

Deutsche
Forschungsgemeinschaft

**Thermodynamic
Properties of
Complex Fluid Mixtures**

Research Report

DFG

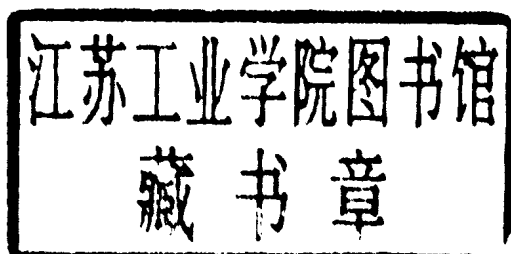
WILEY-VCH

Deutsche
Forschungsgemeinschaft

Thermodynamic Properties of Complex Fluid Mixtures

Edited by
Gerd Maurer

Research Report



WILEY-VCH Verlag GmbH & Co. KGaA

DFG

Deutsche Forschungsgemeinschaft
Kennedyallee 40, D-53175 Bonn, Federal Republic of Germany
Postal address: D-53175 Bonn
Phone: ++49/228/885-1
Telefax: ++49/228/885-2777
E-Mail: postmaster@dfg.de
Internet: <http://www.dfg.de>

This book was carefully produced. Nevertheless, editor, authors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.
--

Library of Congress Card No.: applied for

A catalogue record for this book is available from the British Library.

Die Deutsche Bibliothek – CIP Cataloguing-in-Publication Data
A catalogue record for this publication is available from Die Deutsche Bibliothek

ISBN 3-527-27770-6

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Printed on acid-free paper.

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Cover Design and Typography: Dieter Hüsken
Composition: ProSatz Unger, Weinheim
Printing: betz-druck gmbh, Darmstadt
Bookbinding: Litges & Dopf Buchbinderei GmbH, Heppenheim

Printed in the Federal Republic of Germany

Preface

This book presents summaries of the results achieved within a priority program funded by Deutsche Forschungsgemeinschaft (SPP 736) from 1995 to 2002. The main aim of this program was to enable experimental and theoretical work in the area of applied thermodynamics, in particular in phase equilibrium of complex fluid mixtures e.g. in the area of chemical, biotechnological and environmental process sciences. Altogether 27 single research projects were co-ordinated and funded. The research topics range from investigations of fluid systems where the complex behaviour results from chemical reactions (including associating substances) through the phase equilibrium in aqueous solutions of strong electrolytes, aqueous two-phase systems and polymer solutions, to high pressure phase equilibrium phenomena and the properties of microemulsion systems. The priority program was initiated by the editor with support by the late Professor Konrad Bier, Karlsruhe, Professor Klaus Lucas, Aachen, and Professor Karl Stephan, Stuttgart. Professor Dieter Mewes, Hannover, provided strong support within DFG. The project proposals were evaluated and recommended for support by an advisory committee, chaired by Professor Erich Hahne, Stuttgart. Professors Hans-Jürgen Bittrich and Wolfgang Fratzscher, both from Merseburg, Dietrich Wörmann, Köln, Manfred Zeidler, Aachen, and Drs. Bernhard Gutsche, Düsseldorf, and Gerhard Hochgesand, Heusenstamm, served in this committee. Also on behalf of all research grantees, I want to express my gratitude to all those colleagues. Last not least, I appreciate the support by Dr. Walter Lachenmeier of DFG who not only administrated the priority program, but was always open minded to help us to overcome the unavoidable problems during the course of the projects. This book is not only to present the research results, but it is dedicated to all the aforementioned institutions and in particular the persons for their generous and long lasting assistance. Without that dedication, it would have been impossible to achieve the goals. Mrs. Maike Petersen of Wiley-VCH, Weinheim, deserves my thanks both for her advice and her patience with us (the authors and the editor). Last not least I want to thank my secretary Mrs. Monika Reim for assisting me in the time consuming and tedious process of editing/proof reading the various manuscripts and following up the correspondence with the authors.

