The Pennsylvania State University
The Graduate School
Materials Science and Engineering

POLYMER SOLUTIONS AND SOLVENT-SUPERCritical CARBON DIOXIDE STUDIES APPLYING PC-SAFT

A Thesis in
Materials Science and Engineering
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

August 2011
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ABSTRACT

In this thesis is presented the phase equilibria predictions for several polymer solutions and polymer-solvent-solvent systems with the presence of supercritical carbon dioxide (scCO₂) applying Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT). Two main studies were presented to calculate vapor-liquid, liquid-liquid and supercritical fluid-phase equilibria.

In the first study, the capabilities and usefulness of several cubic equations of state (PR, SRK, SOF-PR, SOF-RK) as well as a molecular-based equation of state, PC-SAFT were explored. Specifically, the two phase fluid-fluid regions (VLE, LLE) of several demanding binary mixtures of aromatics as well as dichlorobenzoates (alkyl and semi-fluorinated) with supercritical CO₂ were evaluated. Group contribution approaches were used to estimate the pure fluid parameters for the alkyl and semi-fluorinated dichlorobenzoates needed for each equation of state. We showed that these models can capture many important features of the complex phase behavior of highly asymmetric systems composed of supercritical CO₂ and alkyl (nonfluorinated or semi-fluorinated) 2, 5-dichlorobenzotes.

In a second study, the anti-solvent effects of supercritical carbon dioxide in the polystyrene-cyclohexane-carbon dioxide ternary system were predicted with the PC-SAFT model. The results, using polymer parameters calculated with a recently proposed parametrization strategy, satisfactorily predict the phase equilibria behavior of the ternary system and achieve good agreement with experimental data available in literature. Additionally, the swelling behavior of the ternary system as a function of pressure was calculated and several other derivative properties such as the coefficient of isothermal compressibility ($\beta_T$), the coefficient of isobaric thermal expansivity ($\alpha_P$) and the heat capacity, $C_p$, were evaluated.

Conventional problems in many industrial applications and engineering research areas have been solved with cubic equations of state with reasonable results. However, a
powerful advance for industrial applications of polymer solutions and solvent – solvent mixtures under the influence of scCO₂ have been presented in this work. The results using PC-SAFT, a molecular-based equation of state, can also help in the development and study of new polymeric materials.
# TABLE OF CONTENTS

LIST OF FIGURES ............................................................................................................. vii

LIST OF TABLES ............................................................................................................... xvii

ACKNOWLEDGEMENTS ............................................................................................... xix

Chapter 1 Equations of state, theoretical models and phase diagrams .................... 1

1.1 Introduction ................................................................................................................... 1
1.2 Equations of state .......................................................................................................... 1
1.3 Cubic empirical equations of state ............................................................................. 5
   1.3.1 The classical van der Waals EoS ........................................................................ 6
   1.3.2 Redlich-Kwong equation of state ...................................................................... 6
   1.3.3 Soave-Redlich-Kwong equation of state ........................................................... 7
   1.3.4 Peng-Robinson equation of state ........................................................................ 8
1.4 Theoretical models applicable to polymers ............................................................... 10
   1.4.1 Statistical association fluid theory (SAFT) ......................................................... 11
   1.4.2 Perturbed-chain SAFT (PC-SAFT) ................................................................... 12
1.5 Estimation models or group contribution (GC) methods ......................................... 16
   1.5.1 Elliott’s group contribution method (EGC) extended to PC-SAFT .......... 16
   1.5.2 Tihic’s group contribution method (TGC) applying to polymer systems .......... 18
1.6 Phase diagrams for polymer-solvent systems ............................................................ 19
   1.6.1 Class 1 of binary mixture diagrams ................................................................. 20
   1.6.2 Class 2 of binary mixture diagrams .................................................................. 21
1.7 Vapor-liquid and liquid-liquid equilibrium ............................................................... 24
   1.7.1 Vapor-liquid equilibrium ................................................................................. 24
   1.7.2 Liquid-liquid equilibrium ............................................................................... 25

References ....................................................................................................................... 26

Chapter 2 Supercritical carbon dioxide and its phase behavior in polymers ............. 29

2.1 A new equation of state for carbon dioxide ............................................................... 31
   2.1.1 Helmholtz function ......................................................................................... 31
   2.1.2 Phase equilibria of carbon dioxide ................................................................. 32
   2.1.3 The new equation of state ................................................................................ 36
2.2 Interaction of carbon dioxide with polymers and solutes ....................................... 37
2.3 Solubility in carbon dioxide ...................................................................................... 39
2.4 Application of SCF in bioprocess industries and polymer processing ............... 41

References ....................................................................................................................... 44

Chapter 3 Correlation and prediction of fluid-fluid equilibria of carbon dioxide -
aromatics and carbon dioxide - dichlorobenzoates binary mixtures ...................... 49

3.1 Introduction ............................................................................................................... 49
3.2 Methods .................................................................................................................. 52
  3.2.1 Cubic equations of state and the SOF cohesion function .................................. 52
  3.2.2 Statistical Associating Fluid Theory (SAFT) ..................................................... 58
  3.2.3 PC-SAFT ............................................................................................................ 59
  3.2.4 Group contribution approaches ....................................................................... 60
3.3 Results and discussions ........................................................................................... 60
3.4 Conclusions .............................................................................................................. 72
References ..................................................................................................................... 74

Chapter 4. – Modeling anti-solvent effects of supercritical carbon dioxide (scCO₂) in polystyrene- cyclohexane-carbon dioxide (PS-C₆H₁₂-CO₂) system ................................. 79

4.1 The PC-SAFT model ............................................................................................... 81
4.2 PS- C₆H₁₂-CO₂ phase equilibria using Gross and Sadowski´s parameters ............. 83
  4.2.1 Carbon dioxide – cyclohexane (CO₂-C₆H₁₂) .................................................... 83
  4.2.2 Cyclohexane – polystyrene (C₆H₁₂-PS) .............................................................. 87
  4.2.3 Carbon dioxide- polystyrene (CO₂-PS) .............................................................. 90
  4.2.4 Ternary system: polystyrene - cyclohexane-carbon dioxide (PS-C₆H₁₂-CO₂) ........................................................................................................................ 96
4.3 PS- C₆H₁₂-CO₂ phase equilibria using parameters from the recent developed parametrization strategy ............................................................. 100
4.4 Swelling as a function of pressure .......................................................................... 108
4.5 Derivative properties .............................................................................................. 112
  4.5.1 The coefficient of isothermal compressibility (βₚ) ......................................... 113
  4.5.2 The isobaric thermal expansivity coefficient (αₚ) ........................................... 115
4.6 Conclusions .............................................................................................................. 116
References ..................................................................................................................... 117

Chapter 5.- Conclusions and future work .................................................................... 121

5.1 Fluorinated and hydrocarbon ester functionalized poly (p-phenylene) polymers ....................................................................................................................... 121
  5.1.1 Phase behavior of fluorinated and nonfluorinated propyl and octyl ester functionalized PPPs ............................................................................................. 122
5.2 Conclusions .............................................................................................................. 122
References ..................................................................................................................... 129

Appendix A Phase diagrams of scCO₂ + aromatics and scCO₂+ dichlorobenzoates binary systems .............................................................................................................. 133

References ..................................................................................................................... 132

Appendix B Phase behavior of polystyrene - cyclohexane–carbon dioxide (PS-C₆H₁₂-CO₂) ternary system and its binary components mixtures ........................................... 157

References ..................................................................................................................... 156
LIST OF FIGURES

Figure 1-1 Equation-of-state diagram showing the interrelationship between various EoS...........................................3
Figure 1-2 Diagram showing the interrelationship between various EoS and models. ..................4
Figure 1-3 Helmholtz energy contributions of SAFT ........................................................................................................11
Figure 1-4 Helmholtz energy contributions of PC-SAFT ....................................................................................................12
Figure 1-5 Schematic P-T diagrams of Class 1 for binary van der Waals mixtures ......................21
Figure 1-6 Schematic P-T diagrams of Class 2, type-III for binary van der Waals mixtures ........................................................................................................22
Figure 1-7 a) Schematic P-T diagrams of Class 2, type-IV for binary van der Waals mixtures; b) Enlargement of the region of the critical endpoints of the type-IV system ............................................................22
Figure 1-8 a) Schematic P-T diagrams of Class 2, type-V for binary van der Waals mixtures; b) Enlargement of the region of the critical endpoints of the type-V system ............................................................................23
Figure 1-9 a) Schematic P-T diagrams of Class 2, type-V-A for binary van der Waals mixtures; b) Enlargement of the region of the critical endpoints of the type-V-A system ...............................................................23
Figure 2-1 Three-dimensional phase diagram of CO$_2$ ...........................................................................................................30
Figure 3-1 CO$_2$-toluene, T = 352.59K, red experimental data (352.59 K); red dashed line, PR, k$_{ij}$=0; blue continuous line PR, k$_{ij}$ = 0.0845 ........................................................................................................61
Figure 3-2 CO$_2$-toluene, T = 352.59K, red experimental data (352.59 K); thin red line, PCSAFT-GS; pink dashed line, GC-PCSAFT, k$_{ij}$=0; blue continuous line PCSAFT-GS, k$_{ij}$ = 0.115 ........................................................................................................62
Figure 3-3 CO$_2$-benzene, T = 353 K, □ experimental data (353 K); think red line, PR, k$_{ij}$=0; pink dashed line, SOF-PR, k$_{ij}$=0; blue continuous line SOF-PR, k$_{ij}$ = 0.0828 ..................63
Figure 3-4 CO$_2$-benzene, T = 353 K, □ experimental data (353 K); thin red line, PCSAFT-GS; pink dashed line, GC-PCSAFT, k$_{ij}$=0; blue continuous line PCSAFT-GS, k$_{ij}$ = 0.13 ........................................................................................................................................64
Figure 3-5 Fluid-fluid (VLE and LLE) equilibria of CO$_2$-benzoates. Δ methyl benzoate experimental data (313.15 K); thin black line, GC-PCSAFT, k$_{ij}$ = 0.08; gray dashed line, SOF-PR, k$_{ij}$ = 0.0799; □ ethylbenzoate experimental data (318.15 K), gray dotted line SOF-PR, k$_{ij}$ = 0.0759; blue continuous line GC-PCSAFT, k$_{ij}$ = 0.091; ○
propyl 2,5-dichlorobenzoate experimental data (323.15 K); dashed dotted gray line SOF-PR (LLE) $k_{ij} = 0.06299$; purple continuous bold line GC-PCSAFT, $k_{ij} = 0.061$...66

Figure 3-6 Fluid-fluid (LLE) CO$_2$-ADC B. ○ propyl 2,5-dichlorobenzoate experimental data (323.15 K); dashed dotted gray line SOF-PR (LLE) $k_{ij} = 0.06299$, line with orange diamonds GCPC-SAFT $k_{ij} = 0.061$. ◊ octyl 2,5-dichlorobenzoate experimental data, line with blue squares GC-PCSAFT, $k_{ij} = 0.079$; gray dotted line SOF-PR, $k_{ij} = 0.0763$.................................................................................................................................68

Figure 3-7 Fluid-fluid (LLE) CO$_2$-octyl 2, 5-dichlorobenzoate at 348.15 K. ◊ experimental data; gray line SOF-PR, $k_{ij} = 0.083$; line with green triangles GC-PC-SAFT $k_{ij} = 0.069$, red dashed-dotted line PR-SOF, $k_{ij} = 0.1$; blue continuous line GCPC-SAFT, $k_{ij} = 0.1$.................................................................................................................................69

Figure 3-8 Fluid-fluid (LLE) CO$_2$- FDCB at 323.15 K. Δ 13FO$_2$,5-DCB experimental data; ○ 5FP2,5-DCB experimental data; gray dotted line SOF-PR for 13FO$_2$,5-DCB, $k_{ij} = 0.0646568$; gray solid line SOF-PR for 5FP2,5-DCB, $k_{ij} = 0.037891$; black thick line GC-PC-SAFT for 13FP2,5-DCB, $k_{ij} = 0.03$; black thin line GC-PC-SAFT for 5FP2,5-DCB, $k_{ij} = 0$... .................................................................................................................................70

Figure 4-1 Phase equilibria description for the binary system CO$_2$-C$_6$H$_{12}$ at $T = 348.15$ K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature...............................................................................84

Figure 4-2 Phase equilibria description for the binary system CO$_2$-C$_6$H$_{12}$ at $T = 373.15$ K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature...............................................................................85

Figure 4-3 Phase equilibria description for the binary system CO$_2$-C$_6$H$_{12}$ at $T = 423.15$ K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature...............................................................................86

Figure 4-4 Phase equilibria description for the binary system PS-C$_6$H$_{12}$ at $T = 303.15$ K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature...............................................................................87

Figure 4-5 Phase equilibria description for the binary system PS-C$_6$H$_{12}$ at $T = 323.15$ K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature...............................................................................88
Figure 4-6 Phase equilibria description for the binary system PS-C₆H₁₂ at T = 333.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with \( k_{ij} = 0 \). Lines with symbols are PC-SAFT correlations with different \( k_{ij} \)'s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature.

Figure 4-7 Phase equilibria description for the binary system PS-CO₂ at temperatures of 373.15 K and 453.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid lines represent PC-SAFT predictions with \( k_{ij} = 0 \). Lines with symbols are PC-SAFT correlations with the corresponding \( k_{ij} \)'s evaluated to fit with the experimental data. Filled symbols correspond to experimental data reported in literature.

Figure 4-8 Phase equilibria description for the binary system PS-CO₂ at temperatures of 373.15 K, 413.15 K and 453.15 K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid lines represent PC-SAFT predictions with \( k_{ij} = 0 \). Lines with symbols are PC-SAFT correlations with the corresponding \( k_{ij} \)'s evaluated to fit with the experimental data. The polymer was modeled using seven pseudocomponents reported in table 4-2. Filled symbols correspond to experimental data reported in literature.

Figure 4-9 Phase equilibria description for the binary system PS-CO₂ at temperatures of 338.22 K, 383.22 K and 402.51K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid lines represent PC-SAFT predictions with \( k_{ij} = 0 \). Dashed lines are PC-SAFT correlations with the corresponding \( k_{ij} \)'s evaluated to fit with the experimental data. The polymer was modeled using seven pseudocomponents reported in table 4-3. Filled symbols correspond to experimental data reported in literature.

Figure 4-10 Phase equilibria description for the binary system PS-CO₂ at temperatures of 373.15 K, 423.15 K and 473.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid lines represent PC-SAFT predictions with \( k_{ij} = 0 \). Dashed lines are PC-SAFT correlations with the corresponding \( k_{ij} \)'s evaluated to fit with the experimental data. The polymer was modeled using seven pseudocomponents reported in table 4-4. Filled symbols correspond to experimental data reported in literature.

Figure 4-11 Pressure-temperature diagram for the ternary system PS-C₆H₁₂-CO₂ with compositions: \( w_{PS}=0.094, w_{C₆H₁₂}=0.856, w_{CO₂}=0.05 \) and \( \text{M}_{w}=100,000 \) g/mol. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid blue line represents PC-SAFT prediction with \( k_{ij} = 0 \). Lines with symbols are PC-SAFT predictions with different sets of \( k_{ij} \)'s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature.

Figure 4-12 Pressure-temperature diagram for the ternary system PS-C₆H₁₂-CO₂ with compositions: \( w_{PS}=0.093, w_{C₆H₁₂}=0.768, w_{CO₂}=0.139 \) and \( \text{M}_{w}=100,000 \) g/mol. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid blue line represents PC-SAFT prediction with \( k_{ij} = 0 \). Diamonds correspond to experimental data reported in literature.
Figure 4-13 Influence of the solvent-antisolvent interaction parameter $k_{\text{cyclohexane-carbon dioxide}}$ in the phase envelope diagrams for the ternary system PS-C$_6$H$_{12}$-CO$_2$. Calculations were made using PC-SAFT parameters taken from table 4-1..............................................99

Figure 4-14 Theoretical results for the phase equilibria of PS ($M_w= 101.4$ kg/mol, $M_w/M_n= 1.09$) with carbon dioxide and cyclohexane at 443 K and 10.1 MPa. Calculations were made using polymer molecular parameters calculated from the parametrization scheme. Dotted lines represent the tie lines. Symbols are experimental data reported in the literature.........................................................101

Figure 4-15 Phase equilibria description for the system PS ($M_w = 330$ kg/mol, PDI=3.08) with carbon dioxide at indicated temperatures. Calculations were made using polymer parameters calculated from the parametrization scheme. Solid lines represent PC-SAFT predictions with $k_{ij}=0$. Dashed lines are PC-SAFT correlations with $k_{ij}$ fitted to the experimental data. Symbols correspond to experimental data reported in literature. The polymer was modeled using seven pseudocomponents. ...........102

Figure 4-16 Phase equilibria description for the binary system PS-C$_6$H$_{12}$ at temperatures 303.15 K, 323.15 K and 333.15 K. Calculations were made using polymer parameters calculated from the parametrization scheme. Solid line represents PC-SAFT prediction with $k_{ij}= 0$. Dashed lines are PC-SAFT correlations with different $k_{ij}$'s evaluated to fit with the experimental data. Symbols correspond to experimental data reported in literature. ..................................................................................102

Figure 4-17 Pressure-temperature diagram for the ternary system PS-C$_6$H$_{12}$-CO$_2$ with compositions: $w_P=0.094$, $w_{C6H12}=0.856$, $w_{CO2}=0.05$ and $M_w=100,000$ g/mol. Calculations were made using PC-SAFT parameters calculated from the parametrization scheme. Solid line is PC-SAFT predictions with different $k_{ij}$'s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature. .................................................................................103

Figure 4-18 Pressure-temperature diagram for the ternary system PS-C$_6$H$_{12}$-CO$_2$ with compositions: $w_P=0.093$, $w_{C6H12}=0.768$, $w_{CO2}=0.139$ and $M_w=100,000$ g/mol. Calculations were made using polymer parameters calculated from the parametrization scheme. Solid blue line represents PC-SAFT prediction with $k_{ij}= 0$. Line with symbols is PC-SAFT predictions with different $k_{ij}$'s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature..........................................................................................104

Figure 4-19 Temperature-composition diagram for the ternary system PS-C$_6$H$_{12}$-CO$_2$. at three pressures of 10.1 MPa, 15.15 MPa and 20.2MPa. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7.........................................................................................105

Figure 4-20 PC-SAFT predictions for the liquid-liquid equilibria (LLE) of the ternary system PS-C$_6$H$_{12}$-CO$_2$. at three pressures of 10.1 MPa, 15.15 Mpa and 20.2 Mpa. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7 .................................................................105
Figure 4-21 Pressure-composition diagram for the ternary system PS-C$_8$H$_{12}$-CO$_2$ at temperatures of 373 K and 408 K. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7 ................................................................. 106

Figure 4-22 Pressure-composition diagram for the ternary system PS-C$_8$H$_{12}$-CO$_2$ at temperatures 443K, 473K and 503K. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7 .................................................................................. 106

Figure 4-23 PC-SAFT predictions for the vapor-liquid-liquid equilibria (VLLE) of the ternary system PS-C$_8$H$_{12}$-CO$_2$ at three temperatures of 443 K, 473 K and 503 K. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7 .................................................................................. 107

Figure 4-24 PC-SAFT predictions for the vapor-liquid-liquid equilibria (VLLE) and binary diagram pressure-composition of the ternary system PS-C$_8$H$_{12}$-CO$_2$ at 443 K. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7 .................................................................................. 107

Figure 4-25 Swelling plots for the ternary system PS-C$_8$H$_{12}$-CO$_2$, at temperatures of 373.15K and 408.15K, as a function of volume and pressure, in the range of 0 to 1 MPa ........................................................................................................ 109

Figure 4-26 Swelling plots for the ternary system PS-C$_8$H$_{12}$-CO$_2$, at temperatures of 373.15K and 408.15K, as a function of volume and pressure, in the range of 0 to 4 MPa ........................................................................................................ 110

Figure 4-27 Swelling plots for the ternary system PS-C$_8$H$_{12}$-CO$_2$, at temperatures of 443K, 473K, and 503K, as a function of volume and pressure, in the range of 0 to 1 MPa ........................................................................................................ 110

Figure 4-28 Swelling plots for the ternary system PS-C$_8$H$_{12}$-CO$_2$, at temperatures of 443K, 473K, and 503K, as a function of volume and pressure, in the range of 0 to 8 MPa ........................................................................................................ 111

Figure 4-29Isothermal compressibility parameters, $\beta_T$, as a function of pressure at temperatures 373.15K and 408.15K ......................................................................................................................... 114

Figure 4-30 Isothermal compressibility parameters, $\beta_T$, as a function of pressure at three temperatures 443K, 473K and 503K ......................................................................................................................... 114

Figure 4-31 Isobaric thermal expansivity coefficients for the ternary system PS-C$_8$H$_{12}$-CO$_2$, at three different pressures 10,100 kPa, 15,150 kPa and 20,200 kPa as a function of temperature ......................................................................................................................... 115

Figure 4-32 Heat capacities of the ternary system PS-C$_8$H$_{12}$-CO$_2$, as a function of temperature at three different pressures ......................................................................................................................... 116
Figure 5-1 Schematic representation of the synthesis of alkyl and fluoroalkyl monomers... 122

Figure 5-2 Schematic representation of the synthesis of alkyl and fluoroalkyl polymers..... 122

Figure 5-3 Pressure-temperature diagram for the binary systems PPO2+CO₂ with $M_{wPPO2}$ = 11,880 g/mol, PDI=1.65 and composition: $w_{PPO2}=0.013$, $w_{CO2}=0.987$. Calculations were made using PC-SAFT parameters taken from table 5-1. For the polydisperse calculations seven pseudo-components were used as showed in table 5-2. Dashed line is PC-SAFT prediction for a monodisperse system with $k_{ij} = 0$. Line with solid diamonds represent PC-SAFT prediction for a polydisperse system with PDI=1.65, 1.3 wt% of PPO2 and $k_{ij}=0$. Continuous line is PC-SAFT predictions modeling the system with PDI=1.65, 1.3 wt% of PPO2 and $k_{ij}=-0.15$. Diamonds correspond to experimental data reported in literature... 123

Figure 5-4 Pressure-temperature diagrams for the binary systems of PPPs+CO₂ and PPOs+CO₂. Phase equilibria diagram calculated as polydisperse systems, with seven presudocomponents as shown in table 5-2. The four mixtures have 1.3% wt of the polymer and $M_m$ ranging from 11,880 g/mol to 30,492 g/mol. Calculations were made using PC-SAFT parameters taken from table 5-1. Lines with symbols are PC-SAFT predictions... 124

Figure 5-5 Pressure-temperature diagram for the binary systems PPP1+CO₂ and PPP2+CO₂ with $w_{PPP}=0.013$, $w_{CO2}=0.987$ and $M_{wPPP_1} = 18,060$ g/mol and $M_{wPPP_2} = 30,492$ g/mol. Calculations were made using PC-SAFT parameters taken from table 5-1. For the polydisperse calculations seven pseudo-components were used as shown in table 5-2. Lines with symbols are PC-SAFT predictions with $k_{ij} = 0$. Dashed lines are PC-SAFT predictions calculated as monodisperse systems... 126

Figure 5-6 Pressure-temperature diagram for the binary systems PPO1+CO₂ and PPO2+ CO₂ with compositions: $w_{PPO1}=0.013$, $w_{CO2}=0.987$ and $M_{wPPO1} = 27,720$ g/mol and $M_{wPPO2} = 11,880$ g/mol. Calculations were made using PC-SAFT parameters taken from table 5-1. For the polydisperse calculations seven pseudo-components were used as shown in table 5-2. Lines with symbols are PC-SAFT prediction with $k_{ij} = 0$. Dashed lines are PC-SAFT predictions calculated as monodisperse systems. Diamonds correspond to experimental data reported in literature.... 127

Figure 5-7 Isothermal pressure-composition section for PE + ethylene system .......... 128

Figure A-1 Pressure – composition isotherms for the systems carbon dioxide – benzene.
(a) T = 353K and $k_{ij} = 0.081$; (b) T = 373.5K and $k_{ij} = 0.081$; (c) T = 393.2K and $k_{ij} = 0.081$; the calculations were made using Peng-Robinson Equation of State (EoS). (d) T = 353K and $k_{ij} = 0.083$; (e) T = 373.5K and $k_{ij} = 0.083$; (f) T = 393.2K and $k_{ij} = 0.083$; the calculations were made using Peng-Robinson SOF EoS; (g) T = 353K and $k_{ij} = 0.084$; (h) T = 373.5K and $k_{ij} = 0.084$; (i) T = 393.2K and $k_{ij} = 0.084$; the calculations were made using Soave-Redlich-Kwong EoS. (j) T = 353K and $k_{ij} = 0.077$; (k) T = 373.5K and $k_{ij} = 0.077$; (l) T = 393.2K and $k_{ij} = 0.077$; the calculations were made using Redlich-Kwong SOF EoS. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature............... 134
Figure A-2  Pressure – composition isotherms for the systems carbon dioxide – benzene.

(a) T = 353K and \( k_{ij} = 0.115 \); (b) T = 373.5K and \( k_{ij} = 0.115 \); (c) T = 393.2K and \( k_{ij} = 0.115 \); the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski.  (d) T = 353K and \( k_{ij} = 0.13 \); (e) T = 373.5K and \( k_{ij} = 0.12 \); (f) T = 393.2K and \( k_{ij} = 0.12 \); the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with \( k_{ij}=0 \). Symbols correspond to experimental data reported in literature .......................................................... 135

Figure A-3  Pressure – composition isotherms for the systems carbon dioxide – toluene.

(a) T = 353.4K and \( k_{ij} = 0.085 \); (b) T = 373.2K and \( k_{ij} = 0.085 \); (c) T = 393.2K and \( k_{ij} = 0.085 \); the calculations were made using Peng-Robinson EoS. (d) T = 353.4K and \( k_{ij} = 0.087 \); (e) T = 373.2K and \( k_{ij} = 0.087 \); (f) T = 393.2K and \( k_{ij} = 0.087 \); the calculations were made using Peng-Robinson SOF EoS; (g) T = 353.4K and \( k_{ij} = 0.09 \); (h) T = 373.2K and \( k_{ij} = 0.09 \); (i) T = 393.2K and \( k_{ij} = 0.09 \); the calculations were made using Soave-Redlich-Kwong EoS. (j) T = 353.4K and \( k_{ij} = 0.081 \); (k) T = 373.2K and \( k_{ij} = 0.081 \); (l) T = 393.2K and \( k_{ij} = 0.081 \); the calculations were made using Redlich-Kwong SOF EoS. Solid lines are correlations with \( k_{ij}=0 \). Symbols correspond to experimental data reported in literature .......................................................... 136

Figure A-4  Pressure – composition isotherms for the systems carbon dioxide – toluene.

(a) T = 353.4K and \( k_{ij} = 0.12 \); (b) T = 373.2K and \( k_{ij} = 0.12 \); (c) T = 393.2K and \( k_{ij} = 0.12 \); the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski.  (d) T = 353.4K and \( k_{ij} = 0.13 \); (e) T = 373.2K and \( k_{ij} = 0.13 \); (f) T = 393.2K and \( k_{ij} = 0.13 \); the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with \( k_{ij}=0 \). Symbols correspond to experimental data reported in literature .......................................................... 137

Figure A-5  Pressure – composition isotherms for the systems carbon dioxide – p-xylene.

(a) T = 353.2K and \( k_{ij} = 0.077 \); (b) T = 373.4K and \( k_{ij} = 0.077 \); (c) T = 393.2K and \( k_{ij} = 0.077 \); the calculations were made using Peng-Robinson EoS. (d) T = 353.2K and \( k_{ij} = 0.08 \); (e) T = 373.4K and \( k_{ij} = 0.08 \); (f) T = 393.2K and \( k_{ij} = 0.08 \); the calculations were made using Peng-Robinson SOF EoS; (g) T = 353.2K and \( k_{ij} = 0.083 \); (h) T = 373.4K and \( k_{ij} = 0.083 \); (i) T = 393.2K and \( k_{ij} = 0.083 \); the calculations were made using Soave-Redlich-Kwong EoS. (j) T = 353.2K and \( k_{ij} = 0.079 \); (k) T = 373.4K and \( k_{ij} = 0.079 \); (l) T = 393.2K and \( k_{ij} = 0.079 \); the calculations were made using Redlich-Kwong SOF EoS. Solid lines are correlations with \( k_{ij}=0 \). Symbols correspond to experimental data reported in literature .......................................................... 138

Figure A-6  Pressure – composition isotherms for the systems carbon dioxide – p-xylene.

(a) T = 353.2K and \( k_{ij} = 0.12 \); (b) T = 373.4K and \( k_{ij} = 0.12 \); (c) T = 393.2K and \( k_{ij} = 0.12 \); the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski.  (d) T = 353.2K and \( k_{ij} = 0.11 \); (e) T = 373.4K and \( k_{ij} = 0.11 \); (f) T = 393.2K and \( k_{ij} = 0.11 \); the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with \( k_{ij}=0 \). Symbols correspond to experimental data reported in literature .......................................................... 139
Figure A-7 Pressure – composition isotherms for the systems carbon dioxide – m-xylene. (a) \(T = 310.9K\) and \(k_{ij} = 0.077\); (b) \(T = 477.6K\) and \(k_{ij} = 0.077\); the calculations were made using Peng-Robinson EoS. (d) \(T = 310.9K\) and \(k_{ij} = 0.08\); (e) \(T = 477.6K\) and \(k_{ij} = 0.08\); (f) \(T = 582.55K\) and \(k_{ij} = 0.08\); the calculations were made using Peng-Robinson SOF EoS; (g) \(T = 310.9K\) and \(k_{ij} = 0.083\); (h) \(T = 477.6K\) and \(k_{ij} = 0.083\); (i) \(T = 582.55K\) and \(k_{ij} = 0.083\); the calculations were made using Soave-Redlich- Kwong EoS. (j) \(T = 310.9K\) and \(k_{ij} = 0.075\); (k) \(T = 477.6K\) and \(k_{ij} = 0.075\); (l) \(T = 582.55K\) and \(k_{ij} = 0.075\); the calculations were made using Redlich-Kwong SOF EoS. Solid lines are correlations with \(k_{ij}=0\). Symbols correspond to experimental data reported in literature............................140

Figure A-8 Pressure – composition isotherms for the systems carbon dioxide – m-xylene. (a) \(T = 310.9K\) and \(k_{ij} = 0.11\); (b) \(T = 477.6K\) and \(k_{ij} = 0.11\); (c) \(T = 582.55K\) and \(k_{ij} = 0.11\); the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski. (d) \(T = 310.9K\) and \(k_{ij} = 0.11\); (e) \(T = 477.6K\) and \(k_{ij} = 0.11\); (f) \(T = 582.55K\) and \(k_{ij} = 0.11\); the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with \(k_{ij}=0\). Symbols correspond to experimental data reported in literature.................................................141

Figure A-9 Pressure – composition isotherms for the systems carbon dioxide – o-xylene. (a) \(T = 312.65K\) and \(k_{ij} = 0.073\); (b) \(T = 338.15K\) and \(k_{ij} = 0.073\); (c) \(T = 366.15K\) and \(k_{ij} = 0.073\); the calculations were made using Peng-Robinson EoS. (d) \(T = 312.65K\) and \(k_{ij} = 0.075\); (e) \(T = 338.15K\) and \(k_{ij} = 0.075\); (f) \(T = 366.15K\) and \(k_{ij} = 0.075\); the calculations were made using Peng-Robinson SOF EoS; (g) \(T = 312.65K\) and \(k_{ij} = 0.075\); (h) \(T = 338.15K\) and \(k_{ij} = 0.075\); (i) \(T = 366.15K\) and \(k_{ij} = 0.075\); the calculations were made using Soave-Redlich-Kwong EoS. (j) \(T = 312.65K\) and \(k_{ij} = 0.074\); (k) \(T = 338.15K\) and \(k_{ij} = 0.074\); (l) \(T = 366.15K\) and \(k_{ij} = 0.074\); the calculations were made using Redlich-Kwong SOF EoS. Solid lines are correlations with \(k_{ij}=0\). Symbols correspond to experimental data reported in literature ......................142

Figure A-10 Pressure – composition isotherms for the systems carbon dioxide – o-xylene. (a) \(T = 312.65K\) and \(k_{ij} = 0.11\); (b) \(T = 338.15K\) and \(k_{ij} = 0.11\); (c) \(T = 366.15K\) and \(k_{ij} = 0.11\); the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski. (d) \(T = 312.65K\) and \(k_{ij} = 0.11\); (e) \(T = 338.15K\) and \(k_{ij} = 0.11\); (f) \(T = 366.15K\) and \(k_{ij} = 0.11\); the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with \(k_{ij}=0\). Symbols correspond to experimental data reported in literature.............................................143

Figure A-11 Pressure – composition isotherms for the systems carbon dioxide – methylbenzoate. (a) \(T = 313.15K\) and \(k_{ij} = 0.05\); the calculations were made using Peng-Robinson EoS. (b) \(T = 313.15K\) and \(k_{ij} = 0.08\); the calculations were made using Peng-Robinson SOF EoS. (c) \(T = 313.15K\) and \(k_{ij} = 0.048\); the calculations were made using Soave-Redlich-Kwong EoS. (d) \(T = 313.15K\) and \(k_{ij} = 0.083\); the calculations were made using Redlich-Kwong SOF EoS. Solid lines are correlations with \(k_{ij}=0\). Symbols correspond to experimental data reported in literature ..........................................................144
Figure A-12 Pressure – composition isotherms for the systems carbon dioxide – methyl benzoate. Temperature = 313.15K and $k_{ij} = 0.08$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.

Figure A-13 Pressure – composition isotherms for the systems carbon dioxide – ethyl benzoate. (a) T = 308.15K and $k_{ij} = 0.07$; (b) T = 318.15K and $k_{ij} = 0.07$; (c) T = 328.15K and $k_{ij} = 0.07$; the calculations were made using Peng-Robinson EoS. (d) T = 308.15K and $k_{ij} = 0.076$; (e) T = 318.15K and $k_{ij} = 0.076$; (f) T = 328.15K and $k_{ij} = 0.076$; the calculations were made using Peng-Robinson SOF EoS; (g) T = 308.15K and $k_{ij} = 0.071$; (h) T = 318.15K and $k_{ij} = 0.071$; (i) T = 328.15K and $k_{ij} = 0.071$; the calculations were made using Soave-Redlich-Kwong EoS. (j) T = 308.15K and $k_{ij} = 0.079$; (k) T = 318.15K and $k_{ij} = 0.079$; (l) T = 328.15K and $k_{ij} = 0.079$; the calculations were made using Redlich-Kwong SOF EoS. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.

Figure A-14 Pressure – composition isotherms for the systems carbon dioxide – ethyl benzoate. (a) T = 308.15K and $k_{ij} = 0.091$; (b) T = 318.15K and $k_{ij} = 0.091$; (c) T = 328.15K and $k_{ij} = 0.091$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.

Figure A-15 Pressure – composition isotherms for the systems carbon dioxide – propyl 2,5- dichlorobenzoate. (a) T = 298.15K; (b) T = 323.15K; (c) T=348.15K; the calculations were made using Peng-Robinson and Peng-Robinson SOF EoS, with $k_{ij} = 0.069$ and $k_{ij} = 0.063$ respectively; (d) T = 298.15K; (e) T = 323.15K; (f) T = 348.15K; the calculations were made using Soave-Redlich-Kwong and Redlich-Kwong SOF EoS, with $k_{ij} = 0.072$ and $k_{ij} = 0.069$ respectively. Symbols correspond to experimental data reported in literature.

Figure A-16 Pressure – composition isotherms for the systems carbon dioxide – propyl 2, 5- dichlorobenzoate. (a) T = 298.15K and $k_{ij} = 0$; (b) T=313.15 K and $k_{ij} = 0.064$; (c) T= 323.15K and $k_{ij} = 0.061$; (c) T = 348.15K and $k_{ij} = 0.045$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.

Figure A-17 Pressure – composition isotherms for the systems carbon dioxide – octyl 2,5- dichlorobenzoate. (a) T = 298.15K; (b) T = 323.15K; (c) T = 348.15K; the calculations were made using Peng-Robinson and Peng-Robinson SOF EoS, with $k_{ij} = 0.0868$ and $k_{ij} = 0.0822$ respectively; (d) T = 298.15K; (e) T = 323.15K; (f) T = 348.15K; the calculations were made using Soave-Redlich-Kwong and Redlich-Kwong SOF EoS, with $k_{ij} = 0.0971$ and $k_{ij} = 0.0939$ respectively. Symbols correspond to experimental data reported in literature.

Figure A-18 Pressure – composition isotherms for the systems carbon dioxide – octyl 2,5- dichlorobenzoate. (a) T = 298.15K and $k_{ij} = 0.085$; (b) T= 323.15K and $k_{ij} =
0.079; (b) T = 348.15K and $k_{ij} = 0.071$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.

Figure A-19 Pressure – composition isotherms for the systems carbon dioxide – pentafluoro propyl 2,5- dichlorobenzoate. (a) T = 298.15K; (b) T = 323.15K; (c) T = 348.15K; the calculations were made using Peng-Robinson and Peng-Robinson SOF EoS, with $k_{ij} = 0.047$ and $k_{ij} = 0.038$ respectively; (d) T = 298.15K; (e) T = 323.15K; (f) T = 348.15K; the calculations were made using Soave-Redlich-Kwong and Redlich-Kwong SOF EoS, with $k_{ij} = 0.051$ and $k_{ij} = 0.039$ respectively. Symbols correspond to experimental data reported in literature.

Figure A-20 Pressure – composition isotherms for the systems carbon dioxide – pentafluoro propyl 2,5- dichlorobenzoate. (a) T = 298.15K and $k_{ij} = 0.05$; (b) T = 323.15K and $k_{ij} = 0$; (c) T = 348.15K and $k_{ij} = -0.02$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.

Figure A-21 Pressure – composition isotherms for the systems carbon dioxide – tridecafluoro octyl 2,5- dichlorobenzoate. (a) T = 298.15K; (b) T = 323.15K; (c) T = 348.15K; the calculations were made using Peng-Robinson and Peng-Robinson SOF EoS, with $k_{ij} = 0.069$ and $k_{ij} = 0.065$ respectively; (d) T = 298.15K; (e) T = 323.15K; (f) T = 348.15K; the calculations were made using Soave-Redlich-Kwong and Redlich-Kwong SOF EoS, with $k_{ij} = 0.084$ and $k_{ij} = 0.080$ respectively. Symbols correspond to experimental data reported in literature.

Figure A-22 Pressure – composition isotherms for the systems carbon dioxide – tridecafluoro octyl 2,5- dichlorobenzoate. (a) T = 298.15K and $k_{ij} = 0.050$; (b) T = 323.15K and $k_{ij} = 0.03$; (c) T = 348.15K and $k_{ij} = 0.015$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.
LIST OF TABLES

Table 1-1 Modifications of the attractive term of van der Waals Equation ..................................................5
Table 2-1 Some properties for supercritical carbon dioxide ........................................................................30
Table 2-2 Selected specific isobaric heat capacity of carbon dioxide ............................................................35
Table 2-3 Coefficients for the equations 2.15 and 2.16, for $c_p^0$ and $\varnothing^0$, respectively ..........................37
Table 2-4 Physical properties of some supercritical solvents ......................................................................41
Table 3-1 Schematic representation of compounds studied in this work ......................................................51
Table 3-2 Estimated properties of pure alkyl 2, 5-dichlorobenzoates ...............................................................58
Table 3-3 PC-SAFT parameters ..................................................................................................................71
Table 3-4 Temperature independent binary interaction parameters ($k_{ij}$'s) used in this work .......................71
Table 3-5 Temperature dependant binary interaction parameters ($k_{ij}$'s) used in this work for GC PC-SAFT ...........................................................................................................................................................................71
Table 3-6 Temperature dependant binary interaction parameters ($k_{ij}$'s) used in this work for the cubic EoS ...........................................................................................................................................................................72
Table 4-1 PC-SAFT parameters used in this work .........................................................................................82
Table 4-2 Pseudocomponents determined from the experimental data $M_w$ and $M_n$ values for modeling the molecular weight of PS with carbon dioxide presented in figure 4-8 .................................................................................92
Table 4-3 Pseudocomponents determined from the experimental data $M_w$ and $M_n$ values for modeling the molecular weight of PS with carbon dioxide presented in figure 4-9 .................................................................94
Table 4-4 Pseudocomponents determined from the experimental data $M_w$ and $M_n$ values for modeling the molecular weight of PS with carbon dioxide presented in figure 4-10 .........................................................................................95
Table 4-5 Equations for $k_{ij}$'s determined from the experimental data at different temperatures for the systems PS-CO$_2$ ..................................................................................................................................................96
Table 4-6 Studied sets of $k_{ij}$'s parameters for the ternary system PS-C$_6$H$_{12}$-CO$_2$ shown in figures 4-11 and 4-12 ................................................................................................................................................97
Table 4-7 Binary interaction parameters, $k_{ij}$’s, for each pair of components of the three binary mixture studied in following sections .........................................................99

Table 4-8 Compositions for the border points of the three phase region of the ternary system PS-C$_6$H$_{12}$-CO$_2$ at 443 K ........................................................................................................108

Table 5-1 PC-SAFT parameters for poly (p-phenylene) polymers used in this work .........123

Table 5-2 Pseudocomponents determined from the reported experimental data, Mw and Mn, used in this work ..........................................................................................................................125

Table A-1 Coefficients for the generalized correlations of equations 3.8a and 3.8b ..........133

Table B-1 Pseudocomponents determined from the experimental data Mw and Mn values for modeling the molecular weight distribution of PS with methyl cyclohexane shown in figure 4-14 ........................................................................................................157

Table B-2 Molecular parameters of the PC-SAFT model for polymer calculated in figure 4-15. .................................................................................................................................157

Table B-3 Pseudocomponents determined from the experimental data Mw and Mn values for modeling the molecular weight distribution of PS with carbon dioxide shown in figure 4-15 ...........................................................................................................158

Table B-4 Isothermal compressibilities, $\beta_T$, and molar volumes calculated at different pressures at two isotherms 373.15K and 408.15K...............................................................158

Table B-5 Isothermal compressibilities, $\beta_T$, and molar volumes calculated at different pressures for two isotherms 443 K, 473K, and 503K.........................................................159

Table B-6 Isobaric thermal expansivities, $\alpha_P$, and molar volumes calculated at different temperatures for three isobars (10,100kPa, 15,150kPa and 20,200kPa) .................160
ACKNOWLEDGEMENTS

This work is the result of more than three years of formation and research in the Materials Science area, which was completely new for me. It means that it would not be possible without the collaboration and help of many people and institutions to whom I’m sincerely grateful.

First, I would like to express my sincere gratitude to my advisers Dr. Coray Colina and Dr. James Runt, who help me in the selection of the topic of this thesis. They always encourage me to continue my preparation and give me support, expert advice and guidance with a lot of patient during my graduate study.

To the Department of Materials Science and Engineering for giving me the opportunity to realize this research with professors, staff members and all resources of this department. With special thanks to Dr. Paul Painter who accept to be part of the committee for the revision of this thesis.

To friends and work group members of the Colina’s research group: Greg Larsen, Kristin Patterson, Lauren Abbott, Kyle Hart and Monica Castellanos; and of the Runt’s research group: Taeyi Choi, Kevin Masser, Amanda McDermott. All of them in several occasions offer me their friendship and expertise.

I cannot forget the valuable opportunity to work with Prof. Claudio Olivera-Fuentes and Prof. Sivia Siquier-Soler, both members of the Department of Thermodynamics and Transport Phenomena at Simon Bolivar University, Caracas, Venezuela. Without their collaboration this research would not be possible.

To the Instituto Tecnológico y de Estudios Superiores de Monterrey, Campus San Luis Potosí, Mexico, for the confidence and financial support during all these years out of my country.
To my only son Oscar Rubén, who learnt and grew up beside me. He became the principal reason to maintain the enthusiasm to finish and to reach this goal.

To my family and friends for supporting and encouraging me unconditionally.

Finally, I want to express my gratitude to all people that in anonymous way participated in the elaboration of this research.
Chapter 1

Equations of state, theoretical models and phase diagrams

1.1 Introduction

Solubility of polymers in solvents and the effect of temperature on it have been under considerable attention in polymer processing and applications\(^1\). Therefore, the study of polymer solutions and solvent-mixtures result of interest both in theoretical and experimental aspects.

The use of supercritical fluids in polymer processing and industrial applications is pursued not only in research laboratories but also has been adopted on a commercial scale\(^2\). The solubility of supercritical CO\(_2\) (scCO\(_2\)) depends on temperature and pressure and also on weak interactions with the chain groups in the polymer\(^3\). Therefore, the appropriate equation of state or theoretical model, and the resulting phase diagrams are essential to understanding the regions of distinct chemical and structural behavior of polymer solutions in thermodynamic equilibrium. The properties of a polymer solution or solvent-mixtures, and thus their functionality, sometimes depend critically on what region is used in the preparation of the material. When polymers are fabricated, the processing conditions must be maintained in very narrow regions of temperature and composition in order to achieve the desired properties\(^2\).

The theoretical modeling of solubility data is as crucial as experimental measurements for a complete understanding of processes where thermodynamics plays a vital role; and, incidentally, theoretical calculations are inexpensive compared to experiments\(^2\).

1.2 Equations of state

Equations of state have been used to study the phase equilibria of pure components and mixtures. There are many reasons for using equations of state for phase equilibria calculations.
Starting with its applicability, equations of state can be used over a wide range of pressure and temperature. Secondly, they can study mixtures of various components from light gases to heavy liquids. Third, which is the topic of this work, equations of state can be applied to calculate vapor-liquid, liquid-liquid and supercritical fluid-phase equilibria\textsuperscript{4} in systems that involve solvent-scCO\textsubscript{2}, alkyl-scCO\textsubscript{2} and polymer-alkyl-scCO\textsubscript{2}.

There are many ways to compare equations of state (EoS), Wei and Sadus\textsuperscript{4} used the criteria by which the EoS were developed, i.e., by combining separate contributions for the attractive and repulsive interactions. In figure 1-1, are shown the different branches that form this diagram corresponding to different representations of the repulsive interactions. They are the van der Waals, the Carnahan-Starling, the Hard Convex Body (HCB), the Perturbed Hard Chain Theory (PHCT) and the Thermodynamic Perturbation Theory (TPT). Most of the empirical EoS are equations of state that represent a new term, either for the attraction part or for the repulsion part of the equation; nonetheless, all of these equations are capable of predicting phase equilibria. Empirical equations derive almost entirely from the van der Waals repulsive branch. The theoretical equations have many branches depending on which alternative was used to account the repulsion of nonspherical bodies. The different theoretical branches converge on one point, which correspond with the case of hard-sphere repulsion as has been delineated by the Carnahan-Starling equation.

In figure 1-1 is shown the importance of the van der Waals and Redlich-Kwong equations as starting point for the development of several empirical equations. While, the PHCT and the Statistical Association Fluid Theory (SAFT) equations of state are the origin of many theoretical equations.
Another way to present the wide influence of applied thermodynamics and models was discussed by Chen and Mathias\(^5\). According with the diagram shown in figure 1-2, they presented seven branches that converge in one point in which theory, simulation and experiments have to participate to make the best contribution to the practice of the applied thermodynamics.

Three of these branches correspond to EoS. There are the van der Waals, empirical EoS, and theoretical EoS. The van der Waals equations had their origin around 1877, were followed by significant improvements, some equations used mixing and combining rules to describe phase-equilibrium. The model has its principal application in the gas-processing and petroleum industries. The empirical equations, which can be delineated to the virial model enhanced with experienced data fitting and empiricism, developed the branch of multi-parameter EoS. Starting with Beattie-Bridgman equation in 1927 was followed by highly accurate equations of state for pure fluids. The theoretical EoS branch was started with the virial equation of Meyer in 1901. Together with distinct models such as hard-sphere EoS, the BACK model and the perturbed-hard-chain model, provide the first statistical mechanical basis for modeling large molecules as
polymers. The most recent theoretical EoS is the PC-SAFT proposed by Gross and Sadowski in 2001.

Figure 1-2 Diagram showing the interrelationship between various EoS and models.

The remaining four branches correspond to estimation methods, predictive activity coefficient methods, and models specifically for electrolytes and polymers. Advances in activity coefficient methods are principally in the modeling of chemical systems with multifunctional group molecules. Examples of that are in the polymer NRTL and UNIFAC models, including databanks such as NIST Chemistry Webbook, AIChE DIPPR, etc. All of these contributions include model parameters, references, notes, and codes which give reliable and efficient access to evaluate experimental data and correlations. Lastly, for polymer systems, two crucial polymer characteristics, the size effect on the entropy term and the interaction effect on the enthalpy of mixing; were captured in the Flory-Huggins lattice model in 1942. For additional free volume effects, the lattice fluid model was proposed by Sanchez-Lacombe. Successful engineering EoS for polymer solutions are the Hard-sphere-chain models such as SAFT and its recent derivatives.
They integrate the segment concept with local composition models and with segment-based mixing rules for copolymers.

The interrelationships between models and equations of state have been of interest of many research projects. People in the experimental area and people in the simulation area use EoS and models. They compare results and analyze them in the way to understand their interrelationships. Then, they are exporting these ideas to new interesting research. We present through this work different applications using both, empirical equations and theoretical models, to predict phase behavior.

1.3 Cubic empirical equations of state

The origin of empirical EoS is attributed to the need to predicting the thermodynamic state of gases and liquids. The simplest EoS for this objective is the Ideal Gas Law. In 1662, Robert Boyle, after performing several experiments, wrote the first expression of an EoS. Other equations were proposed during the subsequent centuries. As example we found the Law of Charles and Gay-Lussac (1787) and Dalton’s law of partial pressures (1801). This increasing development of empirical EoS also allowed the appearance of two other important equations: the ideal gas law (1834) and the Van der Waals equation of state.

Cubic equations are actually the most widely used models for numerous industrial, chemical-process and practical applications. The calculations of binary mixture properties and phase equilibria are still performed regularly in industry with cubic EoS with satisfactory results.

Table 1-1 Modifications of the attractive term of van der Waals Equation

<table>
<thead>
<tr>
<th>Equation</th>
<th>Attractive term ((-Z_{at}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redlich-Kwong (RK) (1949)</td>
<td>(\frac{a}{RT^{1.5}(V + b)})</td>
</tr>
<tr>
<td>Soave-Redlich-Kwong (SRK) (1972)</td>
<td>(\frac{aT}{RT(V + b)})</td>
</tr>
<tr>
<td>Peng-Robinson (PR) (1976)</td>
<td>(\frac{a(T)V}{RT[V(V + b) + b(V - b)]})</td>
</tr>
</tbody>
</table>
In table 1-1 has been summarized three important modifications to the attractive term of the van der Waals EoS. We will perform calculations only with these important modifications of the cubic EoS and then compare with PC-SAFT results.

1.3.1 The classical van der Waals EoS

In 1873, J.D. van der Waals proposed the first equation of state to predict vapor-liquid coexistence.\(^{10}\)

\[
Z = \frac{V}{V - b} - \frac{a}{RTV}
\]

(1.1)

where \(Z\) is the compressibility factor (\(Z = \frac{PV}{RT}\)), \(T\) is the temperature, \(V\) is the volume, \(P\) is the pressure, and \(R\) is the molar universal gas constant (\(R = 8.31447 \text{ J/molK}\)). The attractive forces between the molecules are included in the parameter \(a\), and the covolume occupied by the molecules are represented by the parameter \(b\). Both parameters, \(a\) and \(b\), can be calculated from the critical properties of the compound. Equation 1.1 is defined by two terms which account for the contributions of repulsive and attractive intermolecular interactions. The van der Waals equation of state gives qualitative predictions for many systems. Based on this equation, hundreds of empirical equations have been proposed.

1.3.2 Redlich-Kwong equation of state

The Redlich-Kwong\(^{11}\) equation of state was introduced in 1949 as an improvement of the van der Waals EoS. This equation containing two individual coefficients was proposed for obtaining satisfactory results above the critical temperature for any pressure. It is represented by

\[
Z = \frac{V}{V - b} - \frac{a}{RT^{1.5}(V + b)}
\]

(1.2)

It will be used in the form:

\[
Z = \frac{1}{1 - h} - \frac{(\frac{a}{b})^h}{(1 + h)}
\]

(1.3)

where \(Z = \frac{PV}{RT}\); \(h = \frac{BP}{Z} = \frac{b}{V}\) and
The relations between the coefficients $a$ and $b$ or $A^2$ and $B$ and the critical temperature $T_c$ and critical pressure $P_c$, follow from the critical conditions. All relations proposed by Redlich and Kwong were able to give reasonable results independently if only the critical temperature and pressure were known; or if sometimes $P-V-T$ data for some or all the components exist; or if sometimes a complete set of data for mixtures are available. The method proposed does not require an unreasonable amount of time. However, after many applications it is known that RK EoS performs poorly with respect to the liquid phase and thus is not completely successful when vapor-liquid equilibria calculation is performed.

1.3.3 Soave-Redlich-Kwong equation of state

In 1972, Giorgio Soave proposed a modified Redlich-Kwong EoS. As Soave denoted, his proposed EoS resulted from the fact that using the original Redlich-Kwong EoS to multicomponent -VLE calculations gives poor results; so, it must be attributed to the equations’ lack of efficiency in expressing the influence of temperature. Then he replaced part of the attraction term of the original RK EoS by the following expression

$$Z = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

(1.6)

Giving:

$$V = z \frac{RT}{Z}$$

(1.7)
The SRK EoS can also be found:

\[ A = \frac{aZ}{R^2T^2} \]  \hspace{2cm} (1.8)

\[ B = \frac{bZ}{RT} \]  \hspace{2cm} (1.9)

The SRK EoS can also be found:

\[ Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \]  \hspace{2cm} (1.10)

The proposed equation nearly reproduce vapor pressures of pure components by assuming the parameter \( a \) in the original equation to be temperature-dependent. Additionally, he introduced the acentric factor as a third parameter, to derive a generalized correlation for the modified parameter. For mixtures, a notable improvement at limited pressure ranges (up to 6.8 – 13.8 MPa) was realized using a proper value of the acentric factor. However, empirical corrections were necessary for systems containing carbon dioxide, hydrogen and polar compounds. In such cases an empirical correction factor needs to be used. In such manner, the generalized mixing rules presented as \( a_{ij} = (a_i a_j)^{1/2} \) has to be changed by \( a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \) where \( k_{ij} \) the empirical correction factor is determined from the experimental data for each binary present in the mixture. Each \( k_{ij} \) can be determined independent of system temperature, pressure and composition.

1.3.4 Peng-Robinson equation of state

In 1976, Peng and Robinson\textsuperscript{13} published the development of a new modification of the van der Waals EoS in which the attractive pressure term was changed. Four goals should be satisfied: the involved parameters should be describable in terms of the critical properties and the acentric factor; the compressibility factor and liquid density should be calculated with moderate accuracy near the critical point; the mixing rules should use only a single binary interaction
parameter independent of temperature, pressure and composition; and the resulting equation should be relevant for all fluid properties.