Kaiserslautern, July 2003

Gerd Maurer

Contents

I	Chemical Reactive Systems	
1	Experimental and Theoretical Investigations at the System $\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$	3
	<i>Matthias Behmann, Sae-Hoon Kim, Hans-Jürgen Kofß, and Klaus Lucas</i>	
1.1	Abstract	3
1.2	Introduction	3
1.3	Experimental Methods	4
1.3.1	Apparatus	4
1.3.2	Materials	5
1.3.3	Calibration and Analysis of Raman Signals	5
1.4	Theory	9
1.5	Results and Discussion	12
1.5.1	The System $\text{CH}_3\text{OH} + \text{H}_2\text{O}$	13
1.5.2	The System $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$	13
1.5.3	The System $\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$	17
1.5.4	The System $\text{CH}_3\text{SO}_4\text{H} + \text{CH}_3\text{OH}$	18
1.5.5	The System $\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ with $\text{CH}_3\text{SO}_4\text{H}$	18
1.5.6	The System $\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ with $\text{CH}_3\text{SO}_4\text{H}$ and $(\text{CH}_3)_2\text{O}$	21
1.6	Conclusion	22
	References	23
	Nomenclature	24
2	Measurement of Binary Phase Equilibria of Esterification Systems	26
	<i>Marko Tischmeyer and Wolfgang Arlt</i>	
2.1	Abstract	26
2.2	Introduction	26
2.3	Fundamentals	27
2.3.1	Calculation of Liquid and Vapor Phase Fugacities	27
2.3.2	Reaction Space and Coordinates Transformation	28
2.3.3	Standard State in VLE Calculation with Chemical Equilibrium	31
2.3.4	Kinetic Modelling	32
2.4	Experimental	34

2.4.1	Chemicals	34
2.4.2	Equipment and Experimental Procedure	35
2.5	Results	39
2.6	Conclusion	45
	References	45
	Nomenclature	46
3	Solubility of Carbon Dioxide in Aqueous Alkanolamine Solutions in the Temperature Range 313 to 353 K and Pressures up to 2.7 MPa	48
	<i>Dirk Silkenbäumer, Bernd Rumpf, and Rüdiger N. Lichtenhaler</i>	
3.1	Abstract	48
3.2	Introduction	48
3.3	Experimental	49
3.3.1	Apparatus	49
3.3.2	Procedure	50
3.3.3	Materials	51
3.4	Results	51
3.4.1	Test of Procedure: Results for the System $\text{CO}_2 + \text{H}_2\text{O}$	51
3.4.2	Results for the System $\text{CO}_2 + \text{MDEA} + \text{H}_2\text{O}$	52
3.4.3	Results for the System $\text{CO}_2 + \text{AMP} + \text{H}_2\text{O}$	54
3.4.4	Results for the System $\text{CO}_2 + \text{MDEA} + \text{AMP} + \text{H}_2\text{O}$	57
3.5	Modeling	58
3.6	Comparison with Literature Data	64
3.7	Conclusions	66
	References	66
	Nomenclature	67
4	The Influence of NO_2 on Complex Phase and Reaction Equilibria in Wet Flue Gas Cleaning Processes	69
	<i>Mohammad A. Siddiqi, Jens Petersen, and Klaus Lucas</i>	
4.1	Abstract	69
4.2	Introduction	69
4.3	Experimental	71
4.3.1	Apparatus	71
4.3.2	Materials	72
4.4	Experimental Results	73
4.4.1	Studies at 298.65 K	73
4.4.2	Studies at 318.45 K and 333.35 K	77
4.5	Model Calculations	78
4.6	Results and Discussion	85
	References	88
	Nomenclature	90