The proposed two-constant equation has the following form

\[
Z = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}
\]  

Equation 1.11 can be expressed as

\[
Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0
\]  

where

\[
A = \frac{aP}{RT^2}
\]  

\[
B = \frac{bP}{RT}
\]  

\[
Z = \frac{PV}{RT}
\]  

The mixing rules in equation 1.12 can be defined by

\[
a = \sum_i \sum_j x_i x_j a_{ij}
\]  

\[
b = \sum_i x_i b_i
\]

where

\[
a_{ij} = (1 - k_{ij})a_{i}^{1/2}a_{j}^{1/2}
\]

In this equation \( k_{ij} \) is a binary interaction coefficient determined empirically from the characterization of the binary mixture with components \( i \) and \( j \).
The PR EoS can be used to precisely predict the liquid densities of many materials, especially nonpolar ones. But in general, its performance is similar than Soave RK EoS.

**1.4 Theoretical models applicable to polymers**

The modelings of polymer solutions phase equilibria by the use of cubic equations of state like van der Waals and its related modifications in not possible. These equations were developed for small molecules and its application to macromolecules, i.e. polymers is outside their scope. Thus, during the last four decades different approaches have been proposed to overcome this and other limitations: chain-like structure of polymers and the interactions between molecules.

The early approach of the lattice models was proposed by Flory and Huggins. Other equations of state originated on the almost the same idea are the Lattice-Fluid Theory from Sanchez and Lacombe and Mean-Field Lattice-Gas theory from Kleintjens and Koningsveld. Based on the partition function of a system derived from statistical mechanics, new approaches emerged. One of them is the Perturbed Hard-Chain Theory (PHCT) introduced by Beret and Prausnitz.

Another option for polymer phase equilibria calculations is the application of so-called perturbation theories. The assumption is that the residual part of the Helmholtz energy of a system \( A^{\text{res}} \) can be described as the sum of different contributions. Some perturbations of the contribution to the Helmholtz energy, \( A^{\text{pert}} \) which are not covered by the reference system are

\[
A = A^{\text{id}} + A^{\text{res}} = A^{\text{id}} + A^{\text{ref}} + A^{\text{pert}}
\]  

\[
p = p^{\text{id}} + p^{\text{res}} = p^{\text{id}} + p^{\text{ref}} + p^{\text{pert}}
\]
An applicable reference system for small molecules is the hard-sphere (hs) system. In this system, the molecules are considered to be spheres of a fixed diameter and without any attractive interactions; covering in this way the repulsive interactions of the molecules.

Other independent contributions have to be accounted by the perturbation terms: dispersion (attractive interactions), association (formation of hydrogen bonds), and formation of chains (due to the nonspherical shape of the molecules). These contributions resulted in different models. The Statistical Association Fluid Theory (SAFT) appears as a result of this idea, and was developed by Chapman et al.\textsuperscript{17,18}, Huang and Radosz\textsuperscript{19,20}.

1.4.1 Statistical association fluid theory\textsuperscript{21} (SAFT)

In SAFT, solvent molecules or polymers (chain-like molecules) are considered to be a chain of \( m \) identical spherical segments. Arising from a reference system \( (A^{\text{hs}}) \), the model contemplates three perturbation contributions: chain formations \( (A^{\text{chain}}) \), attractive interactions \( (A^{\text{disp}}) \), and association sites \( (A^{\text{assoc}}) \) (Figure 1-3):

\[
A^{\text{res}} = \frac{mA^{\text{hs}} + A^{\text{chain}}}{} + mA^{\text{disp,SAFT}} + A^{\text{assoc}} \tag{1.21}
\]

![Figure 1-3 Helmholtz energy contributions of SAFT\textsuperscript{21}](image-url)
After the SAFT model, several perturbations theories were formulated based on SAFT EoS, but they show different types of perturbations. Examples are SAFT-VR\textsuperscript{22} and PC-SAFT.

1.4.2 Perturbed-chain SAFT\textsuperscript{6,21} (PC-SAFT)

In polymers and chain-like molecules, the Perturbed-Chain SAFT model\textsuperscript{6,23,24} is a widely used model. The main advancement in PC-SAFT is that considers the hard chain as a reference system (more convenient for polymers and other chain-like molecules) (Figure 1-4).

The hard-chain system is achieved as the sum of the hard-sphere and chain-formation contributions $A^\text{hs}$ and $A^\text{chain}$, similar to the SAFT model. Whereas the dispersion term $A^\text{disp,PC-SAFT}$ includes the attraction of chain molecules rather than the nonbonded segments, it emerges as a function of chain length $m$:

$$A^{res} = A^{hc} + A^{\text{disp,PC-SAFT}}(m) + A^{\text{assoc}}$$ \hspace{1cm} (1.22)

![Figure 1-4 Helmholtz energy contributions of PC-SAFT](image)

For phase equilibria calculations three pure-component parameters for non-associating molecules are needed. The first is the segment diameter $\sigma$, which corresponds to the van der
Waals parameter $b$. The second one, $\varepsilon$, is the interaction energy between segments, which corresponds to the van der Waals parameter $a$. The third, the segment number $m$, is considered the deviation from the spherical shape of the molecules. This last parameter is proportional to the molecular weight for polymer systems. When the PC-SAFT approach is used to predict binary mixture behavior, sometimes is necessary to include an additional parameter ($k_{ij}$), to improve accuracy that can be attributed to deviations of the geometric mean of the energy parameter.

The various contributions included in equation 1.22 require several expressions. The hard-chain contribution pronounces as:

$$\frac{A^{hc}}{NkT} = \bar{m} \frac{A^{hs}}{NkT} = \sum_i x_i (m_i - 1) \ln g_{i_i}(d_{i_i}^n)$$

(1.23)

$$\frac{A^{hs}}{NkT} = \frac{1}{\zeta_0} \left[ \frac{3 \zeta_1 \zeta_2}{(1-\zeta_3)} + \frac{\zeta_3^2}{(1-\zeta_3)^2} + \left( \frac{\zeta_3^2}{\zeta_3^2} - \zeta_0 \right) \ln (1 - \zeta_3) \right]$$

(1.24)

$$\bar{m} = \sum_i x_i m_i$$

(1.25)

$$\zeta_n = \frac{\pi}{6} \rho \sum_i x_i m_i a_i^n ; \quad \zeta_3 = \eta$$

(1.26)

where $g$, is a the radial distribution function, which is a function of the distance of two segments. Hence, $g(d^{+})$ is the value of the radial distribution function at contact. It can be determined as:

$$\ln g_{ij}(d_{ij}^n) = \frac{1}{1 - \zeta_3} + \frac{d_{ij}}{(d_i + d_j)} \frac{3 \zeta_2}{(1-\zeta_3)^2} + \left( \frac{d_{ij}}{(d_i + d_j)} \right)^2 \frac{2 \zeta_3^2}{(1-\zeta_3)^2}$$

(1.27)
To calculate the (temperature-dependent) segment diameter $d$, from the temperature-independent one, the following expression is used

$$d_i = \sigma_i \left[ 1 - 0.12 \exp \left( \frac{-3\varepsilon_{ij}}{kT} \right) \right]$$ (1.28)

The attractive interaction contributions of segments of different chains $A^{\text{disp,PC-SAFT}}$ is established as a power series with respect to reversed temperature. If we only take into account two terms of these series and compute their dependence on segment number and density, $A^{\text{disp,PC-SAFT}}$ reads as:

$$\frac{A^{\text{disp,PC-SAFT}}}{kTN} = \frac{A_1}{kTN} + \frac{A_2}{kTN}$$ (1.29)

$$\frac{A_1}{kTN} = -2\pi \rho l_1(\eta, \bar{m}) \sum_j \Sigma_i x_i x_j m_i m_j \left( \frac{\varepsilon_{ij}}{kT} \right) \sigma_{ij}^3$$ (1.30)

$$\frac{A_2}{kTN} = -\pi \rho \bar{m} \left( 1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho} \right)^{-1} l_2(\eta, \bar{m}) \sum_j \Sigma_i x_i x_j m_i m_j \left( \frac{\varepsilon_{ij}}{kT} \right)^2 \sigma_{ij}^3$$ (1.31)

where:

$$l_1(\eta, \bar{m}) = \sum_{i=0}^{6} a_i (\bar{m}) \eta^i$$ and $$l_2(\eta, \bar{m}) = \sum_{i=0}^{6} b_i (\bar{m}) \eta^i$$ (1.32)

and:

$$a_i = a_{0i} + \frac{\bar{m}-1}{\bar{m}} a_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} a_{2i}$$ (1.33)
The variables included in equations 1.33 and 1.34 are model constants and are given in tables presented in the original literature. The binary interaction parameter, $k_{ij}$, included in equation 1.35 has to be fitted to binary experimental data. The remaining contribution, $A_{assoc}$, captures the Helmholtz energy change due to the formation of hydrogen bonds. The corresponding expressions are described by Chapman et al. For modeling associating molecules PC-SAFT require two more parameters: the association volume $\kappa_{AA}$ (representing the potential energy width $r_{AA}$) and the association strength $\varepsilon_{AA}$ (representing the potential energy depth).

Finally the mixture components, chemical potentials and system pressure can be evaluated by using the following relations:

\[
p = -\left(\frac{\partial A}{\partial V}\right)_{T,n_i}
\]

and

\[
RT\ln \phi_i = \left(\frac{\partial A_{res}}{\partial n_i}\right)_{T,V,n_{j\neq i}} - RT \ln z \quad \text{with} \quad z = \frac{pV}{NkT}
\]

For all components $i$ of the mixture, to perform phase-equilibrium calculations must to follow the classical phase-equilibrium conditions:
1.5 Estimation models or group contribution (GC) methods

The group of estimation methods was initially based on the regular solution theory of Scatchard-Hildebrand in 1929; however, their actual roots lean on group contribution models. The GC methods can be divided into two classes. The first class are those that estimate the property of a compound as a summation of the contributions of simple first-order groups (FOG) that may occur in the molecular structure, such as CH\(_2\) and OH. This FOG is compelling when there is no theoretical basis for the groups’ identifications and the groups are not able to capture proximity effects or isomer differences. The second class group (SOG) includes those that attempt to capture fine structural differences\(^{27}\). Here we will present two different methodologies extended to the statistical association fluid theory (SAFT) and perturbed-chain statistical associating fluid theory (PC-SAFT).

1.5.1 Elliott’s group contribution method (EGC) extended to PC-SAFT

This methodology\(^{28}\) was developed by Elliott and Natarajan and it can be identified as first-order contribution group. This EGC was extended to SAFT and PC-SAFT. Using this method, they calculated vapor pressure predictions as well as boiling temperatures of a database of 871 organic compounds. For PC-SAFT the model identifies each pure component in terms of three parameters. There are the temperature-independent segment diameter, σ, the depth of the potential, \(\epsilon/k\), and \(m\), the number of segments per chain. Additionally, three more parameters are added for hydrogen-bonding species: the number of hydrogen-bonding segments per molecule, \(N_d\); the bonding volume, \(\kappa^{AD}\); and the hydrogen-bonding energy, \(\epsilon^{HB}/k\). Following Elliot and
Natarajan\textsuperscript{29}, the EGC calculates $\varepsilon_{HB}/k$ as an average over bonding sites: 4 kcal/mol for hydroxyl groups and 1.25 kcal/mol for amine, amide, nitrile and aldehydes groups. For the parameter $\kappa^{AD}$, it is correlated in terms of $b$ and $m$, with the expression

$$\kappa^{AD} = 0.035 \frac{b}{m} \quad (1.39)$$

They have assigned two association sites to all associating components (often called 2B model). For estimating the three parameters, they started by estimating the compressibility factor:

$$Z_L^{298} = \frac{0.1 V_L^{298}}{298R} \quad (1.40)$$

where $V_L^{298}$ is the liquid molar volume at 298 K, and $R$ is the universal constant. The extended Hoy\textsuperscript{30} correlation for $V_L^{298}$ has the form

$$V_L^{298} = 12.1 + \sum v_i \Delta V_i \quad (1.41)$$

where $\Delta V_i$ is the UNIFAC group contribution for liquid molar volumes.

Once the compressibility factor have been calculated, the relationship of the solubility parameter can evaluated using

$$\delta = \left[\left(H_{vap}^{298} - 298R\right)/V_L^{298}\right]^{1/2} \quad (1.42)$$

For the calculation of the heat of vaporization, $H_{vap}^{298}$, the Constantinou and Gani\textsuperscript{31} approach can be utilized as follow

$$H_{vap}^{298} = 6.829 + \sum v_i H_i \quad (1.43)$$

And the internal energy departure function also must be calculated with
As third step, the shape factor is determined by

\[
\frac{\delta^2 v_L^{298}}{298 R} = - \frac{U}{298 R}
\]  

(1.44)

As third step, the shape factor is determined by

\[
m = 1 + (\sum v_i \Delta m_i)
\]  

(1.45)

where $\Delta m_i$ is the group contribution and 1 is the number assigned to a spherical molecule. The optimal shape parameters for all compounds were tabulated with the ones in terms of the group contribution correlations. The tables can be consulted in the original paper\(^{28}\).

The use of this EGC approach for different families of compounds and PC-SAFT models will provide new routes to predicting thermodynamic properties when experimental data are not available.

1.5.2 Tihic’s group contribution method (TGC) applying to polymer systems

The second group contribution (TGC) methodology\(^{27}\) uses the Constantinou-Gani method\(^{31}\) in combination with simplified PC-SAFT\(^{32}\) to determine the characteristic molecular PC-SAFT parameters. For nonassociating fluids, three parameters are needed: the segment number ($m$), the hard-core segment diameter ($\sigma$), and the segment-segment interaction energy parameter ($\varepsilon/k$). For associating fluids two additional compound parameters are defined: the association energy ($\varepsilon^{AB}$) and the association volume ($\kappa^{AB}$).

This TGC method, used for predicting physical and thermodynamic properties of compounds at two levels, is a SOG method. This specific methodology can be described in three steps: Step 1. The identification and occurrence of FOG and SOG in each compound. Step 2. The fitting of vapor pressures and liquid density data obtained from DIPPR\(^{33}\) correlations in a reduced temperature ($T_r$) range of $0.5 \leq T_r \leq 0.9$ for generating an extensive parameter table for PC-SAFT
nonassociating compounds. Step 3. The fitting of each of the three GC based parameters to the corresponding DIPPR fitted parameters.

For the estimation of the three PC-SAFT parameter groupings, \( m, m\sigma^3 \), and \( m\varepsilon/k \), the following relations are applied assuming that a given molecule contains \( n_i \) groups of type \( i \)

\[
m_{\text{molecule}} = \sum_i (n_i m_i)_{\text{FOG}} + \sum_j (n_j m_j)_{\text{SOG}}
\]

(1.46)

\[
(m\sigma^3)_{\text{molecule}} = \sum_i (n_i m_i \sigma_i^3)_{\text{FOG}} + \sum_j (n_j m_j \sigma_j^3)_{\text{SOG}}
\]

(1.47)

\[
(m\varepsilon/k)_{\text{molecule}} = \sum_i (n_i m_i \varepsilon_i/k)_{\text{FOG}} + \sum_j (n_j m_j \varepsilon_j/k)_{\text{SOG}}
\]

(1.48)

where \( m_i, \sigma_i \) and \( \varepsilon_i/k \) are the contributions of the first-order group (FOG) of type \( i \) that appears \( n_i \) times; and \( m_j, \sigma_j \) and \( \varepsilon_j/k \) are the contributions of the second-order group (SOG) of type \( j \) that appears \( n_j \) times.

The proposed TCG technique requires only chemical structural information and the molecular weight for determining the presence of FOG and SOG of each compound of interest. And TCG technique is considered a reliable tool for accurate modeling of polymer phase equilibria over a wide range of temperatures and compositions, and different degrees of the chemical complexities.

### 1.6 Phase diagrams for polymer-solvent systems

The phase behavior of polymer mixtures can be complicated. The main reason is due to the polydisperse character of most polymers resulting in multi-component mixtures. Nevertheless, the use of pressure-temperature \((P-T)\) diagrams for simple binary mixtures to describe the phase equilibrium of the system is viable\(^{34}\).
For small molecule mixtures a useful classification of $P$-$T$ diagrams using the van der Waals EoS, was proposed by Scott and Konynenberg\textsuperscript{35}. According to Scott classification, there are three main classes of binary-fluid phase diagrams. The \textit{Classes 1 and 2} are formed for binary mixtures with similar and different gas-liquid critical temperatures, respectively and will be explained in detail later. The \textit{Class 3} groups very complex mixtures exhibiting lower-critical-solution temperatures (LCST). The LCST behavior cannot be represented by only one EoS as van der Waals equation because LCST-phase behavior is a consequence of strong interactions between the two components.

The phase diagrams are also categorized by the presence or absence of three-phase lines (L$_1$L$_2$G) and azeotrope lines (positive and negatives) and by the manner in which they meet the critical lines. Critical lines can finish in different paths. They end at the one-component gas-liquid critical points C$_1$ and C$_2$ and at the limiting upper critical solution point C$_m$ ($T_m^\infty$, $\infty$, $x = \frac{1}{2}$) of a close-packed ($V_m=b$) ‘liquid-liquid’ system. Critical lines also can finish at the ends of three-phase lines, at upper or lower critical endpoints (UCEPs or LCEPs). If the azeotrope lines are present, end at high pressures on critical lines. For the two first groups the possible nine phase diagrams predicted for van der Waals mixtures are classified according to the nature of their $P$-$T$ projections.

1.6.1 Class 1 of binary mixture diagrams

\textit{Class 1} is formed for binary mixtures with similar gas-liquid critical temperatures, in which the critical points of the pure components are continuously connected by a critical line.

I. One critical line: C$_1$ to C$_2$ (G-L)

I-A. The same as I, including a negative azeotrope.
II. Two critical lines: \(C_1\) to \(C_2\) (G-L); \(C_m\) to UCEP (L-L)

II-A. The same as II, including a positive azeotrope.

Figure 1-5 Schematic P-T diagrams of Class 1 for binary van der Waals mixtures

The type-I diagram is the simplest possible phase behavior, when the gas-liquid critical line has positive slope it represents the locus of LCSTs and when the slope is negative the critical points are UCSTs. For the type-I-A diagram, the slopes of both branches of the critical line are positives and imply LCSTs. Type-II diagram shows the phase behavior for a binary mixture, where the two component vapor-liquid equilibrium lines end in the pure component critical points, \(C_1\) and \(C_2\). The curve dashed line is the critical mixture curve continuously connected from \(C_1\) to \(C_2\). Considering that the liquids are not miscible at all temperatures, a liquid-liquid-gas (LLG) line ending in an UCEP appears at temperatures lower than the critical temperature of either component. The vertical dashed line corresponds to a UCST line, beginning at the UCEP and it represents the effect of pressure on the transition from two liquid phases to one liquid phase.

1.6.2 Class 2 of binary mixture diagrams

*Class 2* is formed for binary mixtures with very different gas-liquid critical temperatures, in which the critical points of the pure components are no connected by a critical line.
III-HA. Two critical lines: $C_1$ to UCEP (G-L); $C_m$ to $C_2$ (L-L to G-L). A three-phase line runs from a UCEP to $p=0$, $T=0$ at lower temperatures than the one-component vapor pressure curves, developing ‘heteroazeotrope’ behavior.

III. The same as III-HA except that the three-phase line lies between the two one-component vapor-pressure curves$^{35}$.

![Type-III-HA](image)

**Figure 1-6 Schematic P-T diagrams of Class 2, type-III for binary van der Waals mixtures$^{35}$**

In the type-III diagram shown in figure 1-6, the components differ in size, shape, and/or polarity. The three-phase line LLG is only intercepted once by the critical mixture curve at the UCEP. The other branch of the critical mixture curve, which begins at $C_2$, never meets the LLG line or the critical point of the lighter component$^{35}$.

IV. Three critical lines: $C_1$ to UCEP (G-L); LCEP to $C_2$ (L-L to G-L); $C_m$ to UCEP (L-L).

![Type-IV](image)

**Figure 1-7 a) Schematic P-T diagrams of Class 2, type-IV for binary van der Waals mixtures; b) Enlargement of the region of the critical endpoints of the type-IV system$^{35}$**
In the type-IV phase diagram, the critical mixture curve is not continuous, but intersects a liquid miscibility region near the critical temperature of the light component. There are three critical lines: the critical mixture curve initiates at C_2 and finishes at the LCST, C_m to UCEP, and the branch of the critical mixture curve begins at C_1 and finishes at a UCEP.

V. Two critical lines: C_1 to UCEP (G-L); LCEP to C_2 (L-L to G-L)

![Type-V diagram](image1.png)

Figure 1-8  a) Schematic P-T diagrams of Class 2, type-V for binary van der Waals mixtures;

b) Enlargement of the region of the critical endpoints of the type-V system

V-A. The same diagram as V, including a negative azeotrope.

![Type-V-A diagram](image2.png)

Figure 1-9 a) Schematic P-T diagrams of Class 2, type-V-A for binary van der Waals mixtures;

b) Enlargement of the region of the critical endpoints of the type-V-A system
The importance of these van der Waals diagrams for small systems is that with a very simple EoS, can lead to qualitative agreement with experimental behavior in a wide range of pressure, temperature and composition.  

1.7 Vapor -liquid and liquid -liquid equilibrium  

1.7.1 Vapor-liquid equilibrium  

In studies of phase equilibria frequently occur the coexistence of vapor and liquid phases, therefore, that type of phase equilibria is widely studied and better understood than any others.  

Any type of equilibrium between phases needs equality of P, T, and partial fugacities of each independent compound throughout the system,  

\[ P_{(1)} = P_{(2)} = P_{(3)} \ldots \text{for all phases} \]  

\[ T_{(1)} = T_{(2)} = T_{(3)} \ldots \text{for all phases} \]  

\[ f_{i(1)} = f_{i(2)} = f_{i(3)} \ldots \text{for all phases} \]  

\[(i = 1, 2, 3 \ldots n \text{ compounds})\]

When the condition of equilibrium occurs only in one phase between a vapor and liquid then,  

\[ f_{iV} = f_{iL} \] \hspace{1cm} (1.49)

The same condition of equilibrium gives in terms of fugacity coefficients  

\[ y_i \phi_{iV} P = y_i \phi_{iL} P \] \hspace{1cm} (1.50)

When the condition of equilibrium occurs under the presence of more than one liquid phase equation 1.50 has to be extended to all of them, i.e. for equation 1.51  

\[ y_i \phi_{iV} P = y_i \phi_{iL} P = y_i^* \phi_{iL}^* P \] \hspace{1cm} (1.51)

It is important to take into account that two or three liquid phases can be present.
1.7.2 Liquid-liquid equilibrium

Equilibrium between liquid phases involves the same thermodynamic pattern as that between a liquid and a vapor phase. Therefore, there is no thermodynamic difference between two types of equilibria and three practical distinctions have to be made:

1. From an experimentally point of view, liquid-liquid equilibria is easier to determine, particularly near of room temperature.
2. There is not EoS for liquids for calculating fugacities or activities.
3. In liquid-liquid equilibria the temperature effect is more accentuated\(^3\).

For researchers, these practical distinctions are not completely clear. Some question still under discussion, these are how to predict properties for pure compounds or for mixtures; how to lead with limited data and how to obtain more experimental data.

After we reviewed these methods and EoS, the work presented here constitutes a new strategy to contribute in this research area. It would be used to predict properties and phase behavior, not only for the existent compounds, but for new materials.
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Chapter 2

Supercritical carbon dioxide and its phase behavior in polymers

During the last three decades supercritical fluids (SCF) solvents have been the center of fascinating research and ongoing programs involving polymers systems. Industrial applications of SCF solvents have been known since the beginning of the 20th century. In 1936, Wilson et al. designed a process for phase equilibrium separation. During the last fifty years, many supercritical phase equilibrium applications have been developed for food and pharmaceutical industrial areas. For example, processes where fine particle formation depends greatly on solute solubility in a supercritical solvent at equilibrium is the supercritical anti-solvent process (SAS), proposed by Dixon et al. The supercritical extraction process of essential oils is another example of the potential applications of phase equilibrium. When the phase equilibrium is concerning to polymer-supercritical carbon dioxide systems, we can find research leading to both experimental and modeling aspects. Carbon dioxide (CO₂) has been tested to provide relevant applications using phase equilibrium properties of binary, ternary and complex mixtures.

A supercritical fluid state is a phase which is neither liquid nor gas; it is a state above the critical temperature and the critical pressure (figure 2-1). The end of the vaporization curve at the critical point denotes that beyond the corresponding temperature and pressure it is impossible to establish clearly the gas state from the liquid one. A supercritical fluid has both the gaseous property of high compressibility and the liquid
property of being able to dissolve materials into their components. More often, its density changes to a great extend in an uninterrupted manner\(^4\). Some properties of supercritical carbon dioxide are summarized in table 2-1. For the construction of figure 2-1 was required equilibrium temperatures and pressures for: the sublimation curve (solid and vapor densities, or vapor volumes); the melting curve (solid and liquid densities); and for the saturation curve (liquid and vapor densities).

![Figure 2-1 Three-dimensional phase diagram of CO\(_2\).\(^4\)](image)

Table 2-1 Some properties for supercritical carbon dioxide

<table>
<thead>
<tr>
<th></th>
<th>(T_c) = 304.12K</th>
<th>(p_c) = 73773 kPa</th>
<th>(V_{mc}) = 94.428 cm(^3)/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Critical point</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Triple point</strong></td>
<td>(T_3) = 216.59K</td>
<td>(p_3) = 5180 kPa</td>
<td>(V_{m,3(g)}) = 29.09 cm(^3)/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(V_{m,3(l)}) = 37.338 cm(^3)/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(V_{m,3(g)}) = 3133.79 cm(^3)/mol</td>
</tr>
<tr>
<td><strong>Density(^5)</strong></td>
<td>1.562 g/ml (solid at 1 atm. and -78.5°C)</td>
<td>0.77 g/ml (liquid at 56 atm. and 20°C)</td>
<td>1.977 g/ml (gas at 1 atm. and 0°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>849.6 g/l (supercritical fluid at 150 atm. and 30°C)</td>
</tr>
</tbody>
</table>
Important parameters of productivity in industry, such as, the rate of production, the maximum pressure and the temperature reached by mixtures using CO₂; are some of the factors which are involved by comprehending phase equilibrium of supercritical solutions.  

2.1 A new equation of state for carbon dioxide

The current state-of-the-art equation of state for carbon dioxide was published by Span and Wagner, which was designed to reduce the disadvantages of previous relationships for carbon dioxide. As mentioned above, from an engineering point of view, carbon dioxide has been the most commonly used solvent for SCF extraction and excellent for build up oil recovery. From a thermodynamic point of view, carbon dioxide has been used as a testing fluid for calibration purposes and as a reference molecule because of its strong quadruple moment. However, technically it is more difficult to accurately calculate carbon dioxide’s thermodynamic properties than for other solvents. Refined multi-property fitting procedures and strategies for optimizing the structure of empirical relationships resulted in the basis for the improvement of an empirical equation of state.

2.1.1 Helmholtz function

The fundamental equation given by Span and Wagner is formulated as a function of the Helmholtz energy, A, with density, ρ, and temperature, T, as independent variables.
The dimensionless Helmholtz energy $\Phi = A / RT$ is commonly separated into a part depending on the ideal gas behavior $\Phi^0$ and a second term that includes the residual fluid behavior $\Phi'$, expressly

$$\Phi(\delta, \tau) = \Phi^0(\delta, \tau) + \Phi'(\delta, \tau) \quad (2.1)$$

where $\delta = \rho / \rho_c$ is the reduced density and $\tau = T_c / T$ is the inverse reduced temperature.

According with these authors all thermodynamic properties of a pure substance can be obtained by combining derivatives of equation 2.1. The vapor pressure and the densities of saturated liquid and saturated vapor can be calculated from a specific equation in $\Phi$ by simultaneous solution of the following equations

$$\frac{\rho_s}{RT \rho'} = 1 + \delta' \Phi^r_\delta (\delta', \tau) \quad (2.2)$$

$$\frac{\rho_s}{RT \rho''} = 1 + \delta'' \Phi^r_\delta (\delta'', \tau) \quad (2.3)$$

$$\frac{\rho_s}{RT} \left( \frac{1}{\rho'} - \frac{1}{\rho''} \right) - \ln \left( \frac{\rho'}{\rho''} \right) = \Phi^r(\delta', \tau) - \Phi^r(\delta'', \tau) \quad (2.4)$$

which correspond to the equality of pressure, temperature, and specific Gibbs energy in the coexisting phases.