5	An Infrared Spectroscopic Investigation of the Species Distribution in the System $\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$	92
	<i>Ute Lichtfers and Bernd Rumpf</i>	
5.1	Abstract	92
5.2	Introduction	92
5.3	Phase Equilibria and Quantitative Infrared Spectroscopy in the System $\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$	93
5.4	Experimental	98
5.4.1	Apparatus	98
5.4.2	Materials	99
5.4.3	Results	99
5.4.4	Calibration Measurements	101
5.4.5	Evaluation of Spectra	102
5.4.5.1	Spectra Taken in Calibration Measurements	102
5.4.5.2	Spectra in the System $\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$	103
5.5	Results	106
5.6	Modeling	107
5.7	Prediction of Caloric Effects	112
5.8	Conclusion	114
	Acknowledgements	115
	References	115
	Nomenclature	117
II	Associating Mixtures	121
6	VLLE for Mixtures of Water and Alcohols: Measurements and Correlations	123
	<i>Frank Gremer, Gerhard Herres, and Dieter Gorenflo</i>	
6.1	Abstract	123
6.2	Introduction	123
6.3	Experimental	124
6.4	Experimental Results	127
6.5	Conclusions	132
	References	133
	Nomenclature	134
7	Phase Equilibria in Ternary Systems Containing Phenols, Hydrocarbons, and Water	135
	<i>Jürgen Schmelzer, Klaus Taubert, Antje Martin, René Meinhardt, and Jochen Kempe</i>	
7.1	Abstract	135
7.2	Introduction	135
7.3	Experimental	136
7.3.1	Liquid-Liquid Equilibrium	136
7.3.2	Vapor-Liquid Equilibrium	137

7.3.3	Infrared Spectroscopic Investigations	139
7.3.4	Materials	139
7.4	Theory	139
7.4.1	UNIFAC Group-Contribution Method	139
7.4.2	NRTL and UNIQUAC Gibbs Excess Energy Models	140
7.4.3	ESD Equation of State (ESD-EOS)	140
7.5	Results and Discussions	142
7.5.1	Prediction Using UNIFAC	142
7.5.2	Correlation of Binary Data with NRTL, UNIQUAC, and ESD-EOS	143
7.5.3	Prediction for Ternary Systems with NRTL, UNIQUAC, and ESD-EOS	143
7.6	Conclusions	146
	Acknowledgements	147
	References	147
	Nomenclature	148
8	Influence of Additives on Hydrophobic Association in Polynary Aqueous Mixtures. An NMR Relaxation and Self-Diffusion Study	150
	<i>Manfred Holz and Manghaiko Mayele</i>	
8.1	Abstract	150
8.2	Introduction	150
8.3	Methods and Experimental	152
8.3.1	Theoretical Background of the <i>A</i> -Parameter Procedure	153
8.3.2	Experimental Determination of the <i>A</i> -Parameter	154
8.3.2.1	Measurement of the Intermolecular Relaxation Rate	154
8.3.2.2	PFG NMR for the Determination of Self-Diffusion Coefficients	155
8.3.2.3	Measurement of the Spin Density	155
8.3.3	Experimental	156
8.3.3.1	Apparatus	156
8.3.3.2	Sample Preparation	156
8.3.4	Materials	157
8.4	Results and Discussion	157
8.4.1	The Binary System: Water + <i>tert</i> -Butanol	157
8.4.2	The Ternary System: Water + <i>tert</i> -Butanol + Urea	159
8.4.2.1	Urea Effect on the Translational Dynamics of <i>tert</i> -Butanol and Water	160
8.4.2.2	Influence of Urea on <i>tert</i> -Butanol Self-Association	166
8.4.3	Water + Ethylene Glycol Systems	169
8.4.3.1	The Binary System: Water + Ethylene Glycol	170
8.4.3.2	Ternary Systems: Water + Ethylene Glycol + Additive	172
	The Additive Dioxane	172
	The Additive <i>n</i> -Butanol	174
	Salts as Additives	175
8.5	Conclusions	177
	References	178
	Nomenclature	181

III	Aqueous Solutions of Strong Electrolytes	185
9	Phase Equilibria of Aqueous Solutions Containing Volatile Electrolytes	187
	<i>Jürgen Zipprian, Nils Elm, and Karlheinz Schaber</i>	
9.1	Abstract	187
9.2	Introduction	187
9.3	Experimental	188
9.3.1	Apparatus	188
9.3.2	IR-Spectra and Calibration Curves	190
9.4	Results and Discussion	192
9.4.1	System $\text{NH}_3 + \text{H}_2\text{O}$	192
9.4.2	System $\text{HCl} + \text{H}_2\text{O}$	195
9.4.3	System $\text{HBr} + \text{H}_2\text{O}$	197
9.4.4	System $\text{HCl} + \text{CaCl}_2 + \text{H}_2\text{O}$	198
9.4.5	System $\text{HCl} + \text{HBr} + \text{H}_2\text{O}$	200
9.5	Theory	202
9.6	Results and Discussion	203
9.6.1	Partial Pressure of HCl	203
9.6.2	Partial Pressure of H_2O	204
9.7	Conclusions	204
	References	205
	Nomenclature	206
10	Experimental Determination and Prediction of Phase Equilibria in Systems Containing Strong Electrolytes	208
	<i>Magnus Topp Hoff, Christian Rose, Jörn Kiepe, and Jürgen Gmehling</i>	
10.1	Abstract	208
10.2	Introduction	209
10.3	Group Contribution Model for the Prediction of Activity Coefficients in Systems Containing Strong Electrolytes	210
10.3.1	Thermodynamic Framework	210
10.3.1.1	Estimation of Parameters	213
10.3.2	Results and Discussion for VLE Data	214
10.3.3	Prediction of Solid-Liquid Equilibria	217
10.3.3.1	Theory	218
10.3.3.2	Results and Discussion	218
10.3.4	Prediction of Gas Solubilities	221
10.3.4.1	Modified PSRK Group Contribution Method	222
10.3.4.2	Results and Discussion	224
10.4	Determination of Vapor-Liquid Equilibria for Systems Containing Strong Electrolytes	225
10.4.1	Materials	226
10.4.2	Headspace Gas Chromatography	226
10.4.3	Ebulliometry	226
10.4.3.1	Experimental Results	227

10.4.4	Measurement of Activity Coefficients at Infinite Dilution in Electrolyte Systems Using the Dilutor Technique	228
10.4.4.1	Experimental and Measurement Procedure	228
10.4.4.2	Principle of the Applied Method	230
10.4.4.3	Experimental Results	231
10.4.5	Measurement of the Mean Activity Coefficients of Ions by Determination of the Electromotive Force	233
10.5	Conclusion	235
	References	236
	Nomenclature	238
11	Ion Coordination and Thermodynamic Modeling of Molten Salt Hydrate Mixtures	241
	<i>Wolfgang Voigt, Kay Hettrich, and Dewen Zeng</i>	
11.1	Abstract	241
11.2	Introduction	241
11.3	Experimental	243
11.3.1	Solid-Liquid Equilibria	243
11.3.2	UV-Vis Spectroscopy	243
11.3.3	Raman Spectroscopy	243
11.3.4	Chemicals	244
11.4	Results and Discussion	244
11.4.1	System $\text{MgCl}_2 + \text{CuCl}_2 + \text{H}_2\text{O}$	244
11.4.1.1	Solid-Liquid Equilibria	244
11.4.1.2	UV-Vis Spectroscopy	247
11.4.1.3	Raman Spectra	250
11.4.2	$\text{MgCl}_2 + \text{CsCl} + \text{H}_2\text{O}$	251
11.5	Thermodynamic Modeling	253
11.5.1	Modeling Strategy	253
11.5.2	Computational Problems of Parameter Estimation	254
11.5.3	Model Development for the Systems $\text{MgCl}_2 + \text{KCl} + \text{H}_2\text{O}$ and $\text{MgCl}_2 + \text{CuCl}_2 + \text{H}_2\text{O}$	255
11.5.3.1	Binary Systems	255
	$\text{MgCl}_2 + \text{KCl}$	255
	$\text{KCl} + \text{H}_2\text{O}$	257
	$\text{MgCl}_2 + \text{H}_2\text{O}$	258
11.5.3.2	Ternary Systems	260
	$\text{MgCl}_2 + \text{KCl} + \text{H}_2\text{O}$	260
	$\text{MgCl}_2 + \text{CuCl}_2 + \text{H}_2\text{O}$	261
11.6	Conclusions	263
	Acknowledgements	263
	References	263
	Nomenclature	266