2.1.2 Phase equilibria of carbon dioxide

For an improved wide-range equation of state, an accurate description of phase equilibria by auxiliary equations is important and helpful. For phase equilibria of carbon dioxide the data sets published by Span and Wagner$^6$ were divided in three groups: the
data sets used for the improvement of the corresponding relationships, the data sets available for comparisons and some small data sets of those with rather high uncertainty.

For the inclusion of the data sets of the triple-point, they were collected from the published data between 1933 and 1989 and for the new equation Span and Wagner used the data of Duschek et al

\[ T_t = (216.592 \pm 0.003)K \]  
\[ P_t = (0.51795 \pm 0.00010)K \]

For the incorporation of data sets of the critical-point, they were compared from the published data between 1972 and 1991 in tables and for the new equation Span and Wagner selected the data of Duschek et al

\[ T_c = (304.1282 \pm 0.015)K \]  
\[ P_c = (7.3773 \pm 0.0030)MPa \]  
\[ \rho_c = (467.6 \pm 0.6)kg/m^3 \]

For the group of data sets of the melting pressure, two available sets were found of carbon dioxide (1942 and 1960). Unfortunately the information was incongruent with each other and with recent data of triple point pressure. Then, they presented a correlation for the melting pressure

\[ \frac{P_m}{P_t} = 1 + a_1 \left( \frac{T}{T_t} - 1 \right) + a_2 \left( \frac{T}{T_t} - 1 \right)^2 \]  

Using \( T_t=216.592 \text{ K}, P_t=0.51795 \text{ MPa}, a_1=1955.5390 \text{ and } a_2=2055.4593 \)

In the case of sublimation pressure the available data sets resulted more congruent with the available data. The data sets were selected from 1899 to 1984 and could be described by the correlation equation
\[
\ln \left( \frac{p_{\text{sub}}}{p_s} \right) = \frac{T}{T_c} \left\{ a_1 \left( 1 - \frac{T}{T_c} \right) + a_2 \left( 1 - \frac{T}{T_c} \right)^{1.9} + a_3 \left( 1 - \frac{T}{T_c} \right)^{2.9} \right\}
\]  

(2.11)

With \( T_i = 216.592 \) K, \( P_i = 0.51795 \) MPa, \( a_i = -14.740846 \), \( a_2 = 2.4327015 \) and \( a_3 = 5.3061778 \). The latest value for the sublimation temperature at normal pressure (\( P_0 = 0.101325 \) MPa) is \( T = 194.6857 \) K \( \pm 0.0030 \) K iteration with equation 2.11 yields \( T = 194.6855 \) K.

For the vapor pressure, Span and Wagner\(^6\) collected published data from 1902 to 1994 and they selected the ones of Duschek\(^{12}\) et al and formulated the relationship

\[
\ln \left( \frac{p_s}{p_c} \right) = \frac{T_c}{T} \left[ \sum_{i=1}^{4} a_i \left( 1 - \frac{T}{T_c} \right)^{t_i} \right]
\]

(2.12)

with \( T_c = 304.1282 \) K, \( P_c = 7.3773 \) MPa, \( a_i = -7.0602087 \), \( a_2 = 1.9391218 \), \( a_3 = -4.6008549 \), \( a_4 = -10.11178 \), \( a_5 = -29.742252 \), \( t_1 = 0.340 \), \( t_2 = 1/2 \), \( t_3 = 1 \), \( t_4 = 7/3 \) and \( t_5 = 14/3 \).

Lastly, for the caloric data on the liquid-vapor phase boundary, they were reviewed data sets from 1928 to 1994. The specific heat capacity along the saturated liquid line was transformed by Span and Wagner\(^6\) to the specific isobaric heat capacity at saturated liquid density using the relationship

\[
c_p(T) = c_\sigma(T) - \frac{T}{(\rho s)_T} \left( \frac{\partial p}{\partial T} \right) \left( \frac{\partial s}{\partial p} \right)
\]

(2.13)

For the thermodynamic properties, Span and Wagner\(^6\) reviewed data sets from 1903 to 1997. In the temperatures up to 360K and pressures of up to 13MPa, the best \( \rho PT \) relationships found were the data sets of Duschek \textit{et al}\(^ {12}\) and Gilgen \textit{et al}\(^ {13}\). All these measurements were performed using the "two-sinker" buoyancy method which probably provides the most accurate \( \rho PT \) data available today. For the temperatures between 523 K and 698 K and pressures up to 34MPa, they selected the Fenghour \textit{et al}\(^ {14}\) measurements.
Particularly, the description of the data for the specific isobaric heat capacity was separated into data sets which describe the caloric behavior of the ideal gas and data sets which include the residual behavior. They reviewed data sets from 1932 to 1994. While the data set of Bender et al provides an accurate description in the low density region, the data of Ernst and Hochberg and Ernst et al allow the precise description of caloric properties up to 90 MPa. For the description of the supercritical region the best data sets are of the Rivkin and Gukov. (See table 2-2).

Table 2-2 Selected specific isobaric heat capacity of carbon dioxide

<table>
<thead>
<tr>
<th>Data sets</th>
<th>No. of data</th>
<th>Mean $f^4_{\text{st}}$</th>
<th>Uncertainty estimated by the authors</th>
<th>Uncertainty estimated by Span and Wagner</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rivkin, and Gukov</td>
<td>220</td>
<td>0.17</td>
<td>Δ$T$=10mK, Δ$P$=0.05%, Δ$c_p$=2%</td>
<td>Δ$T$=25mK, Δ$P$=0.05%, Δ$c_p$=2%</td>
</tr>
<tr>
<td>*Bender et al 15</td>
<td>60</td>
<td>1.00</td>
<td>Δ$T$=10mK, Δ$P$=0.01%, Δ$c_p$=0.12%</td>
<td>Δ$c_p$=0.1% -0.15%</td>
</tr>
<tr>
<td>*Ernst, and Hochberg</td>
<td>9</td>
<td>2.25</td>
<td>Δ$T$=20mK, Δ$P$=0.1%, Δ$c_p$=0.2-0.9%</td>
<td>Δ$c_p$=0.2% -0.9%</td>
</tr>
</tbody>
</table>
| *Ernest et al 17 | 55          | 1.92                   | Δ$T$=20mK, Δ$P$=0.1%, Δ$c_p$=0.2-0.9% | *The consistency is given instead of uncertainty | *Corrected values
2.1.3 The new equation of state

The new equation of state for carbon dioxide is a fundamental equation expressed in form of Helmholtz energy \(^6\) (see equation 2.14). In conjunction with expressions 2.16 and 2.17, the fundamental equation is constrained to the critical parameters given in the previous section. This equation is valid for the entire fluid region covered by reliable data, specifically for \(216\text{K} \leq T \leq 1100\text{K}\) and \(0 \text{ MPa} \leq P \leq 800 \text{ MPa}\) in the homogeneous region and on the liquid-vapor phase boundary within their experimental uncertainty.

\[
\frac{A(\rho,T)}{RT} = \Phi(\delta, \tau) = \Phi^0(\delta, \tau) + \Phi^\tau(\delta, \tau) \quad (2.14)
\]

where \(\delta = \rho/\rho_c\) and \(\tau = T_c/T\) with \(\rho_c = 467.6\text{kg/m}^3\) and \(T_c = 304.1282\text{K}\).

The ideal-gas part of the Helmholtz energy is given by

\[
\frac{c_p^0(T)}{R} = 1 + a_3^0 + \sum_{i=4}^{8} a_i^0 \left( \theta_i^0 \tau \right)^2 \frac{\exp \left( \theta_i^0 \tau \right)}{\left[ \exp \left( \theta_i^0 \tau \right) - 1 \right]^2} \quad (2.15)
\]

The expression of \(\Phi^0(\delta, \tau)\), which has been derived from equation 2.15 by integration is

\[
\Phi^0(\delta, \tau) = \ln(\delta) + a_1^0 + a_2^0 \tau + a_3^0 \ln(\tau) + \sum_{i=4}^{8} a_i^0 \ln \left[ 1 - \exp \left( -\tau \theta_i^0 \right) \right] \quad (2.16)
\]

The coefficients \(a_i^0\) and \(\theta_i^0\) are given in table 2-3 and there were published by Span and Wagner\(^6\) with all significant digits.
Table 2-3 Coefficients for the equations 2.15 and 2.16, for \(c_p^0\) and \(\varphi^0\), respectively

<table>
<thead>
<tr>
<th></th>
<th>(a_i^0)</th>
<th>(\varphi_i^0)</th>
<th></th>
<th>(a_i^0)</th>
<th>(\varphi_i^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.373</td>
<td>5</td>
<td>6</td>
<td>0.621</td>
<td>6.112</td>
</tr>
<tr>
<td>2</td>
<td>-3.705</td>
<td>6</td>
<td>7</td>
<td>0.412</td>
<td>6.777</td>
</tr>
<tr>
<td>3</td>
<td>2.500</td>
<td>7</td>
<td>8</td>
<td>1.040</td>
<td>11.324</td>
</tr>
<tr>
<td>4</td>
<td>1.994</td>
<td>3.152</td>
<td>8</td>
<td>0.083</td>
<td>27.088</td>
</tr>
</tbody>
</table>

The residual part of the Helmholtz energy can be formulated

\[
\varphi^r = \sum_{i<j}^{7} n_i \delta^d \varphi^{i+1} + \sum_{i=8}^{34} n_i \delta^d \varphi^{i+1} e^{-\delta^d i} + \sum_{i=35}^{39} n_i \delta^d \varphi^{i+1} e^{-\alpha_i (\delta^d i)^2 - \beta_i (\varphi^d i)^2} + \sum_{i=40}^{42} n_i \Delta^d \varphi^{i+1} e^{-\gamma_i (\delta^d i)^2 - \delta_i (\varphi^d i)^2}
\]

with \(\Delta = \{(1 - \tau) + A_i [(\delta - 1)^2]^{1/(2\beta_i)}\}^2 + B_i [(\delta - 1)^2]^{\alpha_i}\)  

(2.17)

The parameters for equation 2.17 were published by Span and Wagner and can be found in the original publication\(^6\).

For the basic properties of carbon dioxide such as pressure, enthalpy and fugacity, this fundamental equation for carbon dioxide provides good results within the whole region of chemical stability.

2.2 Interaction of carbon dioxide with polymers and solutes

The phase behavior of a polymer in a given solvent depends on polymer molecular weight, polydispersity, degree and type of chain branching as well as solvent quality\(^20\). Carbon dioxide has been promoted as the solvent option for many industrial
applications because it is inexpensive; it has a critical temperature close to room temperature, a moderate critical pressure, and a density higher than most SCF.

To form a stable polymer-SCF solvent solution at a given pressure and temperature, the Gibbs free energy must to be negative and at a minimum\(^\text{21}\). The Gibbs free energy of mixing is

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}
\]

where \(\Delta H_{\text{mix}}\) is the enthalpy of mixing, \(T\) is temperature and \(\Delta S_{\text{mix}}\) is the entropy of mixing. The polymer segment-segment, solvent-segment and polymer segment-solvent interaction energies and the solution density, determine the enthalpic interactions. While, the entropy interactions, so-called equation of state effect, is determined by the combinatorial entropy of mixing and the non-combinatorial contribution associated with the volume change on mixing\(^\text{22}\). The principles of molecular thermodynamics achieve a norm for quantifying the interactions that regulate the phase behavior of polymer-SCF mixtures.

The expected solvent properties of carbon dioxide depend on the previous conditions dictated by the Gibbs free energy of mixing. Therefore, taking into account the CO\(_2\) properties summarized in table 2-1, CO\(_2\) at high temperatures is not expected to be a good solvent\(^\text{20}\). But it does have a strong quadrupole moment due to structural symmetry. This influences its behavior as a solvent. CO\(_2\) is not a strong solvent for very polar polymers especially at low temperatures in which polar interactions are magnified; in contrast, CO\(_2\) is a weak solvent for nonpolar polymers in which its quadrupolar interactions dominate the interchange energy as the temperature is lowered. Kirby and McHugh\(^\text{20}\) reviewed the solvent properties of carbon dioxide. They proved those
hydrocarbon polymers containing fluorinated groups exhibit a good to high degree of solubility in CO$_2$. Also they show both polar and nonpolar character of CO$_2$ and that it does not dissolve polyolefins with molecular weight greater than a few thousands. Thus, the unique solubility properties of CO$_2$ still need to be interpreted, and to evaluate the properties of scCO$_2$ continue been a fascinating topic.

2.3 Solubility in carbon dioxide

There is an increasing interest in continuing development of CO$_2$-soluble polymers. If we can identify CO$_2$-polymer solubility behavior, then more new CO$_2$-soluble polymers can be found. One alternative is to study structure-CO$_2$ solubility relationships. Bray et al$^{23}$ suggested that small structural changes in some polyesters will help to improve CO$_2$ solubility. For solubility of linear alkyl polyesters, fine variations of these compounds influence its solubility in scCO$_2$. Polyesters with odd number of carbon atoms in the diacid moiety exhibit greater solubility than the even-numbered members. For solubility of acyl branched polyesters, they suggested two ways to improve solubility: a) increasing the degree of acylation and, b) increase the length of the acyl chains and molecular weight. Acylation adds a chain branch to the polymer; this increases the free volume of the polymer which enhances solubility in a supercritical solvent$^{24}$. Branching also reduce the intermolecular interactions between polymer segments that arise through short-range molecular orientation offered by a high content of linear segments without pendant groups$^{25}$. This should enhance solubility. Lastly, Bray et al suggested the possibility of designing alkyl polyesters with increased frequency of acyl
branching of varying lengths will result in better solubilities which should increase the number of applications for CO$_2$ as a solvent.

Within the past two decades, there has been increased attention oriented at designing highly functionalized poly (p-phenylenes) (PPPs), along with affordable techniques to process them. Functionalized PPPs can be very soluble in a conventional liquid organic solvent, which suggests that the use of a SCF solvent would also be an alternative$^{26}$. Results show that fluorooctyl poly (p-phenylene) is extremely soluble in CO$_2$ as it only takes ~ 6.8 MPa at 25°C to dissolve this polymer; which show that the family of PPP polymers can be dissolved in SCF solvents at discreet operating conditions.

According with Kirby$^{20}$ et al other important factor that increases SCF solvent quality is the polarizability. Several authors have claimed that the solvent properties of CO$_2$ should be compared to those of toluene$^{27}$, acetone$^{28}$ and hexane$^{27}$ (see table 2-4). However, the reduction in cloud-point pressure is less dramatic as the size of the solvent increases or, stated differently, as the solvent quality increase. An example of experimental co-polymer-SCF data, Bungert$^{29}$ et al, showed $P$-$T$ results for polystyrene/cyclohexane/carbon dioxide. The temperature range studied was 140-240 °C at pressures from 0 to 160 bars. Their experiments considered polystyrene molecular weights from 40,000 to 160,000 g/mol.

In the case of cosolvent or antisolvent effects, Kirby$^{20}$ et al mentioned several factors that can be associated with enhancing solubility. Some cosolvent factors are free volume differences, favorable physical interactions, combination of polar co-solvent with polar polymers, and hydrogen bonding interactions. Other co-solvent studies have been
performed when a SCF solvent is added into solution with the deliberate intent of decreasing the solvent quality of the liquid solvent to precipitate the polymer from solution. In this instance, the SCF is an antisolvent. The antisolvent effect is magnified when the operating temperatures are well above the critical point of the supercritical solvent.

Table 2-4 Physical properties of some supercritical solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_c$ (°C)</th>
<th>$P_c$ (bar)</th>
<th>$\alpha \times 10^{25}$ (cm$^3$)</th>
<th>Dipole moment $\mu$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>235.05</td>
<td>48.4</td>
<td>63.30</td>
<td>2.9</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>31.0</td>
<td>73.8</td>
<td>27.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>32.3</td>
<td>48.8</td>
<td>45.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Hexane</td>
<td>234.1</td>
<td>29.7</td>
<td>118.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>320.05</td>
<td>41.1</td>
<td>123.1</td>
<td>0.36</td>
</tr>
<tr>
<td>Trifluromethane</td>
<td>26.2</td>
<td>48.6</td>
<td>26.5</td>
<td>1.6</td>
</tr>
</tbody>
</table>

2.4 Application of SCF in bioprocess industries and polymer processing

Biotechnological applications such as removal of biostatic agents from fermentation broths, supercritical disruption of microorganisms, destruction of industrial waste, gas-antisolvent crystallization and micro-size particle formation, have been topics of increased interest. Supercritical-carbon dioxide is the most commonly used fluid and its low critical temperature and pressure make it an ideal medium for processing volatile
products. Non-toxicity, non-flammability, the selectivity of the process, and the ease of recovery are the more important features. Processes that use CO$_2$ do not add directly to the house green effect but rather add in the reduction of emitted CO$_2$. Introduction of scCO$_2$ to a liquid decrease the overall viscosity and thus facilitates the handling of the compound and enhances mass transfer from the liquid to SC phase. To enumerate all the applications in bioprocesses of many SCF are beyond the scope of this work; thus, only few of them that involve scCO$_2$ and polymeric materials will be presented here.

In the polymer industry, scCO$_2$ extraction can be an alternative for the de-solvent process of polymer solutions. The drying process can be reduced due to scCO$_2$ capability of complete recovery by depressurizing. ScCO$_2$ can dissolve typical polymerization solvents, n-hexane or toluene at higher temperatures. The design of the de-solvent process requires quantitative information on the distribution of organic solvent between the polymer solution and the scCO$_2$ phase.

In the biomedical industry, supercritical fluid extraction of residual cyclics from medical devices is attractive. Cyclic and low molecular weight oligomer content can be as high as 4 wt%, and extraction with scCO$_2$ can reduce the level of these species to less than 10 ppm.

The possibility of produce different solid shapes and structures at low temperature with minimum amount of residual organic solvents is other advantage of applying SCF in polymer processing. ScCO$_2$ has been employed as an antisolvent for processing value added materials e.g. hyaluronic acid-base biopolymers.

A major disadvantage in SCF application for biomolecules is the difficulty in measurement and prediction of their solubility in SCF at various pressures and
temperatures for process optimization\textsuperscript{34}. This fact is one of our motivations of this work in which solubility of alkyl chains and other compounds will be studied.
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Chapter 3

Correlation and prediction of fluid-fluid equilibria of carbon dioxide - aromatics and carbon dioxide - dichlorobenzoates binary mixtures

3.1 Introduction

The use of low molecular weight fluorine-containing compounds in supercritical CO$_2$ and other supercritical fluids is becoming increasingly important in the design of medicines, pesticides and herbicides, polymerization, materials processing, lithographic processes, biomaterials and film deposition [see references 1, 2, 3, 4, 5, 6 and references therein]. Recently, it has been shown$^7$ that alkyl ester functionalized poly-$p$-phenylene polymers (PPP) can be dissolved in supercritical CO$_2$ at modest conditions. The building blocks in the synthesis of PPP are the 2,5-dichlorobenzoates. Moreover, the presence in the monomer ring molecule of an alkyl ester chain of appropriate length, especially if fluorinated, may make the poly-$p$-phenylene polymers CO$_2$-philic. This opens the possibility of using supercritical CO$_2$ as a suitable solvent for the separation, synthesis and dissolution of these PPP materials$^8$. Unfortunately, highly fluorinated compounds are expensive, and thus there is great incentive to design new, inexpensive CO$_2$-philic groups. In order to design these new fluorinated compounds, with tailored solubility in CO$_2$, knowledge and understanding of the phase equilibria of these mixtures is essential.

Some experimental and theoretical phase equilibria data are available in the open literature for the neat perfluoralkane-CO$_2$ systems. For example, Iezzi et al.$^9$ obtained the phase behavior of CO$_2$ + $n$-hexane and CO$_2$ + $n$-perfluorohexane and showed that the differences in phase behavior between both binary systems are consistent with the differences in pure component critical parameters. SAFT-VR was used by Colina et al.
for the prediction of vapor-liquid (VLE) and vapor-liquid-liquid equilibria (VLLE) of binary and ternary systems of \( \text{CO}_2/n\text{-perfluoroalkane}/n\text{-alkane} \)\(^{10,11}\).

For mixtures of \( \text{CO}_2 \) with several semi-fluorinated, FDCB, and non-fluorinated, ADCB, Shen \textit{et al.}\(^{12}\) reported experimental isopleths and solution densities. They found that the solubility of the alkyl 2, 5-dichlorobenzoates decreases significantly as the alkyl chain length increases, although this effect is less pronounced when the chain is fluorinated, especially for the longer alkyl chains. They noted that the pressure needed to dissolve a benzoate in \( \text{CO}_2 \) exhibits a minimum with respect to alkyl chain length, even when the alkyl chain is fluorinated. They also reported that when using the cubic equation of state (EoS) of Peng and Robison\(^{22}\), their modeling was not able to capture the non-monotonic behavior of the change in mixture-critical pressure with increasing alkyl chain length observed with the FDCB.

It is amply known that \( \text{CO}_2 \) and aromatics have strong quadrupole moments, and that dichlorobenzoates exhibit both dipolar (ester linkage) and quadrupolar (aromatic) interactions. Additionally it is also known that \( \text{CO}_2 \) forms a weak interaction with fluorine atoms, decreasing the fluid-fluid immiscibility region. Thus, it might appear at first unreasonable to attempt to correlate the phase equilibria of these systems with cubic EoS or even with “simpler” versions of molecular-based EoS which make no explicit provision for such complex interactions. Nevertheless, our objective here is to test the possibility of using these algebraically simple EoS to correlate the experimental phase behavior of these challenging systems. To accomplish this, the influence of \( \text{CO}_2 \) quadrupole moment on the properties of the binary mixtures can be accounted for effectively through a binary interaction parameter, \( k_{ij} \). Moreover, this binary interaction
parameter might be constant for each system (i.e. independent of temperature and composition in the range of study) and thus provide an effective way to account for the different (polar) interactions in binary systems composed of (supercritical) CO$_2$ and aromatics or ADBC. Although the study of the VLLE at conditions close to the critical point of CO$_2$ is outside the scope of the present work, it is worth mentioning that the representation of type III phase diagrams, including VLLE lines, is well within the capabilities of both cubic EoS $^{13}$ and the SAFT approach$^{11}$.

Specifically, therefore, in this work we explore the capabilities and usefulness of several cubic EoS (PR, SRK, SOF-PR, SOF-RK) as well as a molecular-based EoS, PC-SAFT, for correlating the two phase fluid-fluid regions of several demanding binary mixtures of aromatics as well as dichlorobenzoates (alkyl and semi-fluorinated) with supercritical CO$_2$.

Table 3-1 Schematic representation of compounds studied in this work

<table>
<thead>
<tr>
<th>AROMATICS</th>
<th>DICHLOROBENZOATES</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>STRUCTURE</strong></td>
<td><strong>NAME</strong></td>
</tr>
<tr>
<td></td>
<td><strong>C$_6$H$_6$</strong></td>
</tr>
<tr>
<td>BORONITE</td>
<td>TOLUENE</td>
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<tr>
<td></td>
<td>m-XYLENE</td>
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<tr>
<td></td>
<td>o-XYLENE</td>
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<td></td>
<td>p-XYLENE</td>
</tr>
<tr>
<td></td>
<td>METHYLbenzoate</td>
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<td></td>
<td>ETHYLbenzoate</td>
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</tbody>
</table>
3.2 Methods

3.2.1 Cubic equations of state and the SOF cohesion function

Cubic equations of state are the simplest thermodynamic models capable of representing fluid phase equilibrium. For example, they have been the foundation of the well-known theoretical global phase diagrams of van Konynenburg and Scott\textsuperscript{14}, were the van der Waals EoS was used for a wide variety of binary fluid mixtures. Although cubic EoS lack the more rigorous theoretical foundation of molecular-based models, their semi-empirical nature may actually work to their advantage, giving them a flexibility that is absent from more complex EoS. A case in point is the temperature dependence of “2P1T” cubic EoS, so called because they contain two fluid-specific parameters $a$ and $b$, with only $a$ depending on temperature. This class of cubic EoS can be written in general as

$$
\begin{align*}
\frac{P}{RT} = & \frac{a_c \alpha(T_r)}{Q(v)} - \frac{a_c \alpha(T_r)}{Q(v)} \\
Q(v) = & v^2 + k_1 bv + k_2 b^2
\end{align*}
$$

(3.1)

where $b$ is the covolume parameter, $a$ is the attraction parameter which has the value $a_c$ at the critical temperature $T_c$, and $\alpha \equiv a/a_c$ is the cohesion parameter or alpha function which depends on reduced temperature $T_r \equiv T/T_c$. The names given to these parameters reflect the common reading of Eq. (3.1) as a sum of repulsive and attractive pressures, despite the fact that the same EoS can be derived in many alternative ways, each supporting a different interpretation\textsuperscript{15}, and that neither the repulsion nor the attraction term is theoretically correct\textsuperscript{16}. The repulsion term gives only a first-order approximation to the virial expansion of hard-sphere fluids \textsuperscript{17} and works in practice only by using a covolume that is a fraction of the true value derived from molecular diameters\textsuperscript{18}. Rather than
improving this term, however, cubic EoS developers have sought to counteract its shortcomings by modifying the complementary attraction term, which has evolved from $k_1 = k_2 = 0$ in the van der Waals EoS$^{19}$, to $k_1 = 1$, $k_2 = 0$ in the Redlich-Kwong EoS$^{20,21}$, $k_1 = 2$, $k_2 = -1$ in the Peng-Robinson EoS$^{22}$, and many other empirical forms that can be justified only in terms of *ad hoc* intermolecular potentials or partition functions$^{23,24}$.

In earlier EoS of the 2P1T class, the alpha function was an integral part of the model, e.g. $\alpha = 1$ (constant $a$) in the original van der Waals EoS or $\alpha = T_r^{-1/2}$ in the Redlich-Kwong EoS$^{20}$. However, Wilson$^{25}$ and Soave$^{21}$ showed that the temperature dependence could be tailored to fit the experimental saturation pressure of pure fluids, improving the general prediction of fluid properties and especially phase equilibria. Many such functions have been proposed in the literature; several reviews are available$^{16,26,27}$. Most of these proposals adhere to the debatable repulsion/attraction interpretation of the EoS, limiting for instance $\alpha$ to positive values only$^{28,29}$. This is the case for instance with the alpha function originally proposed by Soave$^{21}$ and later adopted also by Peng and Robinson$^{22}$,

$$\alpha = \left[ 1 + m \left( 1 - T_r^{1/2} \right) \right]^2 \quad (3.2)$$

Given that the attraction term is essentially empirical, there is no real reason to rule out negative values of $\alpha$. Such values, if they arise, should appear at supercritical temperatures, because $\alpha$ equals unity by definition at the critical temperature, and decreases with increasing temperature. Mollerup$^{30}$ computed supercritical values of $\alpha$ from the critical isochore, which is a natural extension of the vapor pressure curve, and found that $\alpha$ for nitrogen, became negative at high temperatures (although he felt obliged to call these negative values “deprived [of] any physical significance”). Colina *et al.*$^{31}$
showed that negative supercritical values of $\alpha$ also follow naturally from second virial coefficients and Joule-Thomson inversion curves, and from extrapolation of subcritical (i.e. based on vapor pressures) values using $\alpha$ functions not constrained artificially to positive values only. Abbott$^{15}$ remarked that even if the repulsion term in Eq. (3.1) was replaced by a more accurate hard-body formula, the attraction term would still become negative at high temperatures due to contributions from soft repulsions.

The prohibition of negative $a$ or $\alpha$ may have originated in the behavior of the original van der Waals EoS, for which $a$ is a constant and the residual internal energy is given by

$$u^g - u \equiv -u^r = \frac{a}{v}$$

(3.3)

From physical arguments $-u^r$ should be positive, because energy must be supplied to separate the molecules of a real fluid to convert it into an ideal gas. This implies that $a$ should not be negative, and justifies its interpretation as an energy parameter$^{32}$ or cohesion parameter, because $-u^r$ is usually identified with the cohesive energy of a fluid$^{33}$. This convenient interpretation, however, disappears once $a$ is made temperature dependent, as in all modern 2P1T cubic EoS. In this case, the above expression becomes$^{34}$

$$-u^r = \frac{a}{v} - T \left( \frac{da}{dT} \right) = \frac{a_c}{v} \frac{d(\alpha / T_r)}{d(1/T_r)} \equiv \frac{a_c}{v} \beta(T_r)$$

(3.4)

Results for other 2P1T EoS are similar, differing only in the volume term$^{31,35}$. The requirement is thus that $\beta$, not $a$ or $\alpha$, be positive, i.e. that $\alpha/T_r$ be an increasing function of $1/T_r$. 

\[ \beta \equiv \frac{d(\alpha / T_r)}{d(1/T_r)} > 0 \]  

(3.5)

The inverse relation, giving \( \alpha \) in terms of \( \beta \),

\[ \alpha(T_r) = T_r \left[ 1 - \int_1^{T_r} \frac{\beta}{T_r^2} dT_r \right] \]  

(3.6)

shows clearly that \( \alpha \) may become negative if the upper integration limit is high enough.

We use in the present work the previously developed SOF cohesion function based on the above considerations\(^{34,35} \)

\[ \beta = \frac{m}{T_r^{n-2}} \Rightarrow \alpha = T_r \left[ 1 + \frac{m}{n-1} \left( \frac{1}{T_r^{n-1}} - 1 \right) \right] \]  

(3.7)

The two characteristic constants, \( m \) and \( n \) have been determined for 846 fluids taken from the DIPPR\(^ {36} \) compilation. Parameter sets are available for use with the van der Waals, Redlich-Kwong and Peng-Robinson EoS. Extended corresponding-states correlations, in terms of acentric factor \( \omega \) and critical compressibility factor \( Z_c \), have also been developed to estimate parameters for fluids not in the database\(^ {35} \)

\[ m = c_0 + c_1 Z_c + c_2 \omega \]  

(3.8a)

\[ N = \frac{0.7 l - n - 1}{n - 1} = \frac{d_0 + d_1 \omega}{m} \]  

(3.8b)

with coefficients given in reference 35 and presented in Appendix A, Table A-1, for completeness. Below, we present a polynomial approximation that avoids iterative solution of Eq (3.8b) and yields parameter \( n \) with accuracy better than \( 1 \times 10^{-5} \) in \( 1 < n < 4 \):

\[ n = -154.54120445 N^6 + 538.50604746 N^5 - 802.39608278 N^4 + 665.38319777 N^3 \\
-335.57724443 N^2 + 108.56966563 N - 16.02899516 \]  

(3.9)
Modeling the CO₂–DCB phase equilibria with cubic EoS requires estimation of critical properties and acentric factors of the ADCB and FDCB. We have used estimation tools reviewed in the most current edition of The Properties of Gases and Liquids. Estimates of $T_c$, $P_c$, $V_c$ and normal boiling temperature $T_b$ were obtained using the group contribution methods of Constantinou and Gani, Marrero and Gani and the Joback and Lydersen techniques as implemented in the Cranium Lite® software by Molecular Knowledge Systems, Inc. (free download). The only group contribution method that permits direct estimation of acentric factors, due to Constantinou et al., is unfortunately not applicable to the ADCBs, because parameters are not available for the first-order groups ACCl, CF₂, COO and second-order group ACCOO. Acentric factors were therefore estimated in all cases from $T_c$, $P_c$ and $T_b$ using the corresponding states correlation of saturation pressures by Ambrose and Walton as recommended by Poling et al.

It follows that neither $Z_c$ (computed as $P_cV_c/(RT_c)$) nor $\omega$ used to obtain the SOF parameters $m$ and $n$ from Eq (3.8) are direct estimate, but is derived from other estimates. As pointed out by Liu and Chen, this greatly increases the uncertainty of these predicted properties. In order to gain an approximate idea of the reliability and suitability of the above-mentioned methods for the compounds in the present study, properties were estimated for the simpler related fluids benzene, toluene, xylene (o-, m- and p-), methylbenzoate and ethylbenzoate. Comparison of the estimates against reference values read from the DIPPR compilation showed that the methods of Constantinou and Gani, and Marrero and Gani, with second order contributions as required, gave substantially
lower maximum and average errors. The resulting values of \( m \) and \( n \) computed from Eq. (3.8) were quite similar to the optimal values already available for the same fluids in the SOF database. Finally, considering that the Marrero and Gani method is the only one to include (as a second order contribution) the effect of the triple substitution on the aromatic ring (two Cl, one COO-R in the present case for all the ADCBs studied), we selected this method as appropriate for the task in hand. The estimated critical properties, acentric factor and SOF parameters are summarized in Table 3-2. For CO\(_2\) we used the following values taken from the DIPPR compilation: \( T_c = 304.19 \) K, \( P_c = 7361.73 \) kPa, \( Z_c = 0.274 \), \( \omega = 0.226446 \), with SOF parameters RK: \( m = 1.8474 \), \( n = 2.3144 \) and PR: \( m = 1.6885 \), \( n = 2.3817 \).

Finally, application of cubic EoS to mixtures requires a prescription for the computation of the mixture parameters \( a_m \), \( b_m \) from those of the pure constituents \( a_{ii} \), \( b_{ii} \). We use in this work the simplest mixing and combination rules of the van der Waals one-fluid type,

\[
\begin{align*}
  a_m &= \sum_i \sum_j (1-k_{ij}) (a_{ii} a_{jj})^{1/2} \\
  b_m &= \sum_i x_i b_{ii}
\end{align*}
\]

where \( k_{ij} \) are the binary interaction parameters. For binary mixtures, such as considered in the present work, a single interaction parameter \( k_{12} = k_{21} \) is required, because \( k_{11} = k_{22} = 0 \) by definition.
Table 3-2 Estimated properties of pure alkyl 2, 5-dichlorobenzoates

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_e$ / K(a)</th>
<th>$P_e$ / bar(a)</th>
<th>$Z_e^{(a)}$</th>
<th>$\omega^{(a)}$</th>
<th>$m^{(c)}$</th>
<th>$\rho^{(c)}$</th>
<th>$m^{(e)}$</th>
<th>$n^{(e)}$</th>
</tr>
</thead>
</table>
| Non-fluorinated
| Propyl 2,5-DCB | 776.63        | 25.261        | 0.23662     | 0.47922       | 2.06417   | 2.45776     | 2.23085   | 2.44522   |
| Octyl 2,5-DCB  | 824.84        | 17.435        | 0.22532     | 0.52003       | 2.11622   | 2.48481     | 2.28671   | 2.47254   |
| Semi-fluorinated
| Pentfluoro Propyl 2,5-DCB | 772.94        | 20.47         | 0.21792     | 0.43047       | 1.97885   | 2.48339     | 2.1386    | 2.47181   |
| Tridecafluoro Octyl 2,5-DCB | 808.83        | 14.12         | 0.23532     | 0.42615       | 1.98498   | 2.45001     | 2.14553   | 2.43776   |

(a) Method of Marrero and Gani\(^{38}\) with second-order contributions
(b) Method of Ambrose and Watson\(^{41}\)
(c) From equations (3.8a, b) and (3.9)

3.2.2 Statistical Associating Fluid Theory (SAFT)

SAFT\(^{43}\) and its variations is a widely used molecular based equation of state (MBEoS) for solution thermodynamics\(^{44,45}\). It has a strong theoretical basis, and its accuracy for many different systems has made it an increasingly popular model in the chemical process industry. SAFT was used by Colina et al.\(^{46}\) for the calculation of the phase behavior of a fluorinated polymer, poly (1, 1, 2, 2-tetrahydroperfluorooctyl acrylate) or PTAN, in supercritical CO\(_2\). Linear and perfluorinated alkanes have been studied within the SAFT-VR approach by McCabe et al.\(^{47}\), and by Dias et al. within the soft-SAFT approach\(^{48}\) among others. In a recent application, SAFT-VR was also used by Colina et al. for the prediction of VLE, LLE and VLLE of binary and ternary systems of CO\(_2\)/n-perfluoroalkane/n-alkane\(^{10,11}\). Comparisons against the available experimental and molecular simulation\(^{49}\) data showed that the predicted diagrams provide a good representation of the phase equilibria.
In the last few years, dipolar, quadrupolar and mixed interactions have been incorporated explicitly into several molecular-based EoS $^{50, 51, 52, 53}$. The polar terms are generally rooted to the perturbation theory of Stell and co-workers for simple polar fluids$^{54}$. Crossover terms have also been recently develop for some MB-EoS $^{55, 56, 57}$. In this work, however, we are interested in comparing on equal terms the performance of several cubic EoS with the widely use PC-SAFT model, and thus we intentionally avoid for now the inclusion of additional terms to account explicitly for associating and polar interactions. The reader is referred to the works by Gross and Sadowski$^{60}$ and Tumakaka and Sadowski$^{58}$ for further details.

### 3.2.3 PC-SAFT

The PC-SAFT EoS proposed by Gross and Sadowski$^{59, 60}$ assumes (non-associating) molecules to be chains formed by $m$ spherical segments of identical diameter $\sigma$, and characteristic energy, $\varepsilon/k$. For relatively small molecules, they are usually fitted to vapor pressure and liquid density data. Associating fluids (not considered in this work) require two additional compound parameters, the association energy ($\varepsilon_{AB}$) and the association volume ($\kappa_{AB}$). The compressibility factor, $Z$, is of the form: $Z = 1 + Z_{\text{ref}} + Z_{\text{chain}} + Z_{\text{disp}} + Z_{\text{assoc}}$. Here $Z_{\text{ref}}$ is the contribution of the hard-sphere chain reference system, $Z_{\text{chain}}$ is the additional contribution due to the formation of chain, $Z_{\text{disp}}$ is the dispersion component, and $Z_{\text{assoc}}$ is the contribution due to association. The reader is referred to the works by Gross and Sadowski$^{59, 60}$ for more details.
3.2.4 Group contribution approaches

Several group contribution methods are available in the literature for the SAFT-type EoS. As discussed in section 3.2.1 the second class GC approaches include methods that attempt to capture fine structural differences by additionally introducing second-order groups. Considering that the GC parameters for PC-SAFT are available in the literature using the second order contribution of Constantinou and Gani, we elected to choose this method for the PC-SAFT approach. Tihic et al. based their work on a database of 400 low-molecular weight compounds, and estimated the group contribution (GC) parameters for the PC-SAFT EoS by fitting experimental liquid densities and vapor pressures. This method does not consider explicitly, however, the effect of the triple substitution (two Cl, one COO-R) on the ADCB aromatic ring.

3.3 Results and discussions

Predicted VLE for the CO₂-toluene binary system from the PR and PC-SAFT equations (with \( k_{ij} = 0 \)) are shown in Figures 3-1 and 3-2 respectively, together with the experimental values reported by Ng and Robinson. Also shown are the results for the best fit (as determined by minimizing the error among the calculated and experimental pressures at different temperatures.)

In Fig. 3-1 it can be seen that the PR EoS gives a reasonable agreement with the experimental data even with \( k_{ij} = 0 \). The largest deviations from the predicted curve occur, as expected, in the liquid branch, and can be considerably reduced by using \( k_{ij} = 0.0845 \) for better agreement with the experimental data available. Overall, these
predictions can be considered very good, given the pseudo-empirical model used. Similar results were obtained for the SRK, SOF-RK, PR, and SOF-PR EoS for 353.4 K, 373.2 K, and 393.2 K as shown in figure A-3 of the appendix A. For example the predictions obtained for the SOF-PR at 352.59 K visually overlap with the PR predictions and thus are not shown in figure 3-1. It is also important to highlight that only a temperature independent binary interaction parameter was used for each EoS as reported in Table 3-4.

![Figure 3-1 CO₂-toluene, T = 352.59K, △ experimental data; red dashed line, PR, kᵢⱼ=0; blue continuous line PR, kᵢⱼ = 0.0845.](image)

In figure 3-2 is shown the predictions obtained with the original PC-SAFT EoS, with parameters given by Gross and Sadowski and reported in Table 3-3. In this case the shape of the curve in the liquid branch is concave instead of slightly convex. However, when a small temperature independent binary interaction parameter is included, the correct behavior is obtained. Also shown in Fig 3-2, are the results for this system using the GC-PC-SAFT. It can be observed that the results are practically equivalent to those
obtained with the PC-SAFT parameters reported by Gross and Sadowski (PC-SAFT). Similar results were obtained at 353.4 K, 373.2 K and 393.2 K as reported in figure A-4 of the appendix A.

![Figure 3-2 CO₂-toluene, T = 352.59K, Δ experimental data; thin red line, PC-SAFT; pink dashed line, GC-PC-SAFT, k_ij=0; blue continuous line PC-SAFT, k_ij = 0.12.](image)

In figures 3-3 and 3-4 are shown the predictions for the system CO₂-benzene at 353 K (as well as in figures A-1 and A-2 for other temperatures). In figure 3-3 we compare the results of the predictions obtained with the PR EoS and the SOF-PR EoS with k_ij = 0. The behavior is similar to that obtained in figure 3-1. Although in this case the amount of experimental data available is scarce, it is clear from figures 3-1 and 3-3 that these cubic EoS (as well as SRK and SOF-RK) with constant (nonzero) k_ij parameters are able to correlated (and predict) adequately the phase behavior for the system under study.
Similarly in figure 3-4 the predictions for the PC-SAFT EoS exhibit a concave shape that is readjusted with the use of a constant $k_{ij}$. Again, predictions with the GC-PC-SAFT are similar to those obtained with the PC-SAFT parameters obtained from saturation pressures and liquid densities by Gross and Sadowski. It can also be observed that the inclusion of a higher $k_{ij}$ for the PC-SAFT models, unlike the case of the cubic EoS studied, has a noticeable impact on the predicted compositions of the vapor phase.

Similar results were obtained for the VLE of several systems, e.g. CO$_2$ with $p$-, $m$-, $o$- xylene as shown in the appendix A (figures A-5 to A-10). In general, for these small molecule binary systems, the simpler cubic EoS appear to be able to capture correctly the VLE region, and in better agreement when compared with the PC-SAFT. This might be related with the well-know over-prediction of the critical point from the original versions of the SAFT approach (without cross-over terms), whereas cubic EoS satisfy this critical point exactly for the pure fluids.

Figure 3-3 CO$_2$-benzene, $T = 353$ K, □ experimental data$^{68}$; think red line, PR, $k_{ij}$=0; pink dashed line, SOF-PR, $k_{ij}$=0; blue continuous line SOF-PR, $k_{ij} = 0.0828$
It is know that comparisons of any model with experimental LLE data provide a much more rigorous test. Thus, we now turn our attention to not only LLE but to most the demanding systems such as the CO$_2$-benzoates family. As mentioned before, when polar compounds such as methylbenzoate are treated, the SAFT equations can be extended by adding a multipolar term to account for dipolar or quadrupolar interactions, e.g. as recently reported$^{64}$ for the case of binary mixtures of methylbenzoate with some alkanes. However, this consideration is outside the scope of this work, since our main objective is to test the “simpler” cubic EoS for these systems, and for comparison we are presenting results obtained with the original PC-SAFT EoS as well. In figure 3-5 are shown the VLE and LLE of CO$_2$-methylbenzoate, ethylbenzoate and propyl 2, 5 -dichlorobenzoate binary systems. For these organic compounds neither the critical properties and acentric factor required for the application of the cubic EoS, nor are the PC-SAFT parameters, are available. As discussed in section 3.2.1, critical properties were estimated from the group
contribution approach of Marrero and Gani\textsuperscript{38} for use with the cubic EoS, and GC-PC-SAFT parameters where obtained as explained in section 3.2.4 with the group contribution approach of Tihic and coworkers\textsuperscript{66}.

Results obtained using the $k_{ij}$ as reported in table 3-4 are shown. It can be seen that only VLE is obtained for the methylbenzoate-CO$_2$ system at 313.15 K from the SOF-PR cubic and PC-SAFT EoS, in agreement with available experimental data (other equations are shown in the appendix A, figures A-11 and A-12). However, for the ethylbenzoate-CO$_2$ system at 318.15 K the presence of VLE and LLE is evident and predicted by both approaches (see also figures A-13 and A-14, in the Appendix A). A VLLE is also present (not shown) around an ethylbenzoate mole fraction of 0.25. Thus this diagram suggest the existence of a LLE for the ethylbenzoate-CO$_2$ below an ethylbenzoate mole fraction of 0.25 with a predicted UCSP of $\sim$13,300 kPa at 318.15 K from the SOF-PR and $\sim$15,500 kPa from the GC-PCSAFT. In other words, a LLE region of immiscibility is predicted ($0 < x < 0.25$) where higher pressures are need to obtain a single phase region. To the best of our knowledge, no experimental data has been reported in this region to allow verification of these theoretical predictions.

We also show in figure 3-5 that the LLE is also correlated for the propyl 2, 5-dichlorobenzoate system at 323.15 K by both the SOF-PR and GC-PC-SAFT EoS. The difference in selected temperatures for the different systems shown is dictated by the available experimental data. However, predictions at other temperatures are presented in figures A-15 and A-16 for the cubic and GC-PC-SAFT EoS respectively. The presence of VLE and LLE regions for the propyl 2, 5-dichlorobenzoate system at 323.15 K is clearly predicted from both equations.
It is also evident from this figure that the LLE envelop narrows in mole fraction and the upper critical solution pressure (UCSP) increases with the growing alkyl chain. It can also be observed that, according to the GC-PC-SAFT model, the predicted VLE region for the propyl 2, 5-dichlorobenzoate is below the methyl and ethyl benzoates VLE regions about benzoate compositions greater than 0.3-0.4. The PR-SOF model however does not predict this crossing of the bubble point lines.

Figure 3-5 Fluid-fluid (VLE and LLE) equilibria of CO$_2$-benzoates. △ methylbenzoate experimental data$^{69}$ (313.15 K); thin line, GC-PC-SAFT, $k_{ij} = 0.08$; dashed line, SOF-PR, $k_{ij} = 0.0799$; □ ethylbenzoate experimental data$^{70}$ (318.15 K), dotted line SOF-PR, $k_{ij} = 0.0759$; bold line GC-PC-SAFT, $k_{ij} = 0.091$; ○ propyl 2,5-dichlorobenzoate experimental data$^{12}$ (323.15 K); dashed dotted line SOF-PR (LLE) $k_{ij} = 0.0630$; dashed double dotted line GC-PC-SAFT, $k_{ij} = 0.061$.

In figure 3-6, the LLE for a longer ADCB chain, octyl 2, 5-DCB is shown together with the available experimental data. Predictions and data for propyl 2, 5-DCB
at 323.15 K are also included for comparison with the previous figure. It can be seen that results for the heavier organic compound are on the whole less successful, which may be a consequence of increasing limitations in the group-contribution techniques used to estimate the properties of these compounds. Larger (in absolute value) interaction parameters $k_{ij}$ will be required to compensate for any systematic deviations in this respect, and this might explain why Shen et al.\textsuperscript{12} found that the PR EOS failed to correlate their experimental data with $k_{ij}$ values as large as $\pm 0.022$. In Figure 3-6, we have used $k_{ij} = 0.061$ for the GC-PC-SAFT EoS, and $k_{ij} = 0.0763$ for the SOF-PR EoS, both indicative of substantially smaller cross-attraction effects between CO$_2$ and the ADCB. We may remark however that these are not inordinately large values, as binary interaction parameters go.

It is important to note also that for the longer ADCB chains it was not sufficient to use a single temperature-independent $k_{ij}$ parameter for the GC-PC-SAFT, and in some cases for the cubic EoS, because the predicted phase diagrams are extremely sensitive to the value of $k_{ij}$. This value must be finely tuned for the attractive effects to overcome the large repulsive interactions that arise naturally at the high experimental pressures. For example, the PR-SOF EoS results for the octyl-2, 5 DCB in figure 3-6 correspond to a $k_{ij} = 0.0763$ chosen for best reproduction of the critical solution pressure (UCSP), albeit at a DCB concentration somewhat in excess of the experimental value. In figure 3-7, it can be seen that a value of $k_{ij} = 0.083$ predicts the existence of a second region of immiscibility (LCSP) at above 100 MPa, attributable to increased molecular repulsions. Also shown in figure 3-7 are SOF-PR EoS results for $k_{ij} = 0.088$ and 0.100; as the value of $k_{ij}$ increases, the UCSP and LCSP approach each other, and eventually the two regions of
immiscibility merge into a single hour-glass shaped phase envelope, i.e. repulsion effects dominate and the system never achieves completely solubility. Thus, a variation of less than 0.02 in $k_{ij}$ completely changes the nature of the predicted phase equilibrium. Similar behavior was observed with all the cubic models and cohesion functions studied.

For the GC-PC-SAFT EoS, the best fit at 323.15 K is also shown in figure 3-6 ($k_{ij} = 0.079$). The GC-PCSAFT underpredicts the pressure at higher compositions. This might be related again to the predictions of the PC-SAFT parameters from a GC approach whose uncertainties increase with molecular weight. However, the GC-PC-SAFT does predict a UCSP phase envelop even with different $k_{ij}$ (i.e. $k_{ij} = 0.1$) as shown in figure 3-7 for comparison. In the Appendix A can be found figures for this system (A-17 and A-18) with predictions for this system at different temperatures from all the EoS used in this study. It is worth noting that predictions at 298.15 K are generally “flatter” in accordance with experimental results.

Figure 3-6 Fluid-fluid (LLE) CO$_2$-ADCB. ○ propyl 2,5-dichlorobenzoate experimental data$^{12}$ (323.15 K); dashed double dotted line SOF-PR $k_{ij} = 0.06299$, continuous line with orange
symbols GC-PC-SAFT \( k_{ij} = 0.061 \). ◊ octyl 2,5-dichlorobenzoate experimental data\(^{12}\) (323.15 K), dotted line with blue symbols GC-PC-SAFT, \( k_{ij} = 0.079 \); dashed dotted line SOF-PR, \( k_{ij} = 0.0763 \).

Figure 3-7 Fluid-fluid (LLE) \( \text{CO}_2 \)-octyl 2, 5-dichlorobenzoate at 348.15 K. \( \Delta \) experimental data\(^{12}\); thin line SOF-PR (UCSP/LCSP) \( k_{ij} = 0.083 \), bold line GC-PC-SAFT \( k_{ij} = 0.071 \), dotted line SOF-PR, \( k_{ij} = 0.088 \); dashed dotted line GC-PC-SAFT, \( k_{ij} = 0.1 \); -x- line SOF-PR, \( k_{ij} = 0.1 \).

In figure 3-8 we show the results for the FDCB together with the available experimental data. In this figure, data for the pentafluoro propyl 2, 5-DCB - \( \text{CO}_2 \) and tridecafluoro octyl 2, 5-DCB – \( \text{CO}_2 \) systems at 323.15 K are compared with computations from the SOF-PR and GC-PC-SAFT EoS. In general, it can be seen that the cubic EoS does a more credible job than the molecular-based EoS in fitting the experimental data. In keeping with the previous results, we may attribute this to the less reliable estimation of the pure fluid properties for use with this model. We may also recall that both the cubic
and the PC-SAFT EoS are being used in simplified form, the first by employing a single interaction parameter, the second by omitting multipolar and association contributions. Inspection of figure 3-8, for instance, shows that the SOF-PR EoS here again overpredicts the DCB compositions at equilibrium (the phase envelope is displaced to the right of the diagram), most noticeably for the 13F-octyl 2, 5-DCB. This might indicate that the simple van der Waals mixing rules are not flexible enough to model the changes in molecular interactions with composition for these highly asymmetric mixtures, and that a composition-dependent rule might be in order.

Figure 3-8 Fluid-fluid (LLE) CO\textsubscript{2}- FDCB at 323.15 K. ∆ 13FO2,5-DCB experimental data\textsuperscript{12}; ○ 5F-propyl 2,5-DCB experimental data\textsuperscript{12}; gray dotted line SOF-PR for 13FO2,5-DCB, $k_{ij} = 0.0646568$; gray solid line SOF-PR for 5FP2,5-DCB, $k_{ij} = 0.037891$; black thick line GC-PC-SAFT for 13FO2,5-DCB, $k_{ij} = 0.03$; black thin line GC-PC-SAFT for 5FP2,5-DCB, $k_{ij} = 0$. 
Table 3-3 PC-SAFT parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gross &amp; Sadowski</th>
<th>GC-PC-SAFT</th>
<th>Gross &amp; Sadowski</th>
<th>GC-PC-SAFT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m$</td>
<td>$\sigma (\AA)$</td>
<td>$\varepsilon$ (K)</td>
<td>$m$</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>2.073</td>
<td>2.785</td>
<td>169.21</td>
<td>2.073</td>
</tr>
<tr>
<td>benzene</td>
<td>2.465</td>
<td>3.648</td>
<td>287.35</td>
<td>2.198</td>
</tr>
<tr>
<td>toluene</td>
<td>2.815</td>
<td>3.717</td>
<td>285.69</td>
<td>2.669</td>
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<tr>
<td>$o$-xylene</td>
<td>3.136</td>
<td>3.760</td>
<td>291.05</td>
<td>3.139</td>
</tr>
<tr>
<td>$m$-xylene</td>
<td>3.186</td>
<td>3.756</td>
<td>283.98</td>
<td>3.139</td>
</tr>
<tr>
<td>$p$-xylene</td>
<td>3.172</td>
<td>3.778</td>
<td>283.77</td>
<td>3.139</td>
</tr>
<tr>
<td>methylbenzoate</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>3.926</td>
</tr>
<tr>
<td>ethylbenzoate</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>4.310</td>
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<tr>
<td>propyl 2,5-dichlorobenzene</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>5.438</td>
</tr>
<tr>
<td>octyl 2,5-dichlorobenzene</td>
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<td>N/A</td>
<td>N/A</td>
<td>7.360</td>
</tr>
<tr>
<td>pentfluoro propyl 2,5-</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>dichlorobenzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tridecafluoro octyl 2,5-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dichlorobenzene</td>
<td></td>
<td></td>
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<td></td>
</tr>
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</table>

Table 3-4 Temperature independent binary interaction parameters ($k_{ij}$'s) used in this work

<table>
<thead>
<tr>
<th>CO$_2$/</th>
<th>Binary interaction parameter ($k_{ij}$)</th>
<th>Temperature range (K)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>PR</td>
<td>SOF-PR</td>
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<tr>
<td>benzene</td>
<td>0.0807</td>
<td>0.0028</td>
</tr>
<tr>
<td>toluene</td>
<td>0.0845</td>
<td>0.0073</td>
</tr>
<tr>
<td>$o$-xylene</td>
<td>0.0730</td>
<td>0.0064</td>
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<td>$m$-xylene</td>
<td>0.0774</td>
<td>0.0084</td>
</tr>
<tr>
<td>$p$-xylene</td>
<td>0.0772</td>
<td>0.0079</td>
</tr>
<tr>
<td>methylbenzoate</td>
<td>0.0600</td>
<td>0.0799</td>
</tr>
<tr>
<td>ethylbenzoate</td>
<td>0.0699</td>
<td>0.0759</td>
</tr>
<tr>
<td>propyl 2,5-DCB</td>
<td>0.0693</td>
<td>0.0630</td>
</tr>
<tr>
<td>SF propyl 2,5-DCB</td>
<td>0.0465</td>
<td>0.0379</td>
</tr>
<tr>
<td>13F octyl 2,5-DCB</td>
<td>0.0691</td>
<td>0.0647</td>
</tr>
</tbody>
</table>

Table 3-5 Temperature dependent binary interaction parameters ($k_{ij}$'s) used in this work for the GC-PC-SAFT.