12	Effects of Salts on Excess Enthalpies of Binary Liquid Mixtures	268
	<i>Peter Ulbig, Thorsten Frieze, and Katrin Wagner</i>	
12.1	Abstract	268
12.2	Introduction	268
12.3	Experimental/Methods	269
12.3.1	Apparatus	269
12.3.1.1	Calorimetric Measurements	269
12.3.1.2	Solubility Measurements	271
12.3.1.3	Conductivity Measurements	272
12.3.1.4	Measurement of the Excess Volume	273
12.3.2	Materials	273
12.3.3	Analysis	273
12.4	Results and Discussion	275
12.4.1	Excess Enthalpy	275
12.4.1.1	Effect of the Salt Concentration	275
12.4.1.2	Effect of Temperature	275
12.4.1.3	Effect of Different Alcohols	275
12.4.1.4	Effect of Different Salts	278
12.4.2	Solubility	279
12.4.3	Conductivity	279
12.4.4	Excess Volume	280
12.5	Theory	280
12.5.1	The HEACE Model	280
12.5.2	Conductivity Theory	282
12.6	Results and Discussion	283
12.7	Conclusion	286
	Acknowledgements	287
	References	287
	Nomenclature	288
13	Hydrate Equilibria in Aqueous Solutions Containing Inhibitors	290
	<i>Armin M. Rock and Lothar R. Oellrich</i>	
13.1	Abstract	290
13.2	Introduction	290
13.3	Fundamental Hydrate Structural and Phase Behavior	292
13.4	Experimental	296
13.4.1	Apparatus	296
13.4.2	Procedure	298
13.5	Theory	300
13.5.1	Thermodynamic Framework	300
	Solid Hydrate Phase	301
	Fluid Phases	304
13.5.2	Estimation of Hydrate Cavity Interaction Parameters	306
13.6	Results and Discussion	308
13.7	Conclusions	315
	Acknowledgement	316

	References	316
	Nomenclature	319
IV	Phase Equilibrium of Aqueous Two-Phase Systems	321
14	Experimental and Theoretical Investigations on the Precipitation of Polyelectrolytes from Aqueous Solutions by Neutral Polymers	323
	<i>Thomas Grünfelder and Gerd Maurer</i>	
14.1	Abstract	323
14.2	Introduction	323
14.3	Experimental/Methods	325
14.3.1	Materials	325
14.3.2	Experimental Procedures	326
14.3.2.1	Turbidity Measurements	326
14.3.2.2	Compositions of Coexisting Phases	328
	Freeze Drying	328
	Atomic Absorption Spectroscopy	329
	Polymer Concentrations	329
14.4	Results and Discussion	329
14.4.1	Overview	329
14.4.2	Cloud Points	330
14.4.3	Composition of Coexisting Phases	331
14.4.4	Influence of Molecular Weight on the Phase Behavior	332
14.4.5	Influence of Temperature on the Phase Behavior	332
14.5	Modeling	334
14.5.1	Introduction to VERS-PE	334
14.5.2	Determination of Parameters of the VERS-PE Model	338
14.5.3	Results of Correlations/Predictions with the VERS-PE Model	340
14.6	Conclusions	341
	Acknowledgements	341
	References	342
	Nomenclature	342
15	Experimental and Theoretical Studies on Partitioning of Native and Unfolded Enzymes in Aqueous Two-Phase Systems	345
	<i>Maria-Regina Kula and Christian Rämisch</i>	
15.1	Abstract	345
15.2	Introduction	345
15.3	Material and Methods	346
15.3.1	Chemicals and Lysozyme Mutants	346
15.3.2	Determination of Phase Diagrams	347
15.3.3	Protein Conformation	347
15.3.4	Partition Coefficients	348
15.4	Results and Discussion	348
15.4.1	Phase Diagrams of Quaternary Systems	348