<table>
<thead>
<tr>
<th>CO$_2$/</th>
<th>GCPC-SAFT/ Binary interaction parameter ($k_{ij}$)</th>
<th>Temperature-dependent equations</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298.15K 313.15K 323.15K 348.15K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>propyl 2,5-DCB</td>
<td>N/A</td>
<td>0.0640</td>
<td>0.0610</td>
</tr>
<tr>
<td>octyl 2,5-DCB</td>
<td>0.0850</td>
<td>-</td>
<td>0.0790</td>
</tr>
<tr>
<td>SF propyl 2,5-DCB</td>
<td>0.0500</td>
<td>-</td>
<td>0.0000</td>
</tr>
<tr>
<td>13F octyl 2,5-DCB</td>
<td>0.0500</td>
<td>-</td>
<td>0.0150</td>
</tr>
</tbody>
</table>

* For temperature of 298.15K this relationship is valid for molefraction of octyl 2,5-dichlorobenzene < 0.13625
Table 3-6. Temperature dependent binary interaction parameters used in this work for the cubic EoS.

<table>
<thead>
<tr>
<th>CO₂/</th>
<th>Temperature (K)</th>
<th>PR</th>
<th>SOF-PR</th>
<th>SRK</th>
<th>SOF-RK</th>
</tr>
</thead>
<tbody>
<tr>
<td>octyl 2,5-dichlorobenzoate</td>
<td>298.15</td>
<td>0.0695</td>
<td>0.0664</td>
<td>0.0787</td>
<td>0.0763</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>0.0802</td>
<td>0.0763</td>
<td>0.0896</td>
<td>0.0874</td>
</tr>
<tr>
<td></td>
<td>348.15</td>
<td>0.0875</td>
<td>0.0830</td>
<td>0.0972</td>
<td>0.0940</td>
</tr>
</tbody>
</table>

3.4 Conclusions

We have shown that two simple thermodynamic models, cubic equations of state (PR and SRK in original form and modified by use of the SOF cohesion function) and molecular-based equations of state (PC-SAFT with fluid-specific and GC predicted parameters) can capture many important features of the complex phase behavior of highly asymmetric systems composed of supercritical CO₂ and alkyl (nonfluorinated or perfluorinated) 2, 5-dichlorobenzoates.

The present results are open to quantitative improvement, and in this sense our work must be seen as a first effort towards a fully predictive treatment. The estimation of pure component properties is a main source of uncertainties, especially for the fluorinated compounds where the contributions of the fluorine atoms are still largely missing from the published correlations. A second factor is that we have purposely used simplified versions of both types of EoS; thus, the PC-SAFT EoS has lacked terms that might account explicitly for the multipolar and association effects known to exist in these
systems, and the cubic EoS have included a single binary interaction parameter (temperature independent wherever practicable), instead of the more complex, composition-dependent mixing and combination rules known to be required even for much simpler binary mixtures \(^{69}\). As more experimental data become available, however, we are confident from these results that thermodynamic modeling can be perfected to provide reliable correlation and prediction of the phase behavior of these and related systems.
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Chapter 4

Modeling anti-solvent effects of supercritical carbon dioxide (scCO$_2$) in polystyrene - cyclohexane –carbon dioxide (PS-C$_6$H$_{12}$-CO$_2$) system

In the early 1960s, lower critical solution temperature (LCST) phase behavior was found to exist for all polymer solutions unless the polymer thermally degrades before the necessary temperature is reached$^1$. The phase splitting technique is based on the experimental observations first made by Freeman and Rowlinson$^2$. In this process a miscible polymer solution is split in two liquid phases when the system temperature approaches the critical temperature of the solvent. Thus, the polymer can be recuperated from solution by heating the polymer solution until it splits into two phases, a solvent rich phase, and a polymer rich phase. Inducing a polymer-solvent phase split results in an alternative less energy intensive process$^{3,4}$ when compared against stream stripping$^5$. In the 1970’s, several patents appeared suggesting that phase splitting at the LCST is more efficient than stream stripping. However, one limitation in the use of this technique is that the solution must be heated to temperatures in which the solvent is close to its critical temperature; and thus for “good solvents” this temperature can be extremely high for industrial applications.
To overcome the problem of shifting the LCST to lower temperatures, Irani and Cozewith suggested adding a light supercritical fluid (SCF) additive to the polymer solution. The SCF additive has the effect of lowering the critical point of the solvent and, as consequence, the LCST separation occurs at much lower temperatures. In doing so, the possibility of polymer degradation decreases as well as the thermal energy requirements for processing.

Nowadays, liquid-liquid phase separation induced by the addition of a SCF to a liquid mixture is a prominent technique applied to separate polymers. In the context of industrial applications the system PS-\(\text{C}_6\text{H}_{12}\)-CO\(_2\) is being used as a model for the improvement of environmental processes. In this work, we study the phase equilibria of such ternary system, with special interest on understanding the effect of using CO\(_2\) as separation agent. As mentioned in chapter 2, CO\(_2\) is an attractive SCF due to its critical properties (\(T_c = 31.05^\circ\text{C}\), \(P_c = 7.34\) MPa) are within accessible experimental and industrial conditions.

Bungert et al. showed experimentally that for the system PS-\(\text{C}_6\text{H}_{12}\)-CO\(_2\) it is possible to obtain an almost polymer-free solvent-rich phase. They obtained a polymer-rich phase with increased polymer content on a solvent-free basis, reducing the energy requirements for the drying steps by solvent evaporation. Additionally, the separation occurred at lower temperatures reducing the possibility of polymer degradation.

This system has also been of interest to modelers. Lotfollahi et al. calculated the ternary thermodynamic phase behavior for PS-\(\text{C}_6\text{H}_{12}\)-CO\(_2\) using the Sanchez-Lacombe model and then compared it with the reported results obtained by the perturbed hard-sphere chain model (PHSC) and experimental data available. Recently, ter Horst et al.
also studied this system with the Huang-Radosz version of the SAFT-EoS. They found that the equation of state largely over predicts cloud-point pressures for the system if the compounds are modeled as non-associating, and the polymer modeled as monodisperse. Therefore, a qualitative correlation of the polymer-solvent system was possible, but with the introduction of temperature-dependent binary interaction parameters. Behme et al\textsuperscript{12} modeled both monodisperse and polydisperse polystyrene-cyclohexane- carbon dioxide systems with the SAFT EoS. The binary interaction parameters were calculated by minimizing the absolute average deviation of mole fractions in the two phases at 344.15 K (71° C) and 473.15 K (200° C). The best approximation resulted in temperature dependent $k_{ij}$ parameters. For example, for the CO\textsubscript{2}-C\textsubscript{6}H\textsubscript{12} the following equation was proposed

$$k_{CO_2-cyclohexane} = -2.59416 \times 10^{-4}T[K] + 0.23765 \quad (4.1)$$

The objective of this work is to use the Perturbed Chain Statistical Associating Fluid Theory, PC-SAFT, to model the anti-solvent effects of scCO\textsubscript{2} in the polystyrene-cyclohexane system to evaluate its effectiveness.

### 4.1 The PC-SAFT model

Among models based on equations of state, those developed within the framework of the thermodynamic perturbation theory have received increasing attention because of their predictive power. Here we used the Perturbed Chain Statistical Associating Fluid Theory, PC-SAFT.
As mentioned before in Chapter 1, in the framework of PC-SAFT molecules are assumed to be chains of freely jointed spherical segments exhibiting attractive forces among each other\textsuperscript{13}. In terms of the compressibility factor, $Z$, the equation of state is given as:

$$Z = 1 + Z^{hc} + Z^{disp} + Z^{assoc}$$

(4.2)

where $Z^{hc}$ is the contribution of the hard chain and chain-formation; $Z^{disp}$ is the dispersion term; and $Z^{assoc}$ is the contribution due to association. For more details, the reader is referred to 1.4.2 in this thesis.

For non-associating molecules three pure-component parameters are needed and the parameters used in this chapter are listed in table 4-1

Table 4-1 PC-SAFT parameters used in this work

<table>
<thead>
<tr>
<th>Compound</th>
<th>$m$</th>
<th>$\sigma$ (Å)</th>
<th>$\varepsilon/k$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1926.60</td>
<td>4.1071</td>
<td>267.00</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>1845.48</td>
<td>4.1606</td>
<td>267.84</td>
<td>14</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{12}</td>
<td>2.5303</td>
<td>3.8499</td>
<td>278.11</td>
<td>15</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>2.0729</td>
<td>2.7852</td>
<td>169.21</td>
<td>15</td>
</tr>
</tbody>
</table>

Recently, we have presented\textsuperscript{14} a parameterization strategy that allows the calculation of polymer molecular parameters from macroscopic properties of binary polymer solutions. Using polymer parameters calculated from the proposed parameterization strategy, the PC-SAFT model satisfactorily predict the phase equilibria behavior of binary and ternary polymer solutions with different solvents, including
nonassociating compounds such as n-alkanes, polar compounds such as ethers, esters and ketones, and associating compounds such as alcohols.

In this work, we evaluate the prediction capabilities of this parameterization strategy for the system PS-C₆H₁₂-CO₂ and compared the results with the polymer parameters proposed by Gross and Sadowski

4.2 PS-C₆H₁₂-CO₂ phase equilibria using Gross and Sadowski’s parameters

In order to predict ternary phase behavior, binary interaction parameters, $k_{ij}$, are generally needed and obtained by fitting each binary and/or ternary experimental data available (CO₂-C₆H₁₂, PS-CO₂, PS-C₆H₁₂, CO₂-PS-C₆H₁₂). Thus, each of these binary systems is first studied below.

4.2.1 Carbon dioxide- cyclohexane (CO₂-C₆H₁₂)

The first binary mixture corresponds to solvent-solvent interactions, carbon dioxide- cyclohexane (CO₂-C₆H₁₂). We selected experimental data from Anderson et al at three different temperatures 348.15 K, 373.15 K and 423.15 K. The results are shown in figures 4-1, 4-2 and 4-3.
Figure 4-1 Phase equilibria description for the binary system CO$_2$-C$_6$H$_{12}$ at T = 348.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$'s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature$^{16}$.

For the temperature 348.15 K, predicted VLE for the CO$_2$-cyclohexane with PC-SAFT ($k_{ij} = 0$) are shown in figure 4-1 together with the experimental values reported by Anderson$^{16}$. Several values of $k_{ij}$'s were tested with the aim to find an independent temperature interaction parameter. The two $k_{ij}$'s presented give a reasonable agreement with the experimental data. $k_{ij} = 0$ is also shown for comparison. The best fit (as determined by minimizing the error among the calculated and experimental pressures) corresponds to $k_{ij} = 0.08$. 
Figure 4-2 Phase equilibria description for the binary system \( \text{CO}_2-\text{C}_6\text{H}_{12} \) at \( T = 373.15 \) K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with \( k_{ij} = 0 \). Lines with symbols are PC-SAFT correlations with different \( k_{ij} \)’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature\(^{16}\).

For the temperature 373.15 K, predicted VLE for the \( \text{CO}_2 \)-cyclohexane with PC-SAFT \((k_{ij} = 0)\) are shown in figure 4-2. The two \( k_{ij} \)’s presented give a reasonable agreement with the experimental data, where \( k_{ij} = 0.068 \) was obtained from the best fit (as determined by minimizing the error among the calculated and experimental pressures.) Similar results, were obtained for 423.15 K, and presented in figure 4-3.
Figure 4-3 Phase equilibria description for the binary system CO$_2$-C$_6$H$_{12}$ at T = 423.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature$^{16}$.

These results confirmed that for the system CO$_2$-C$_6$H$_{12}$ the binary interaction parameter is temperature-dependent. While the temperature tends to increase, the necessary $k_{ij}$ tends to decrease. A simple linear equation ($R^2 = 0.9947$), similar to that presented by Behme et al$^{12}$ for the SAFT Huang-Radosz equation, was found in this work for the temperature range 348.15 – 423.15 K:

$$K_{ij}(T) = -6.085714 \times 10^{-4} \times T(K) + 0.2931598571$$ (4.3)

Bellow, we present our calculations for the polymer-solvent mixtures (polymer solutions). Some experimental data is available for both binary systems$^{17,18,19}$. First, we evaluate the binary interaction parameter in a range of at least 100 degrees Celsius and
with a small polydispersity index (PDI ≤ 1.2), i.e. we model the polymer as monodisperse. Then, we study the effect of polydispersity.

4.2.2 Cyclohexane- polystyrene (C₆H₁₂-PS)

For the binary system that corresponds to the polymer solution PS-C₆H₁₂, we selected experimental data from Bae et al [20], at three different temperatures 303.15 K, 323.15 K and 333.15 K. In this case, polystyrene can be considered monodisperse (PDI<1.2) with Mₘ=100,000 g/mol. The results are shown in figures 4-4, 4-5 and 4-6.

Figure 4-4 Phase equilibria description for the binary system PS-C₆H₁₂ at T = 303.15 K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with kᵢⱼ = 0. Lines with symbols are PC-SAFT correlations with different kᵢⱼ’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature [20].

In figure 4-4 are shown the predicted LLE for the PS-cyclohexane with PC-SAFT (kᵢⱼ = 0) at 303.15 K. Two additional lines are presented that give reasonable agreement
with the experimental data. The calculated $k_{ij}$ that shown the best agreement with the experimental data corresponds to $k_{ij} = 0.014$.

Figure 4-5 Phase equilibria description for the binary system PS-\(\text{C}_6\text{H}_{12}\) at \(T = 323.15\text{K}\). Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature\(^\text{20}\).

For the temperature 323.15 K predicted LLE for the PS-cyclohexane with PC-SAFT ($k_{ij} = 0$) are shown in figure 4-5. Two additional $k_{ij}$’s are presented that give a reasonable agreement with the experimental data, with a small under prediction for $k_{ij} = 0.017$. At 323.15 K the calculated $k_{ij}$ that shown better agreement with the experimental data corresponds to $k_{ij} = 0.021$. 
Figure 4-6 Phase equilibria description for the binary system PS-C₆H₁₂ at T = 333.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with different $k_{ij}$'s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature²⁰.

For the temperature of 333.15 K predicted LLE for the PS-cyclohexane with PC-SAFT ($k_{ij} = 0$) are shown in figure 4-6. Only two additional $k_{ij}$’s are presented that give a good agreement with the experimental data. At 333.15 K the calculated $k_{ij}$ that shown the best agreement with the experimental data corresponds to $k_{ij} = 0.014$.

It is important to observed that in figures 4-4 to 4-6 all values of $k_{ij}$’s need to “adjust” the experimental data are very small ($<< 0.1$) and in a narrow range (0.014-0.021). These results suggest that for the monodisperse system PS-C₆H₁₂ the binary interaction parameter can be considered temperature-independent in the range under study.
4.2.3 Carbon dioxide- polystyrene (CO$_2$-PS)

For the system CO$_2$-PS we were unable to find experimental data with low PDI. All experimental data available corresponds to PDI > 1.2, and thus to be able to model adequately the phase behavior of this system, we used the concept of pseudocomponents to model these polydisperse systems. In this concept, the continuous molecular weight distribution of polymer is subdivided into a certain number of pseudocomponents each of which is considered as a monodisperse component$^{21}$.

In figure 4-7 and 4-8 are showed the phase behavior of the system PS-CO$_2$ at 373.15 K and 453.15 K, with $M_n = 70,300$ g/mol and $M_w = 187,000$ g/mol, $PDI = 2.66$. For the sake of completeness the results for a monodisperse system are shown.

![Phase equilibrium diagram](image)

Figure 4-7 Phase equilibria description for the binary system PS-CO$_2$ at temperatures of 373.15 K and 453.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid lines represent PC-SAFT predictions with $k_{ij} = 0$. Lines with symbols are PC-SAFT correlations with the corresponding $k_{ij}$'s evaluated to fit with the experimental data. Filled symbols correspond to experimental data reported in literature$^{22}$. 
In figure 4-8 we present the results for the same system, modeling the polydisperse polymer using seven pseudocomponents\(^2\), as listed in table 4-2. For all temperatures it was possible to capture the phase behavior of the binary mixture using a \(k_{ij} = 0.165\) for the temperature of 373.15 K, a \(k_{ij} = 0.176\) for the temperature of 413.15 K and a \(k_{ij} = 0.198\) for the temperature of 453.15 K. Other calculations (not shown) were performed using more pseudocomponents but the results do not shown significant improvement. [The results showed that by modeling the system as polydisperse using the concept of pseudocomponents an improvement of 5 to 15 % was obtained]

Figure 4-8 Phase equilibria description for the binary system PS-CO\(_2\) at temperatures of 373.15 K, 413.15 K and 453.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid lines represent PC-SAFT predictions with \(k_{ij} = 0\). Lines with symbols are PC-SAFT correlations with the corresponding \(k_{ij}\)'s evaluated to fit with the experimental data. The polymer was modeled using seven pseudocomponents reported in table 4-2. Filled symbols correspond to experimental data reported in literature\(^2\).
Table 4-2 Pseudocomponents determined from the experimental data $M_w$ and $M_n$ values for modeling the molecular weight of PS with carbon dioxide presented in figure 4-8.

<table>
<thead>
<tr>
<th>Pseudocomponent $i$</th>
<th>Molar Mass (g/mol)</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>8.65e-06</td>
</tr>
<tr>
<td>2</td>
<td>514.27</td>
<td>1.67e-04</td>
</tr>
<tr>
<td>3</td>
<td>2644.79</td>
<td>3.15e-03</td>
</tr>
<tr>
<td>4</td>
<td>13601.47</td>
<td>5.32e-02</td>
</tr>
<tr>
<td>5</td>
<td>69948.94</td>
<td>5.28e-01</td>
</tr>
<tr>
<td>6</td>
<td>359729.82</td>
<td>4.14e-01</td>
</tr>
<tr>
<td>7</td>
<td>1850000</td>
<td>1.78e-06</td>
</tr>
</tbody>
</table>

In figure 4-9 the phase behavior of the system PS-CO$_2$ at 338.22 K, 383.22 K and 402.51 K, with $M_n$= 70,400 g/mol and $M_w$= 190,000 g/mol, PDI = 2.69 is shown. PC-SAFT results were obtained with the seven pseudocomponents listed in table 4-3. For these systems the PC-SAFT predictions showed good agreement with the experimental data for polystyrene weight fractions ($w_{PS}$) between 0.90 and 0.97. However, for smaller $w_{PS}$ the tendency shows higher deviations, principally for the temperature of 338.22 K. It is important to mention that to be able to capture the phase behavior of binary CO$_2$-polydisperse PS mixture, both the pseudocomponent approach and the use of temperature-dependant $k_{ij}$ ($k_{ij}$ =0.150 for the temperature of 338.15 K, $k_{ij}$ =0.168 for the temperature of 383.22 K and a $k_{ij}$ =0.178 for the temperature of 402.51 K) are needed. This might be a consequence of the pure parameters used for both CO$_2$ and PS that were
adjusted by Gross and Sadowski for a different set of experimental data (cyclohexane at 279-553 K, CO₂ at 216 to 304 K\textsuperscript{15} and polystyrene at pressure range of 10 to 100 MPa\textsuperscript{13}), or it can also be a consequence of the “simple” model that is being use that do not take into account explicitly the electrostatic interaction among CO₂ and PS. In section 4.3 we evaluate the use of a different set of parameters to shed some light into this point.

![Figure 4-9 Phase equilibria description for the binary system PS-CO₂ at temperatures of 338.22 K, 383.22 K and 402.51K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid lines represent PC-SAFT predictions with \( k_{ij} = 0 \). Dashed lines are PC-SAFT correlations with the corresponding \( k_{ij} \)'s evaluated to fit with the experimental data. The polymer was modeled using seven pseudocomponents reported in table 4-3. Filled symbols correspond to experimental data reported in literature\textsuperscript{24}.](image-url)
Table 4-3 Pseudocomponents determined from the experimental data $M_w$ and $M_n$ values for modeling the molecular weight of PS with carbon dioxide presented in figure 4-9.

<table>
<thead>
<tr>
<th>Pseudocomponent</th>
<th>Molar Mass (g/mol)</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>9.552e-06</td>
</tr>
<tr>
<td>2</td>
<td>516.56</td>
<td>1.798e-04</td>
</tr>
<tr>
<td>3</td>
<td>2668.40</td>
<td>3.309e-03</td>
</tr>
<tr>
<td>4</td>
<td>13784.04</td>
<td>5.453e-02</td>
</tr>
<tr>
<td>5</td>
<td>71203.67</td>
<td>5.300e-01</td>
</tr>
<tr>
<td>6</td>
<td>367813.78</td>
<td>4.118e-01</td>
</tr>
<tr>
<td>7</td>
<td>1900000</td>
<td>1.787e-06</td>
</tr>
</tbody>
</table>

In figure 4-10 is showed the phase behavior of the system PS-CO$_2$ at 373.15 K, 423.15 K and 473.15 K, with $M_n$ = 107,000 g/mol and $M_w$ = 330,000 g/mol and a calculated $PDI = 3.08$. The PC-SAFT correlations to fit the experimental data were calculated using seven pseudocomponents listed in table 4-4. For these systems the PC-SAFT predictions shown good agreement with the experimental data for weight fractions of the polystyrene ($w_{PS}$) between 0.93 and 1; however, for smaller $w_{PS}$ the tendency of the correlations start to deviate principally for the temperature of 373.15 K. For all studied temperatures it was possible to capture the phase behavior of the binary mixture using a $k_{ij}$ =0.1685 for 373.15 K, $k_{ij}$ =0.194 for 423.15 K and a $k_{ij}$ =0.22 for 473.15 K.
Figure 4-10 Phase equilibria description for the binary system PS-CO$_2$ at temperatures of 373.15 K, 423.15K and 473.15K. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid lines represent PC-SAFT predictions with $k_{ij} = 0$. Dashed lines are PC-SAFT correlations with the corresponding $k_{ij}$'s evaluated to fit with the experimental data. The polymer was modeled using seven pseudocomponents reported in table 4-4. Filled symbols correspond to experimental data reported in literature$^{25}$.

Table 4-4 Pseudocomponents determined from the experimental data M$_w$ and M$_n$ values for modeling the molecular weight of PS with carbon dioxide presented in figure 4-10.

<table>
<thead>
<tr>
<th>Pseudocomponent $i$</th>
<th>Molar Mass (g/mol)</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>1.020e-05</td>
</tr>
<tr>
<td>2</td>
<td>566.35</td>
<td>1.780e-04</td>
</tr>
<tr>
<td>3</td>
<td>3207.53</td>
<td>3.047e-03</td>
</tr>
<tr>
<td>4</td>
<td>18165.90</td>
<td>4.747e-02</td>
</tr>
<tr>
<td>5</td>
<td>102882.76</td>
<td>4.669e-01</td>
</tr>
<tr>
<td>6</td>
<td>582677.55</td>
<td>4.824e-01</td>
</tr>
<tr>
<td>7</td>
<td>3300000</td>
<td>8.011e-06</td>
</tr>
</tbody>
</table>
For the systems PS-CO₂ presented in figures 4-7, 4-8 and 4-9 three linear equations were obtained and summarized in table 4-5.

Table 4-5. Equations for \( k_{ij} \)'s determined from the experimental data at different temperatures for the system PS-CO₂.

<table>
<thead>
<tr>
<th>PDI</th>
<th>Range of temperature</th>
<th>Temperature-dependent equations</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.66</td>
<td>373.15 K to 453.15 K</td>
<td>( k_{ij} = 0.00047[K] ) – 0.0092</td>
<td>0.9643</td>
</tr>
<tr>
<td>2.69</td>
<td>338.22 K to 402.51 K</td>
<td>( k_{ij} = 0.00047[K] + 0.0027</td>
<td>0.9943</td>
</tr>
<tr>
<td>3.08</td>
<td>373.15 K to 473.15 K</td>
<td>( k_{ij} = 0.00057[K] ) – 0.0238</td>
<td>1</td>
</tr>
</tbody>
</table>

4.2.4 Ternary system: polystyrene- cyclohexane- carbon dioxide (PS- C₆H₁₂-CO₂)

The PC-SAFT parameters used for these calculations were listed in table 4-1. First we focus our attention for a “monodisperse” system, i.e. systems were the polystyrene polydispersity was reported as PDI=1.09.

In figure 4-11 the ternary system PS-C₆H₁₂-CO₂ has “feed” compositions given by: \( w_{PS} = 0.094 \), \( w_{C₆H₁₂} = 0.856 \), \( w_{CO₂} = 0.05 \) and \( M_w = 100,000 \) g/mol.
Figure 4-11 Pressure-temperature diagram for the ternary system PS-C₆H₁₂-CO₂ with compositions: \( w_{PS} = 0.094 \), \( w_{C₆H₁₂} = 0.856 \), \( w_{CO₂} = 0.05 \) and \( M_w = 100,000 \) g/mol. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid blue line represents PC-SAFT prediction with \( k_{ij} = 0 \). Lines with symbols are PC-SAFT predictions with different sets of \( k_{ij} \)'s evaluated to fit with the binary experimental data. Diamonds correspond to experimental data reported in literature⁹.

In figure 4-11, the PC-SAFT predictions, \( k_{ij} = 0 \), for the ternary system are shown together with several sets of \( k_{ij} \)'s parameters (previously determined in sections 4.2.1 to 4.2.3) and summarized on table 4-6. It is important to note that the \( k_{ij} \)'s presented in this table, were not fitted to this (or any) ternary experimental data, but to previously independent binary data. Thus the results here presented, can be considered predictive in the sense that not ternary data has been adjusted. The results with all the sets are similar, and thus indicate that for the monodisperse PS/Cyclohexane/CO₂ system appears good predictions can be obtained not only in the LLE region (as compared with the experimental data available) but also at the VLE region.

Table 4-6 Studied sets of \( k_{ij} \)'s parameters for the ternary system PS-C₆H₁₂-CO₂ shown in figures 4-11 and 4-12.

<table>
<thead>
<tr>
<th>Kij parameters</th>
<th>CO₂-C₆H₁₂</th>
<th>PS-CO₂</th>
<th>PS-C₆H₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Set 1</strong></td>
<td>0.08</td>
<td>0.181</td>
<td>0.0153</td>
</tr>
<tr>
<td><strong>Set 2</strong></td>
<td>0.035</td>
<td>0.163</td>
<td>0.014</td>
</tr>
<tr>
<td><strong>Set 3</strong></td>
<td>0.068</td>
<td>0.18</td>
<td>0.014</td>
</tr>
</tbody>
</table>
Figure 4-12 Pressure-temperature diagram for the ternary system PS-C6H12-CO2 with compositions: \( w_{PS} = 0.093, w_{C6H12} = 0.768, w_{CO2} = 0.139 \) and \( M_w = 100,000 \) g/mol. Calculations were made using PC-SAFT parameters taken from table 4-1. Solid blue line represents PC-SAFT prediction with \( k_{ij} = 0 \). Diamonds correspond to experimental data reported in literature\(^9\).

Thus, in figure 4-12, we evaluated the influence of the solvent/antisolvent proportions for the same monodisperse system at slightly different conditions (“feed” compositions: \( w_{PS} = 0.093, w_{C6H12} = 0.768, w_{CO2} = 0.139 \). Here the PS composition is practically the same as in figure 4-11, but the solvent/antisolvent proportions change from \( w_{C6H12} / w_{CO2} = 0.856 / 0.05 \) to \( 0.768/0.139 \). In this figure we show the predictions obtained with \( k_{ij} = 0 \). As can be seen, the general VLE and LLE regions are quantitative predicted. However, the LLE is “off” by approximately 100 K, and the VLLE point appears overpredicted as well, and thus this is considered unacceptable.

The next logical step was to obtain the predictions with the same \( k_{ij} \) parameters used for figure 4-11, and reported in table 4-6, but this was not possible. A strong influence of the solvent/antisolvent binary interaction parameter was found in the prediction of the ternary phase equilibria at these conditions. In figure 4-13 are shown, as
example, the dependence of the ternary phase equilibria on the value of the solvent/antisolvent $k_{ij}$.

Figure 4-13 Influence of the solvent-antisolvent interaction parameter $k_{\text{cyclohexane-carbon dioxide}}$ in the phase envelope diagrams for the ternary system PS-$\text{C}_6\text{H}_{12}-\text{CO}_2$. Calculations were made using PC-SAFT parameters taken from table 4-1.

For figures 4-13a and 4-13c only at low pressures is possible to obtain the phase envelope. For figure 4-13b an unphysical behavior is predicted around 20 MPa. Only when the binary interaction parameter is increased to 0.105 the correct phase enveloped is obtained. As consequence, appears that the ternary phase equilibria cannot be obtained in a predicted manner from interaction parameters obtained only from binary phase data. This is a daunting system (even for the monidisperse case), but the results obtained so far are consistent with previous work reported in the literature.

Table 4-7 Binary interaction parameters, $k_{ij}$’s, for each pair of components of the three binary mixture studied in following sections

<table>
<thead>
<tr>
<th>Binary mixture</th>
<th>$k_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide – cyclohexane ($\text{CO}_2$-$\text{C}<em>6\text{H}</em>{12}$)</td>
<td>0.105</td>
</tr>
<tr>
<td>Polystyrene – carbon dioxide (PS-$\text{CO}_2$)</td>
<td>0.180</td>
</tr>
<tr>
<td>Polystyrene- cyclohexane (PS-$\text{C}<em>6\text{H}</em>{12}$)</td>
<td>0.014</td>
</tr>
</tbody>
</table>
4.3 PS-C₆H₁₂-CO₂ phase equilibria using parameters from the recent developed parameterization strategy

A similar approach to section 4.2 was followed for the determination of the binary interaction parameters for the PC-SAFT equation when the pure compound parameters obtained from the parameterization strategy are used. As mentioned before, we recently presented a parameterization strategy that allows the calculation of polymer molecular parameters from macroscopic properties of binary polymer solutions. The parameterization scheme was developed in terms of the polymer-solvent interaction parameter (χ) and the Hildebrand parameter (δ), which are readily available in the literature for a large variety of solvents and polymers. Using polymer parameters calculated from the proposed parameterization strategy, the PC-SAFT model satisfactorily predicted the phase equilibria behavior of binary and ternary polymer solutions with different solvents, including nonassociating compounds such as n-alkanes, polar compounds such as ethers, esters and ketones, and associating compounds such as alcohols.

In previous work figure 4-14, the phase equilibria of the ternary system PS (Mₗₑ = 101.4 kg/mol, Mₘₑ/Mₙₑ = 1.09)/cyclohexane/carbon dioxide system at 443 K and 10.1 MPa is shown along with the experimental values reported in the literature. In the case of ternary systems, the parameterization equations (Equations 8 and 10 in the original co-reference) can be used to calculate polymer parameters using the experimental information (δᵥ and χ) corresponding to the solvent with higher concentration (cyclohexane for the system under investigation). It can be seen that the parameterization
strategy gives a good description of the experimental phase diagram, where the addition of carbon dioxide promotes a liquid-liquid demixing, which boundaries a vapor-liquid-liquid region. The liquid-liquid demixing is predicted somewhat too narrow in concentration. However, in general, the calculated values are in reasonable agreement with the experimental data; indicating that the parameterization approach might provide sets of polymer parameters that yield satisfactory results modeling both binary and ternary polymer solutions exhibiting UCST- and LCST-phase behavior as well as UCST-LCST behavior.

Figure 4-14 Theoretical results for the phase equilibria of PS ($M_w = 101.4$ kg/mol, $M_w/M_n = 1.09$) with carbon dioxide and cyclohexane at 443 K and 10.1 MPa. Calculations were made using polymer molecular parameters calculated from the parametrization scheme. Dotted lines represent the tie lines. Symbols are experimental data reported in the literature\textsuperscript{13}.

Similar than in figures 4-4 to 4-10, we present the phase equilibria calculations for the systems PS/Carbon dioxide at 373 K, 423 K and 473 K (figure 4-15) and for the system PS/Cyclohexane at 303.15 K, 323.15 K and 333.15 K (figure 4-16), using the polymer parameters calculated from the parametrization scheme (second row of table 4-
The results showed adequate agreement with the experimental data reported in literature\textsuperscript{25,20}.

Figure 4-15. Phase equilibria description for the system PS ($M_n = 330$ kg/mol, PDI=3.08) with carbon dioxide at indicated temperatures. Calculations were made using polymer parameters calculated from the parameterization scheme. Solid lines represent PC-SAFT predictions with $k_{ij}=0$. Dashed lines are PC-SAFT correlations with $k_{ij}$ fitted to the experimental data. Symbols correspond to experimental data reported in literature\textsuperscript{26}. The polymer was modeled using seven pseudocomponents (see tables B2 and B3 from the appendix B).

Figure 4-16 Phase equilibria description for the binary system PS-C$_6$H$_{12}$ at temperatures 333.15 K, 323.15 K and 303.15K. Calculations were made using polymer parameters calculated from the
parameterization scheme. Solid line represents PC-SAFT prediction with $k_{ij} = 0$. Dashed lines are PC-SAFT correlations with different $k_{ij}$'s evaluated to fit with the experimental data. Symbols correspond to experimental data reported in literature$^{20}$.

We now use the same ternary systems used in figures 4-11 and 4-12, to evaluate the use of the polymer parameters calculated from the parametrization scheme. In both, figure 4-17 and figure 4-18, the pressure-temperature diagrams result in good agreement with the experimental data$^9$ and a correct phase envelope is obtained.

![Figure 4-17](image)

Figure 4-17 Pressure-temperature diagram for the ternary system PS-$C_6H_{12}$-CO$_2$ with compositions: $w_{PS}=0.094$, $w_{C_6H_{12}}=0.856$, $w_{CO_2}=0.05$ and $M_w=100,000$ g/mol. Calculations were made using polymer parameters calculated from the parameterization scheme. Solid blue line represents PC-SAFT prediction with $k_{ij} = 0$. Line with symbols is PC-SAFT prediction with different $k_{ij}$'s evaluated to fit the binary experimental data. Diamonds correspond to experimental data reported in literature$^9$. 
Figure 4-18 Pressure-temperature diagram for the ternary system PS-C₆H₁₂-CO₂ with compositions: $w_{PS}=0.093$, $w_{C₆H₁₂}=0.768$, $w_{CO₂}=0.139$ and $M_w=100,000$ g/mol. Calculations were made using polymer parameters calculated from the parameterization scheme. Solid blue line represents PC-SAFT prediction with $k_{ij} = 0$. Line with symbols is PC-SAFT prediction with different $k_{ij}$’s evaluated to fit with the experimental data. Diamonds correspond to experimental data reported in literature⁹.

Thus, after a rigorously determination of the appropriate set of values for the $k_{ij}$’s interaction parameters, we present below the results of the PVT calculations for the system (PS-C₆H₁₂-CO₂) at several thermodynamic conditions.

In figure 4-19 is shown a temperature/composition phase diagram for the ternary system, in this case, as a function of PS mass fraction. From this figure, the influence of pressure is clearly observed in the closed-loop regions of liquid-liquid immiscibility for the ternary mixture. Also the predicted curves showed the LCST and UCST for each pressure. The lower UCST’s values seem to be almost at the same temperature of 356±2 K. The LCST’s values for the contrary presented more significant difference in
temperature when the pressure is increased, with values of 446 K, 472 K and 502 K, respectively for pressures of 10.1 MPa, 15.15 MPa and 20.2 MPa. The ternary composition diagrams for each pressure are shown for completeness in figure 4-20.

Figure 4-19 Temperature-composition diagram for the ternary system PS-C₆H₁₂-CO₂ at three pressures of 10.1 MPa, 15.15 MPa and 20.2 MPa. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7.

Figure 4-20 PC-SAFT predictions for the liquid-liquid equilibria (LLE) of the ternary system PS-C₆H₁₂-CO₂ at three pressures of 10.1 MPa, 15.15 Mpa and 20.2 Mpa. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7.
Similar calculations were performed in the ternary system but at constant temperatures. At temperatures of 373 K and 408 K, the system only presents two phases in equilibrium VLE or LLE) under the range of interest. In the LLE, the cloud-point pressures at compositions close to \( w_{PS} = 0.16 \) rapidly increase (figure 4-21).

Figure 4-21 Pressure-composition diagram for the ternary system PS-\( \text{C}_6\text{H}_{12}\)-CO\(_2\) at temperatures of 373 K and 408 K. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7.

Figure 4-22 Pressure-composition diagram for the ternary system PS-\( \text{C}_6\text{H}_{12}\)-CO\(_2\) at temperatures of 443K, 473 K and 503 K. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7.
Figure 4-23 PC-SAFT predictions for the vapor-liquid-liquid equilibria (VLLE) of the ternary system PS-C₆H₁₂-CO₂ at three temperatures of 443 K, 473 K and 503 K. Calculations were made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7.

In figure 4-22 is show the phase equilibria as a function of pressure for three different temperatures. Here, it is important to observe that for the temperature of 503 K at 4500 kPa the pressure remains constant from \( w_{PS} = 0.2 \) to \( w_{PS} = 0.52 \) just when the mixture separates into three phases; while for the others two temperatures this phase equilibria does not occur. The ternary composition diagrams for each temperature showed in figure 4-23 as a function of composition, displayed the three different phases as a function of pressure.

Figure 4-24 PC-SAFT predictions for the vapor-liquid-liquid equilibria (VLLE) and binary diagram pressure-composition of the ternary system PS-C₆H₁₂-CO₂ at 443 K. Calculations were
made using PC-SAFT parameters taken from table 4-1 and the binary interaction parameters shown in table 4-7.

As an example, six points in the VLLE region were selected to delineate the three phases present. The specific compositions for these six points are presented in table 4-8.

Table 4-8 Compositions for the border points of the three phase region of the ternary system PS-C₆H₁₂-CO₂ at 443 K.

<table>
<thead>
<tr>
<th></th>
<th>W CO₂</th>
<th>W PS</th>
<th>W C₆H₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.1289</td>
<td>0.0037</td>
<td>0.8673</td>
</tr>
<tr>
<td>P2</td>
<td>0.1118</td>
<td>0.1162</td>
<td>0.7720</td>
</tr>
<tr>
<td>P3</td>
<td>0.6423</td>
<td>1e-71</td>
<td>0.3577</td>
</tr>
<tr>
<td>P4</td>
<td>0.1553</td>
<td>0.0001</td>
<td>0.8447</td>
</tr>
<tr>
<td>P5</td>
<td>0.1196</td>
<td>0.1938</td>
<td>0.6866</td>
</tr>
<tr>
<td>P6</td>
<td>0.6619</td>
<td>1e-71</td>
<td>0.3381</td>
</tr>
</tbody>
</table>

4.4 Swelling as a function of pressure

Swelling is related with an increase of volume of the material due to absorption of a solvent. The concept of free volume was introduced in the 1950s as an explanation for molecular transport in liquids and glasses. Experimentally, swelling has been measured with different polymers, over a wide range of pressures and temperatures. Bonavoglia et al. performed experiments with poly(methyl methacrylate) (PMMA), copolymer tetrafluoroethylene-perfluoromethylvinylether (MFA), poly (tetrafluroethylene) (PTFE), and poly (vinylidiene fluoride) (PVDF). They found different phase equilibria behavior.
for each polymer when in the presence of CO₂, depending on their chemical and physical properties. Some polymer properties such as $T_g$, degree of crystallinity, degree of cross linking and chemical structure are affected when sorption occurs. In the case of CO₂, when a polymer has an affinity with it, the polymer expands when CO₂ is sorbed. This phenomenon is related with the CO₂ diffusion between the polymer chains in the matrix and the corresponding expansion of free volume between them. Spyriouni et al.²⁹ presented a strategy to compute sorption isotherms of CO₂ in glassy atactic polystyrene under high pressure and then compared them with experimental data available.

In this work we present the swelling as a function of pressure for the ternary mixture PS-C₆H₁₂-CO₂, at five different temperatures 373.15K, 408.15K, 443K, 473K and 503K at low pressures [0.2 – 1 MPa] and high pressures [1 to 20 MPa]; using the PC-SAFT EoS. The results are shown in figures 4-25 to 4-28. These temperatures were selected above the $T_g$ of the polymer ($T_g$ of PS =368 K) and below its melting temperature ($T_{melting} = 515$ K).

![Swelling plots](image)

Figure 4-25 Swelling plots for the ternary system PS-C₆H₁₂-CO₂, at temperatures of 373.15K and 408.15K, as a function of volume and pressure, in the range of 0 to 1 MPa.
Figure 4-26 Swelling plots for the ternary system PS-C₆H₁₂-CO₂, at temperatures of 373.15K and 408.15K, as a function of volume and pressure, in the range of 0 to 4 MPa.

Swelling as a function of pressure is shown in figures 4-25 and 4-26 for 373.15 K and 408.15 K. A distinct peak shows around 0.2 MPa for the temperature of 373.15K and around 0.55 MPa for the temperature of 408.15K. These peaks would represent the maximum change in volume of the ternary mixture.

Figure 4-27 Swelling plots for the ternary system PS-C₆H₁₂-CO₂, at temperatures of 443K, 473K, and 503K, as a function of volume and pressure, in the range of 0 to 1 MPa.
Figure 4-28 Swelling plots for the ternary system PS-C₆H₁₂-CO₂, at temperatures of 443K, 473K, and 503K, as a function of volume and pressure, in the range of 0 to 8 MPa.

For the temperatures of 443 K, 473 K and 503 K shown in figures 4-27 and 4-28, at lower pressures the systems remain with similar tendencies. At 443 K the increase in volume is higher (about 0.2 cm³/g), than for the other two temperatures (~0.03 cm³/g to 0.05 cm³/g). In the volume-pressure plot the change in volume that these ternary systems experiment when different phases are present is evident. Particularly at 503 K a discontinuity appears at 4.5 MPa. This change is related to those observed in figure 4-22 (pressure-mass fraction PS plot) when the VLLE phase behavior was predicted. After these conditions the change in the volume is almost insignificant for the three temperatures, when ternary mixtures reach the one phase region in the range of 8.1 MPa to 20.5 MPa depending on the temperature.

Finally several other derivatives properties of interest such as the coefficient of isothermal compressibility ($\beta_T$), the coefficient of isobaric thermal expansivity ($\alpha_P$) and the heat capacity, $C_p$, were also studied, and are discussed below.
4.5 Derivative properties

For small systems, i.e. solvent, anti-solvent, the coefficient of isothermal compressibility ($\beta_T$) and the coefficient of isobaric thermal expansivity ($\alpha_P$) are of great interest both for theoretical and industrial applications. However, the experimental availability of these coefficients is limited. Different experimental techniques have been used to calculate these properties\textsuperscript{30}. For example, $\alpha_P$ is measured with dilatometric or with densitometric techniques. In the case of $\beta_T$ can be directly obtained through the adiabatic compressibility $\beta_S$ by using the expression

$$\beta_T = \beta_S + \alpha_P^2 TV/C_P$$ \hspace{1cm} (4.4)

where $C_P$ is the heat capacity at constant pressure. The adiabatic compressibility is easily evaluated when the speed of sound $u$ and the density $\rho$ are known ($\beta_S = 1/\rho u^2$), but it is required $\alpha_P$ and $C_P$, which are not always available. Therefore, new methods to predict these thermo-mechanical coefficients are needed.

The isobaric thermal expansivity and the isothermal compressibility are defined as

$$\alpha_P = V^{-1} \left( \frac{\partial V}{\partial T} \right)_P$$ \hspace{1cm} (4.5)

$$\beta_T = -V^{-1} \left( \frac{\partial V}{\partial P} \right)_T$$ \hspace{1cm} (4.6)

The ratio between both of them is named the thermal pressure coefficient $\gamma = \frac{\alpha_P}{\beta_T}$.

For polymers, these two coefficients are essentially different manners of representing the PVT surface. They are often used to assess potential engineering applications; the isothermal compressibility can be used to calculate the bulk or shear
moduli. Both coefficients increase significantly at temperatures above the glass transition temperature ($T_g$), in some cases experiencing 50% increase in the melt state, and as consequence, can be used to qualitatively understand how rubbery or glassy the polymer of interest is. Some comparisons of these coefficients for a variety of polymers indicate that a more rubbery polymer will exhibit a higher value for both $\alpha_P$ and $\beta_T$. The effects of pressure, volume, and temperature can even be expeditiously studied using $\alpha_P$ as a function of pressure or $\beta_T$ as a function of temperature.

For polymer solutions (and especially with the presence of solvent/antisolvent) there are scarce studies available in literature. Thus, in this work we use the PC-SAFT EoS to evaluate these parameters. In the previous section, we reported the PVT data for the PS-$\text{C}_6\text{H}_{12}\text{-CO}_2$ system between 373 K and 503 K and at pressures from 0.1MPa to 20.5 MPa. Here, the thermal expansivity, $\alpha_P$, and the isothermal compressibility, $\beta_T$, coefficients are calculated. The molecular weight of the polystyrene considered here is $M_w = 101,400$ g/mol.

4.5.1 The coefficient of isothermal compressibility, $\beta_T$

The isothermal compressibility, $\beta_T$, was calculated at temperature range between 373 K and 503 K. The results are shown in figures 4-29 and 4-30. The $\beta_T$ coefficient presents similar trends, for 373.15 K and 408.15 K, reaching a constant value at 0.5 MPa and 1 MPa, respectively. (See table B-4 from the appendix B)
 Isothermal compressibility parameters, $\beta_T$, as a function of pressure at temperatures 373.15K and 408.15K.

For isotherms at 443 K, 473 K, and 503 K the $\beta_T$ coefficients present similar trends, reaching a constant value at 1.5 MPa, 3.0 MPa, and 4.5 MPa, respectively. In these isotherms, however is clearly shown when the ternary mixture changes from two phases to three phases, in which the $\beta_T$ coefficients present a discontinuity and an increase in the value of $\beta_T$. Then the ternary mixture return to two phases (second discontinuity) and almost the same $\beta_T$ coefficient value as before. (See table B-5 from the appendix B).

 Isothermal compressibility parameters, $\beta_T$, as a function of pressure at three temperatures 443K, 473K and 503K.
4.5.2 The isobaric thermal expansivity coefficient, $\alpha_P$

The isobaric thermal expansivity coefficient, $\alpha_P$, was calculated at temperature range between 150 K and 590 K and at three different pressures 10.1 MPa, 15.15 MPa and 20.2 MPa. Our results are shown in figure 4-31. (See table B-6 from the appendix B).

![Isobaric thermal expansivity coefficients for the ternary system PS-C$_6$H$_{12}$-CO$_2$, at three different pressures 10,100 kPa, 15,150 kPa and 20,200 kPa as a function of temperature.](image)

In this figure three explicit regions are observed. At the lowest pressure (10.1 MPa) a first region can be delimited between the melting point of pure CO$_2$ (194.7 K) and its boiling point (216.6 K). In the second region, approximately between 220 K and 350 K, an increase in the value of the thermal expansivity coefficient is observed, starting around the melting point of C$_6$H$_{12}$ (280 K) and it reach its maximum value near the boiling point of C$_6$H$_{12}$ (354 K). Around 370 K and 440 K, 470 K and 500 K; respectively at pressures 10,100 kPa, 15,150 kPa and 20,200 kPa, other important fact is observed, a change in the sign of the $\alpha_P$ values from positive to negative. This change might be related with the $T_g$ of the polymer (for polystyrene 368.5 K). For the pressure plot of
10,100 kPa the fourth region around 550 K presents a peak that probably is related with the melting point of the polymer (Tm ~ 515 K.)

Finally, the heat capacity ($C_p$) of ternary system PS-C$_6$H$_{12}$-CO$_2$, was calculated at three different temperatures. Results are shown in figure 4-32.

![Heat capacity (Cp)](image)

Figure 4-32 Heat capacities of the ternary system PS-C$_6$H$_{12}$-CO$_2$ as a function of temperature, at three different pressures.

4.6 Conclusions

Here, we demonstrated the advantage of using a molecular-based EoS, PC-SAFT, as a powerful advance for the industrial applications of polymer/solvent/anti-solvent mixtures.

Using polymer parameters calculated from a recently proposed parameterization strategy, the PC-SAFT model satisfactorily predicts the phase equilibria behavior of binary and ternary polystyrene, cyclohexane carbon dioxide systems.
References

1 Flory, P. J. Symposium on applications of phase diagrams in polymer science, at NBS, Gaithersburg, MD. Oct. 15-17, 1984.
2 Freeman, P. I., Rowlinson, J. S. Lower critical points in polymer solutions. Polymer 1, 1960, 20-26
5 McClellan, A. K., McHugh, M. A. Separating polymer solutions using high pressure lower critical solution temperature (LCST) phenomena. Polymer Engineering and Science 25, 1985, 1088-1092
11 Favari, F., Bertucco, A., Elvassore, N., Fermeglia, M. Multiphase multicomponent equilibria for mixtures containing polymers by the perturbation theory. Chemical Engineering Science 55, 2000, 2379-2392


Chapter 5

Conclusions and future work

5.1 Fluorinated and hydrocarbon ester functionalized poly (p-phenylene) polymers

The properties of poly (p-phenylene) (PPP)-based materials have been studied for the last decades as a consequence of the “linear and rigid backbone” chain architecture. The superior thermal stability of PPPs increased the interest on the synthesis of its derivatives. Functionalized PPPs can be very soluble in conventional liquid organic solvents, which indicate that it could be possible to dissolve these polymers in SCF solvents. In chapter 3 we studied the phase equilibria behavior of the building blocks (monomers) of the poly (p-phenylenes) in carbon dioxide with both cubic EoS and the molecular-based PC-SAFT EoS. The results were encouraging and thus, here we report preliminary studies for four specific poly (p-phenylene) polymers that were recently synthesized by Wright et al.

According with Wright et al., the alkyl and fluoroalkyl benzoate monomers were synthesized using two different routes, as shown in figure 5-1. The alkyl benzoate monomer propyl 2, 5-dichlorobenzoate and octyl 2, 5-dichlorobenzoate were synthesized using 2, 5-dichloibenzoic acid and the corresponding alcohol in a Fisher esterification reaction. The fluoroalkyl benzoate monomers were more complicated to synthesize, and thus auxiliary treatments of 2, 5-dichlorobenzoyl chloride with the fluoro alcohols were used. Polymers were synthesized using the Ni-catalyzed homo coupling chemistry.
developed by Colon and Kesley\(^4\) (see figure 5-2). The final polymeric materials, after precipitation and drying, were fully characterized by analytical and spectroscopic methods.

Figure 5-1 Schematic representation of the synthesis of alkyl and fluoroalkyl monomers\(^3\).

5.1.1 Phase behavior of fluorinated and nonfluorinated propyl and octyl ester functionalized PPPs.

The experimental results published by Wright \textit{et al.}\(^3\) for the fluorinated polymer PPO2 (poly \((p\)-phenylene) tridecafluoro octyl 2, 5-DCB) in carbon dioxide shown that it is extremely soluble in CO\(_2\). These results, together with our previous findings presented in chapter 3, invited us to study the phase equilibria of these polymers using PC-SAFT EoS. The pressure-temperature diagram for PPO2 is shown in figure 5.3.
Figure 5-3 Pressure-temperature diagram for the binary systems PPO2+CO2 with $M_{wPPO2} = 11,880$ g/mol, PDI=1.65 and composition: $w_{PPO2}=0.013$, $w_{CO2}=0.987$. Calculations were made using PC-SAFT parameters taken from table 5-1. For the polydisperse calculations seven pseudo-components were used as showed in table 5-2. Dashed line is PC-SAFT prediction for a monodisperse system with $k_{ij} = 0$. Line with solid diamonds represent PC-SAFT prediction for a polydisperse system with PDI=1.65, 1.3 wt% of PPO2 and $k_{ij} = 0$. Diamonds correspond to experimental data reported in literature\(^3\).

Table 5-1. PC-SAFT parameters for poly (p-phenylene) polymers used in this work

<table>
<thead>
<tr>
<th>Poly (p-phenylene) polymers</th>
<th>Properties</th>
<th>GC-PC-SAFT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{wPPO}$</td>
<td>$M_{wmon}$</td>
</tr>
<tr>
<td></td>
<td>(g/mol)</td>
<td>(g/mol)</td>
</tr>
<tr>
<td>PPP1 Propyl 2, 5-Dichlorobenzoate</td>
<td>18,060</td>
<td>233.00</td>
</tr>
<tr>
<td>PPO1 Octyl 2, 5-Dichlorobenzoate</td>
<td>27,720</td>
<td>303.23</td>
</tr>
<tr>
<td>PPP2 Pentafiuoro Propyl 2, 5-Dichlorobenzoate</td>
<td>30,492</td>
<td>323.05</td>
</tr>
<tr>
<td>PPO2 Tridecafluoro Octyl 2, 5-Dichlorobenzoate</td>
<td>11,880</td>
<td>537.10</td>
</tr>
</tbody>
</table>
In the P-T diagram of PPO2 (figure 5-3) are shown the predictions for the monodisperse and polydisperse systems. When the polydispersity is taken into account the predicted phase equilibria increases as a function of pressure. Comparing figures 5.3 and 5.4 with figures 4.17 and 4.18 (in section 4.3 of this work) it is possible to affirm that the general phase behavior of PPPs polymers + CO₂ systems is similar to the studied phase behavior of PS + CO₂ systems, in the range under study.

The P-T phase diagrams for the four poly (p-phenylene) polymers with fluorinated and nonfluorinated alkyl chains are shown in figure 5-4, considered as polydisperse systems. From this figure, it is clear that fluorination of alkyl chains improves the solubility conditions of poly (p-phenylene) polymers. However, the chain length size also strongly improves the solubility. For example, PPO2 requires half the pressure conditions to be dissolved in CO₂ when compared against PPP2. These results confirmed that PPP or PPO polymers might be dissolved in carbon dioxide at moderate conditions.
Figure 5-4 Pressure-temperature diagrams for the binary systems of PPPs+CO$_2$ and PPOs+CO$_2$.

Phase equilibria diagram calculated for polydisperse systems, with seven pseudo-components as shown in table 5-2. The four mixtures have 1.3% wt of the polymer and M$_w$ ranging from 11,880 g/mol to 30,492 g/mol. Calculations were made using PC-SAFT parameters taken from table 5-1. Lines with symbols are PC-SAFT predictions.

Table 5-2 Pseudo-components determined from the reported experimental data, Mw and Mn used in this work.

<table>
<thead>
<tr>
<th>Pseudo-components $i$</th>
<th>Molar mass (g/mol)</th>
<th>Massfraction of the polymer</th>
<th>Molar mass (g/mol)</th>
<th>Massfraction of the polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>5.4294E-09</td>
<td>100</td>
<td>8.2595E-10</td>
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<tr>
<td>2</td>
<td>379.77</td>
<td>2.0273E-05</td>
<td>4.3550E-06</td>
<td>1.1893E-05</td>
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<tr>
<td>3</td>
<td>1442.25</td>
<td>6.9161E-03</td>
<td>3.0681E-03</td>
<td>6.982E-03</td>
</tr>
<tr>
<td>4</td>
<td>5477.23</td>
<td>2.1558E-01</td>
<td>1.6197E-01</td>
<td>3.2309E-01</td>
</tr>
<tr>
<td>5</td>
<td>20800.84</td>
<td>6.1394E-01</td>
<td>6.4078E-01</td>
<td>6.0952E-01</td>
</tr>
<tr>
<td>6</td>
<td>78995.26</td>
<td>1.5975E-01</td>
<td>1.8996E-01</td>
<td>5.8401E-02</td>
</tr>
<tr>
<td>7</td>
<td>300000</td>
<td>3.7979E-03</td>
<td>4.2199E-03</td>
<td>2.8420E-04</td>
</tr>
</tbody>
</table>

In figure 5-5 two phase behaviors are shown, the PPP1 (poly ($p$-phenylene) propyl 2, 5-DCB) with $M_w$= 18,060 g/mol and PDI= 2.15 at wt = 1.3%; and the PPP2 (poly ($p$-phenylene) pentafluoro propyl 2, 5-DCB) with $M_w$= 30,492 g/mol and PDI= 1.98. The critical temperature for both polymeric systems is reached around 580-600 K. However, the critical pressure difference is over 25,000 kPa. In other words, at similar conditions the fluorinated propyl chain requires less pressure to dissolve in CO$_2$. 
Figure 5-5 Pressure-temperature diagram for the binary systems PPP1+CO2 and PPP2+CO2 with compositions $w_{PP1}=0.013$, $w_{CO2}=0.987$ and molecular weight $M_wPP1 = 18,060 \text{ g/mol}$ and $M_wPP2 = 30,492 \text{ g/mol}$. Calculations were made using PC-SAFT parameters taken from table 5-1. For the polydisperse calculations seven pseudo-components were used as shown in table 5-2. Lines with symbols are PC-SAFT predictions with $k_{ij} = 0$. Dashed lines are PC-SAFT predictions calculated for the monodisperse systems.