15.4.2	Stability of T 4-Lysozyme Variants	350
15.4.3	Partition of T 4-Lysozyme Variants	352
15.4.4	T 4-Lysozyme Unfolding and Refolding in PEG + Na ₂ SO ₄ Systems	354
15.5	Conclusion	356
	Acknowledgements	356
	References	356
	Nomenclature	357
16	Experimental and Theoretical Investigations on the Partitioning of Proteins in Aqueous Two-Phase Systems	359
	<i>Jochen Brenneisen and Gerd Maurer</i>	
16.1	Abstract	359
16.2	Introduction	359
16.3	Theory	360
16.3.1	Model	360
16.3.2	Gibbs Energy of the Aqueous Solutions	363
16.3.3	Chemical Reactions	363
16.4	Experimental/Methods	364
16.4.1	Liquid-Liquid Equilibrium Measurements	364
16.4.2	Experiments on Subsystems	365
16.4.2.1	Isopiestic Measurements	365
16.4.2.2	Measurement of pH	365
16.4.2.3	Determination of the Protein Net-Charge	366
16.4.3	Materials	366
16.5	Experimental Results/Modelling	367
16.5.1	Parameters for the Gibbs Excess Energy Model	367
16.5.2	Protein Net Charge	371
16.5.3	Protein Partitioning	371
16.6	Conclusions	374
	Acknowledgements	375
	References	375
	Nomenclature	376
V	Phase Equilibrium of Polymer Systems	379
17	Phase Behavior of Quaternary Polymer Solutions	381
	<i>Claudia Barth-Wiedmann, Matthias Wünsch, and Bernhard Anton Wolf</i>	
17.1	Abstract	381
17.2	Introduction	381
17.3	Experimental Part	382
17.3.1	Apparatus and Procedures	382
17.3.1.1	Static Light Scattering	382
17.3.1.2	Headspace-Gaschromatography	382
17.3.1.3	Determination of Phase Diagrams	384
17.3.2	Materials	384

17.4	Theoretical Background	385
17.4.1	Flory-Huggins Interaction Parameters	385
17.4.2	Calculation of Phase Diagrams	387
17.4.3	Calculation of Vapor Pressures	389
17.5	Results and Discussion	390
17.5.1	Binary Systems	390
17.5.1.1	Mixed Solvents	390
17.5.1.2	Polymer Solutions	391
17.5.2	Ternary Systems	393
17.5.2.1	Phase Diagrams	393
17.5.2.2	Vapor Pressures	395
17.5.3	Quaternary Systems	398
17.6	Conclusions	399
	Acknowledgement	399
	References	400
	Nomenclature	401
	Abbreviations	402
18	Calculation of the High Pressure Phase Equilibrium of Mixtures of Ethylene, Poly(ethylene-co-vinylacetate) Copolymers and Vinyl Acetate with a Cubic Equation of State	403
	<i>C. Browarzik, D. Browarzik, and H. Kehlen</i>	
18.1	Abstract	403
18.2	Introduction	403
18.3	Theory	405
18.3.1	Segment-Molar Quantities and Polydispersity	405
18.3.2	Calculation of the Cloud-Point Curves	407
18.3.3	Calculation of the Coexistence Curves	409
18.3.4	Sako-Wu-Prausnitz Equation of State (SWP-EoS)	411
18.3.5	Fit of Pure-Component Parameters	412
18.4	Results and Discussion	414
18.4.1	The Binary System Ethylene (A) + EVA (B)	414
18.4.2	The Binary System Ethylene (A) + VA (C)	421
18.4.3	The Binary System EVA (B) + VA (C)	422
18.4.4	The Ternary System	423
18.5	Conclusions	425
	References	426
	Nomenclature	428
19	Modeling of Copolymer Phase Equilibria Using the Perturbed-Chain SAFT Equation of State	430
	<i>Feely Tumakaka and Gabriele Sadowski</i>	
19.1	Abstract	430
19.2	Introduction	430
19.3	Theory	431
19.3.1	Copolymer Concept	431