In figure 5-6 two phase behaviors are shown, the PPO1 (poly ($p$-phenylene) octyl 2, 5-DCB) with $M_w = 27,720 \text{ g/mol}$ and with PDI= 2.1; and the PPO2 (poly ($p$-phenylene) tridecafluoro octyl 2, 5-DCB) with $M_w = 11,880 \text{ g/mol}$ and with PDI= 1.65. The P-T curve obtained with $k_{ij} = 0$ over predicts the phase behavior of the PPO2 when compared against the experimental data published by Wright et al.$^3$ However, it shows qualitative agreement. Taking in account that these new PPPs polymers are in development, to our knowledge there are no more experimental data to compare with, and thus the predictive
capabilities of the PC-SAFT approach can help direct future experimental endeavors for these systems. Again it is possible to conclude that both, the length of the chain and the fluorinated conditions, improve significantly the solubility of these PPPs in CO$_2$.

Figure 5-6 Pressure-temperature diagram for the binary systems PPO1+CO$_2$ and PPO2+CO$_2$ with compositions: $w_{PPP}=0.013$, $w_{CO_2}=0.987$ and $M_{wPPO1} = 27,720$ g/mol and $M_{wPPO2} = 11,880$ g/mol. Calculations were made using PC-SAFT parameters taken from table 5-1. For the polydisperse calculations seven pseudo-components were used as shown in table 5-2. Lines with symbols are PC-SAFT prediction with $k_{ij} = 0$. Dashed lines correspond to PC-SAFT predictions for the monodisperse system. Diamonds correspond to experimental data reported in literature$^3$.

In figures 5-5 and 5-6 were included the predictions curves for the monodisperse systems. When compared with experimental data our calculations show that when the polydispersity is taken into account the predictions fall above the monodisperse case.
This is in agreement with the work of Jog et al. as shown in figure 5-7. Note that in figure 5-7 the data shown, is pressure as a function of mass fraction of the polymer, and in figures 5-5 and 5-6, the data is pressure as a function of temperature.

Finally, as mentioned recently by Bray et al. identifying CO$_2$/polymer solubility trends will help to enhance the search of CO$_2$-soluble polymers. The preliminary results presented above show that the PC-SAFT approach can help in the design of these polymers, to guide the synthesis efforts of structural diverse polymer libraries.
5.2 Conclusions

Phase equilibria predictions of several polymer solutions and polymer-solvent-solvent systems in the presence of supercritical carbon dioxide (scCO$_2$), applying PC-SAFT and cubic equations of state, were presented in this work.

In the first chapter, a review of equations of state including their applicability and different types of phase behaviors encountered in binary mixtures of polymer + solvent systems was presented.

The second chapter covered a particular review of scCO$_2$ including the multi-parametric equation of state for this compound. Also were presented the general solubility behavior of carbon dioxide with polymeric materials and some biopolymer applications.

In the third chapter, the capabilities and usefulness of several cubic EoS (PR, SRK, SOF-PR, SOF-RK) as well as a molecular-based EoS, PC-SAFT for correlating the two phase fluid-fluid regions of aromatics + scCO$_2$ and dichlorobenzoates + scCO$_2$ systems were presented. In general, for the small-molecule binary systems, the simpler cubic EoS appear to be able to capture correctly the VLE region, and in better agreement when compared with the PC-SAFT. For benzoates, the critical properties were estimated from the group contribution approach of Marrero and Gani for use with the cubic EoS, and GC-PC-SAFT parameters were obtained with the group contribution approach of Tihic and coworkers. For the longer ADCB series it was necessary to use a temperature-dependent $k_{ij}$ parameter and, moreover, variations in the second significant figure for $k_{ij}$ dramatically affect the phase envelope predictions. In general, qualitative results can be obtained with both cubic EoS and the PC-SAFT approach with the use of temperature-dependant binary interaction parameters.

In the fourth chapter of this work, we used the PC-SAFT model to predict the anti-solvent effects of supercritical carbon dioxide in polystyrene-cyclohexane-carbon dioxide ternary system. The phase equilibria behavior in the ternary system was
calculated using PC-SAFT EoS. The results using polymer parameters calculated with a recently proposed parametrization strategy indicate that the parametrization approach might provide sets of polymer parameters that yield satisfactory results modeling both binary and ternary polymer solutions. These results allowed us to use this equation to evaluate the swelling behavior of the ternary system as a function of pressure; and several other derivatives properties of interest, such as the coefficient of isothermal compressibility \((\beta_T)\), the coefficient of isobaric thermal expansivity \((\alpha_P)\) and the heat capacity, \(C_p\).

The predictions curves for the new fluorinated and hydrocarbon ester functionalized poly \((p\)-phenylene) polymers (PPPs) were calculated with the group contribution parameters in PC-SAFT in chapter five. Although we only have experimental results for the fluorinated polymer PPO2 in CO\(_2\) showing that this fluorinated polymer is extremely soluble in CO\(_2\), our predictions showed reasonable qualitative agreement. The P-T diagrams for four new fluorinated and non-fluorinated PPPs, shown that both, the length of the chain and the fluorinated conditions, improve significantly the solubility of these PPPs in CO\(_2\). However, it would be interesting to study the effect of incorporating associating interactions in the description of the fluid-phase behavior. In the future, we can extend our research to other polymeric systems which involves more complicated molecular interactions such as perfluoro-alkyl acrylates. The use of PC-SAFT EoS sometimes is limited for the availability of the parameters for these new compounds. Then, a combination of the recently presented parametrization strategy for the evaluation of polymer molecular parameters from macroscopic properties of binary mixtures; and the group contribution theories to evaluate the two associative parameters for PC-SAFT: kappa \((\kappa^{AB})\) and epsilon \((\epsilon^{HB})\); would result in a reasonable approach to include the associating interactions in binary and ternary mixtures.

Additionally, because of its high solubility in many polymers, scCO\(_2\) is a valuable tool in polymer processing, so a wide range of applications clearly suggest a bright future for scCO\(_2\)-assisted polymer processing. Therefore, with the presentation of this work, we
believe that the need, for deeper understanding of specific interactions in polymer-CO$_2$
systems, for modeling of a variety of experimental phase equilibria data and for
simulations studies to supplement experimental work, were at least lightly improved.
References


Appendix A

Phase diagrams of scCO$_2$+ aromatics and scCO$_2$+ dichlorobenzoates binary systems

Table A-1 Coefficients for the generalized correlations of equations 3.8a and 3.8b

<table>
<thead>
<tr>
<th></th>
<th>Peng-Robinson</th>
<th>Redlich-Kwong</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_0$</td>
<td>1.18742</td>
<td>1.28206</td>
</tr>
<tr>
<td>$c_1$</td>
<td>0.71904</td>
<td>0.7931</td>
</tr>
<tr>
<td>$c_2$</td>
<td>1.47453</td>
<td>1.58828</td>
</tr>
<tr>
<td>$d_0$</td>
<td>0.61856</td>
<td>0.66848</td>
</tr>
<tr>
<td>$d_1$</td>
<td>0.72421</td>
<td>0.77746</td>
</tr>
</tbody>
</table>
Figure A-1 Pressure – Composition isotherms for the systems carbon dioxide – benzene. (a) $T = 353K$ and $k_{ij} = 0.081$; (b) $T = 373.5K$ and $k_{ij} = 0.081$; (c) $T = 393.2K$ and $k_{ij} = 0.081$; the calculations were made using Peng-Robinson Equation of State. (d) $T = 353K$ and $k_{ij} = 0.083$; (e) $T = 373.5K$ and $k_{ij} = 0.083$; (f) $T = 393.2K$ and $k_{ij} = 0.083$; the calculations were made using Peng-Robinson SOF Equation of State; (g) $T = 353K$ and $k_{ij} = 0.084$; (h) $T = 373.5K$ and $k_{ij} = 0.084$; (i) $T = 393.2K$ and $k_{ij} = 0.084$; the calculations were made using Soave-Redlich-Kwong Equation of State. (j) $T = 353K$ and $k_{ij} = 0.077$; (k) $T = 373.5K$ and $k_{ij} = 0.077$; (l) $T = 393.2K$ and $k_{ij} = 0.077$; the calculations were made using Redlich-Kwong SOF Equation of State. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.
Figure A-2 Pressure – Composition isotherms for the systems carbon dioxide – benzene. (a) T = 353K and $k_{ij} = 0.115$; (b) T = 373.5K and $k_{ij} = 0.115$; (c) T = 393.2K and $k_{ij} = 0.115$; the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski$^2$. (d) T = 353K and $k_{ij} = 0.13$; (e) T = 373.5K and $k_{ij} = 0.12$; (f) T = 393.2K and $k_{ij} = 0.12$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach$^3$. Solid lines are PC-SAFT correlations with $k_{ij}$=0. Symbols correspond to experimental data reported in literature$^1$. 
Figure A-3 Pressure – Composition isotherms for the systems carbon dioxide – toluene. (a) T = 353.4K and $k_{ij} = 0.085$; (b) T = 373.2K and $k_{ij} = 0.085$; (c) T = 393.2K and $k_{ij} = 0.085$; the calculations were made using Peng-Robinson Equation of State. (d) T = 353.4K and $k_{ij} = 0.087$; (e) T = 373.2K and $k_{ij} = 0.087$; (f) T = 393.2K and $k_{ij} = 0.087$; the calculations were made using Peng-Robinson SOF Equation of State; (g) T = 353.4K and $k_{ij} = 0.09$; (h) T = 373.2K and $k_{ij} = 0.09$; (i) T = 393.2K and $k_{ij} = 0.09$; the calculations were made using Soave-Redlich-Kwong Equation of State. (j) T = 353.4K and $k_{ij} = 0.081$; (k) T = 373.2K and $k_{ij} = 0.081$; (l) T = 393.2K and $k_{ij} = 0.081$; the calculations were made using Redlich-Kwong SOF Equation of State. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.¹
Figure A-4 Pressure – Composition isotherms for the systems carbon dioxide – toluene.  
(a) T = 353.4K and $k_{ij} = 0.12$; (b) T = 373.2K and $k_{ij} = 0.12$; (c) T = 393.2K and $k_{ij} = 0.12$; the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski$^2$. (d) T = 353.4K and $k_{ij} = 0.13$; (e) T = 373.2K and $k_{ij} = 0.13$; (f) T = 393.2K and $k_{ij} = 0.13$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach$^3$. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature$^1$. 
Figure A-5 Pressure – Composition isotherms for the systems carbon dioxide –p-xylene. (a) T = 353.2K and $k_{ij} = 0.077$; (b) T = 373.4K and $k_{ij} = 0.077$; (c) T = 393.2K and $k_{ij} = 0.077$; the calculations were made using Peng-Robinson Equation of State. (d) T = 353.2K and $k_{ij} = 0.08$; (e) T = 373.4K and $k_{ij} = 0.08$; (f) T = 393.2K and $k_{ij} = 0.08$; the calculations were made using Peng-Robinson SOF Equation of State; (g) T = 353.2K and $k_{ij} = 0.083$; (h) T = 373.4K and $k_{ij} = 0.083$; (i) T = 393.2K and $k_{ij} = 0.083$; the calculations were made using Soave-Redlich-Kwong Equation of State. (j) T = 353.2K and $k_{ij} = 0.079$; (k) T = 373.4K and $k_{ij} = 0.079$; (l) T = 393.2K and $k_{ij} = 0.079$; the calculations were made using Redlich-Kwong SOF Equation of State. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature.
Figure A-6 Pressure – Composition isotherms for the systems carbon dioxide – p-xylene. 
(a) $T = 353.2\, \text{K}$ and $k_{ij} = 0.12$; (b) $T = 373.4\, \text{K}$ and $k_{ij} = 0.12$; (c) $T = 393.2\, \text{K}$ and $k_{ij} = 0.12$; the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski$^2$. (d) $T = 353.2\, \text{K}$ and $k_{ij} = 0.11$; (e) $T = 373.4\, \text{K}$ and $k_{ij} = 0.11$; (f) $T = 393.2\, \text{K}$ and $k_{ij} = 0.11$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach$^3$. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature$^1$. 

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1. Literature reference 1
2. Literature reference 2
3. Literature reference 3
Figure A-7 Pressure – Composition isotherms for the systems carbon dioxide – m-xylene. (a) T = 310.9K and $k_{ij} = 0.077$; (b) T = 477.6K and $k_{ij} = 0.077$; (c) T = 582.55K and $k_{ij} = 0.077$; the calculations were made using Peng-Robinson Equation of State. (d) T = 310.9K and $k_{ij} = 0.08$; (e) T = 477.6K and $k_{ij} = 0.08$; (f) T = 582.55K and $k_{ij} = 0.08$; the calculations were made using Peng-Robinson SOF Equation of State; (g) T = 310.9K and $k_{ij} = 0.083$; (h) T = 477.6K and $k_{ij} = 0.083$; (i) T = 582.55K and $k_{ij} = 0.083$; the calculations were made using Soave-Redlich- Kwong Equation of State. (j) T = 310.9K and $k_{ij} = 0.075$; (k) T = 477.6K and $k_{ij} = 0.075$; (l) T = 582.55K and $k_{ij} = 0.075$; the calculations were made using Redlich-Kwong SOF Equation of State. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature$^{4,5}$. 
Figure A-8 Pressure – Composition isotherms for the systems carbon dioxide – m-xylene.

(a) T = 310.9K and \( k_{ij} = 0.11 \); (b) T = 477.6K and \( k_{ij} = 0.11 \); (c) T = 582.55K and \( k_{ij} = 0.11 \); the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski\(^2\). (d) T = 310.9K and \( k_{ij} = 0.11 \); (e) T = 477.6K and \( k_{ij} = 0.11 \); (f) T = 582.55K and \( k_{ij} = 0.11 \); the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach\(^3\). Solid lines are PC-SAFT correlations with \( k_{ij}=0 \). Symbols correspond to experimental data reported in literature\(^4,5\).
Figure A-9 Pressure – Composition isotherms for the systems carbon dioxide –o-xylene. (a) T = 312.65K and $k_{ij} = 0.073$; (b) T = 338.15K and $k_{ij} = 0.073$; (c) T = 366.15K and $k_{ij} = 0.073$; the calculations were made using Peng-Robinson Equation of State. (d) T = 312.65K and $k_{ij} = 0.075$; (e) T = 338.15K and $k_{ij} = 0.075$; (f) T = 366.15K and $k_{ij} = 0.075$; the calculations were made using Peng-Robinson SOF Equation of State; (g) T = 312.65K and $k_{ij} = 0.077$; (h) T = 338.15K and $k_{ij} = 0.077$; (i) T = 366.15K and $k_{ij} = 0.077$; the calculations were made using Soave-Redlich-Kwong Equation of State. (j) T = 312.65K and $k_{ij} = 0.074$; (k) T = 338.15K and $k_{ij} = 0.074$; (l) T = 366.15K and $k_{ij} = 0.074$; the calculations were made using Redlich-Kwong SOF Equation of State. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature\textsuperscript{6}. 
Figure A-10 Pressure – Composition isotherms for the systems carbon dioxide – o-xylene. (a) $T = 312.65\, \text{K}$ and $k_{ij} = 0.11$; (b) $T = 338.15\, \text{K}$ and $k_{ij} = 0.11$; (c) $T = 366.15\, \text{K}$ and $k_{ij} = 0.11$; the calculations were made using solvent parameters of PC-SAFT reported by Gross and Sadowski$^2$. (d) $T = 312.65\, \text{K}$ and $k_{ij} = 0.11$; (e) $T = 338.15\, \text{K}$ and $k_{ij} = 0.11$; (f) $T = 366.15\, \text{K}$ and $k_{ij} = 0.11$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach$^3$. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature$^6$. 
Figure A-11 Pressure – Composition isotherms for the systems carbon dioxide – methylbenzoate. (a) $T = 313.15\text{K}$ and $k_{ij} = 0.05$; the calculations were made using Peng-Robinson Equation of State. (b) $T = 313.15\text{K}$ and $k_{ij} = 0.080$; the calculations were made using Peng-Robinson SOF Equation of State. (c) $T = 313.15\text{K}$ and $k_{ij} = 0.048$; the calculations were made using Soave-Redlich-Kwong Equation of State. (d) $T = 313.15\text{K}$ and $k_{ij} = 0.083$; the calculations were made using Redlich-Kwong SOF Equation of State. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature\textsuperscript{7}. 
Figure A-12 Pressure – Composition isotherms for the systems carbon dioxide – methylbenzoate. Temperature = 313.15K and $k_{ij} = 0.08$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach\textsuperscript{3}. Solid lines are PC-SAFT correlations with $k_{ij}$=0. Symbols correspond to experimental data reported in literature\textsuperscript{7}.
Figure A-13 Pressure – Composition isotherms for the systems carbon dioxide – ethylbenzoate. 

(a) $T = 308.15$K and $k_{ij} = 0.07$; (b) $T = 318.15$K and $k_{ij} = 0.07$; (c) $T = 328.15$K and $k_{ij} = 0.07$; the calculations were made using Peng-Robinson Equation of State. (d) $T = 308.15$K and $k_{ij} = 0.076$; (e) $T = 318.15$K and $k_{ij} = 0.076$; (f) $T = 328.15$K and $k_{ij} = 0.076$; the calculations were made using Peng-Robinson SOF Equation of State; (g) $T = 308.15$K and $k_{ij} = 0.071$; (h) $T = 318.15$K and $k_{ij} = 0.071$; (i) $T = 328.15$K and $k_{ij} = 0.071$; the calculations were made using Soave-Redlich-Kwong Equation of State. (j) $T = 308.15$K and $k_{ij} = 0.079$; (k) $T = 318.15$K and $k_{ij} = 0.079$; (l) $T = 328.15$K and $k_{ij} = 0.079$; the calculations were made using Redlich-Kwong SOF Equation of State. Solid lines are correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature$^8$. 
Figure A-14 Pressure – Composition isotherms for the systems carbon dioxide – ethylbenzoate. (a) \( T = 308.15K \) and \( k_{ij} = 0.091 \); (b) \( T = 318.15K \) and \( k_{ij} = 0.091 \); (c) \( T = 328.15K \) and \( k_{ij} = 0.091 \); the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach\(^3\). Solid lines are PC-SAFT correlations with \( k_{ij}=0 \). Symbols correspond to experimental data reported in literature\(^8\).
Figure A-15 Pressure – Composition isotherms for the systems carbon dioxide – propyl 2, 5-dichlorobenzoate. (a) T = 298.15K; (b) T = 323.15K; (c) T = 348.15K; the calculations were made using Peng-Robinson and Peng-Robinson SOF Equation of State, with $k_{ij} = 0.069$ and $k_{ij} = 0.063$ respectively; (d) T = 298.15K; (e) T = 323.15K; (f) T = 348.15K; the calculations were made using Soave-Redlich-Kwong and Redlich-Kwong SOF Equations of State, with $k_{ij} = 0.072$ and $k_{ij} = 0.069$ respectively. Symbols correspond to experimental data reported in literature.
Figure A-16 Pressure – Composition isotherms for the systems carbon dioxide – propyl 2, 5-dichlorobenzoate. (a) \(T = 298.15\text{K}\) and \(k_{ij} = 0\); (b) \(T = 313.15\text{K}\) and \(k_{ij} = 0.064\); (c) \(T = 323.15\text{K}\) and \(k_{ij} = 0.061\); (d) \(T = 348.15\text{K}\) and \(k_{ij} = 0.045\); the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach\(^3\). Solid lines are PC-SAFT correlations with \(k_{ij}=0\). Symbols correspond to experimental data reported in literature\(^7\).

For this range of temperatures [313.15 K to 348.15 K] the following temperature-dependant relationship \((R^2=0.9822)\) can be used to calculate the corresponding \(k_{ij}\) for the binary mixture CO\(_2\)-propyl 2, 5-dichlorobenzoate:

\[
k_{ij} = -0.0006*T[\text{K}] + 0.2409
\]
Figure A-17 Pressure – Composition isotherms for the systems carbon dioxide – octyl 2, 5-dichlorobenzoate. (a) T = 298.15K; (b) T = 323.15K; (c) T = 348.15K; the calculations were made using Peng-Robinson and Peng-Robinson SOF Equation of State, with $k_{ij} = 0.0868$ and $k_{ij} = 0.0822$ respectively; (d) T = 298.15K; (e) T = 323.15K; (f) T = 348.15K; the calculations were made using Soave-Redlich-Kwong and Redlich-Kwong SOF Equations of State, with $k_{ij} = 0.0971$ and $k_{ij} = 0.0939$ respectively. Symbols correspond to experimental data reported in literature. 

7
Figure A-18 Pressure – Composition isotherms for the systems carbon dioxide – octyl 2, 5-dichlorobenzoate. (a) T = 298.15K and $k_{ij} = 0.085$; (b) T= 323.15.15K and $k_{ij} = 0.079$; (c) T = 348.15K and $k_{ij} = 0.071$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach$^3$. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature$^7$.

For this range of temperatures *[298.15 K to 348.15 K] the following temperature-dependant relationship ($R^2=0.9932$) can be used to calculate the corresponding $k_{ij}$ for the binary mixture CO$_2$- octyl 2, 5-dichlorobenzoate:

$$k_{ij} = -0.0003*T[K] + 0.1688$$

* For temperature of 298.15K this relationship is valid for molefraction of Octyl 2, 5-Dichlorobenzoate < 0.13625
Figure A-19 Pressure – Composition isotherms for the systems carbon dioxide – pentafluoropropyl 2, 5-dichlorobenzoate. (a) T = 298.15K; (b) T = 323.15K; (c) T = 348.15K; the calculations were made using Peng-Robinson and Peng-Robinson SOF Equation of State, with $k_{ij} = 0.047$ and $k_{ij} = 0.038$ respectively; (d) T = 298.15K; (e) T = 323.15K; (f) T = 348.15K; the calculations were made using Soave-Redlich-Kwong and Redlich-Kwong SOF Equation of State, with $k_{ij} = 0.051$ and $k_{ij} = 0.039$ respectively. Symbols correspond to experimental data reported in literature\textsuperscript{7}. 
Figure A-20 Pressure – Composition isotherms for the systems carbon dioxide – pentafluoro propyl 2, 5-dichlorobenzoate. (a) T = 298.15K and $k_{ij} = 0.05$; (b) T = 323.15K and $k_{ij} = 0$; (c) T = 348.15K and $k_{ij} = -0.02$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach$^3$. Solid lines are PC-SAFT correlations with $k_{ij}=0$. Symbols correspond to experimental data reported in literature$^7$. For this range of temperatures [298.15 K to 348.15 K] the following temperature-dependant relationship ($R^2=0.9423$) can be used to calculate the corresponding $k_{ij}$ for the binary mixture CO$_2$- pentafluoro propyl 2, 5-dichlorobenzoate:

$$k_{ij} = -0.0014\times T[K] + 0.4624$$
Figure A-21 Pressure – Composition isotherms for the systems carbon dioxide – tridecafluoro octyl 2, 5-dichlorobenzoate. (a) $T = 298.15K$; (b) $T = 323.15K$; (c) $T = 348.15K$; the calculations were made using Peng-Robinson and Peng-Robinson SOF Equation of State, with $k_{ij} = 0.069$ and $k_{ij} = 0.065$ respectively; (d) $T = 298.15K$; (e) $T = 323.15K$; (f) $T = 348.15K$; the calculations were made using Soave-Redlich-Kwong and Redlich-Kwong SOF Equations of State, with $k_{ij} = 0.084$ and $k_{ij} = 0.080$ respectively. Symbols correspond to experimental data reported in literature\textsuperscript{7}. 
Figure A-22 Pressure – Composition isotherms for the systems carbon dioxide – tridecafluoro octyl 2, 5-dichlorobenzoate. (a) T = 298.15K and $k_{ij} = 0.05$; (b) T = 323.15K and $k_{ij} = 0.03$; (c) T = 348.15K and $k_{ij} = 0.015$; the calculations were made using solvent parameters of PC-SAFT calculated with group-contribution approach$^3$. Solid lines are PC-SAFT correlations with $k_{ij}$=0. Symbols correspond to experimental data reported in literature$^7$.

For this range of temperatures [298.15 K to 348.15 K] the following temperature-dependant relationship ($R^2$=0.9932) can be used to calculate the corresponding $k_{ij}$ for the binary mixture CO$_2$- tridecafluoro octyl 2, 5-dichlorobenzoate:

$$k_{ij} = -0.0007*T[K] + 0.2579$$
References


6. Mohamed, R. S., Holder, G.D. High pressure phase behavior in systems containing CO$_2$ and heavier compounds with similar vapor pressure. *Fluid Phase Equilibria* 32, **1987**, 295-317


8. Feng, L.-C., Cheng, K.W., Tang, M., Chen, Y.-P. Vapor-liquid equilibria of carbon dioxide with ethyl benzoate, diethyl succinate and isoamyl acetate binary mixtures at elevated pressures. *J. Supercritical Fluids* 21, **2001**, 111-121
Appendix B

Phase behavior of polystyrene - cyclohexane – carbon dioxide (PS-C₆H₁₂-CO₂) ternary system and its binary component mixtures

Table B-1 Pseudocomponents determined from the experimental $M_w$ and $M_n$ values for modeling the molecular weight distribution of PS with Methyl cyclohexane shown in figure 4-14.

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<th>Pseudocomponent $i$</th>
<th>Molar Mass (g/mol)</th>
<th>Mass Fraction</th>
</tr>
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Table B-2 Molecular parameters of the PC-SAFT model for polymer calculated in figure 4-15

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<tr>
<th>Figure</th>
<th>Mixture</th>
<th>$\chi$</th>
<th>$\delta p$</th>
<th>$\delta s$</th>
<th>$M_w$</th>
<th>$m_p/M_w$</th>
<th>$\sigma$ [Å]</th>
<th>$\epsilon/k$ [K]</th>
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</thead>
<tbody>
<tr>
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Table B-3 Pseudocomponents determined from the experimental data $M_w$ and $M_n$ values for modeling the molecular weight distribution of PS with carbon dioxide presented in figure 4-15.

<table>
<thead>
<tr>
<th>Pseudocomponent $i$</th>
<th>Molar Mass (g/mol)</th>
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Table B-4 Isothermal compressibilities, $\beta_T$, and molar volumes calculated at different pressures at two isotherms 373.15K and 408.15K.

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<th>Pressure [MPa]</th>
<th>$\beta_T$ [MPa$^{-1}$]</th>
<th>Volume [cm$^3$/mole]</th>
<th>$\beta_T$ [MPa$^{-1}$]</th>
<th>Volume [cm$^3$/mole]</th>
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Table B-5 Isothermal compressibilities, $\beta_T$, and molar volumes calculated at different pressures for two isotherms 443 K, 473K, and 503K.

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