19.3.2	Perturbed-Chain SAFT and its Extension to Copolymer Systems	432
19.4	Pure-Component Polymer Parameters	434
19.5	Results for Copolymer Systems	437
19.5.1	Poly(ethylene- <i>co</i> -propylene) (PEP) Systems	437
19.5.2	Poly(ethylene- <i>co</i> -1-butene) (EB) Systems	439
19.5.3	Poly(ethylene- <i>co</i> -vinyl acetate) (EVA) Systems	441
19.5.4	Poly(ethylene- <i>co</i> -methyl acrylate) (EMA) Systems	443
19.6	Conclusions	446
	Acknowledgements	447
	References	447
	Nomenclature	449
20	Cloud Point Pressures of Ethene + Acrylate + Poly(ethene-<i>co</i>-acrylate) Systems	451
	<i>Michael Buback and Markus Busch</i>	
20.1	Abstract	451
20.2	Introduction	452
20.3	Experimental Methods	455
20.4	Results and Discussion	458
20.5	Conclusions	468
	References	468
	Nomenclature	470
21	Gas Expanded Polymer Solutions	472
	<i>Bernd Bungert and Wolfgang Arlt</i>	
21.1	Abstract	472
21.2	Introduction	472
21.3	Fundamentals	474
21.3.1	Separation Processes	474
21.3.1.1	Antisolvent Crystallization	474
21.3.1.2	Liquid-Liquid-Phase Separation of Polymer Solutions	475
21.3.1.3	Liquid-Liquid-Vapor to Vitrified Liquid-Vapor Equilibrium	475
21.3.1.4	Change of Properties by the Dissolution of Compressed Gases	477
21.3.2	Thermodynamic Modeling of Phase Equilibrium	477
21.4	Experimental	478
21.4.1	Apparatus and Chemicals	478
21.5	Results	479
21.6	Conclusion	484
	Acknowledgement	484
	References	484
	Nomenclature	486

22	Calculation of the Stability and of the Phase Equilibrium on the System Methylcyclohexane + Polystyrene Based on an Equation of State	488
	<i>Dieter Browarzik and Mario Kowalewski</i>	
22.1	Abstract	488
22.2	Introduction	488
22.3	Theory	490
22.3.1	Calculation of the Cloud-Point and the Shadow Curves	490
22.3.2	Calculation of the Spinodal Curve	492
22.3.3	Calculation of Critical Points	494
22.3.4	Sako-Wu-Prausnitz Equation of State (SWP-EoS)	495
22.4	Results	497
22.4.1	Parameter Fit	497
22.4.2	Formation of the Hour-Glass Curves in the Polydisperse Case	498
22.4.3	Application of the EoS to a Real Polydisperse System MCH + PS	504
22.5	Conclusions	506
	References	506
	Nomenclature	507
VI	High-Pressure Phase Equilibria	509
23	Phase Equilibrium (Solid-Liquid-Gas) in Binary Systems of Poly(ethylene glycols), Poly(ethylene glycol) dimethyl ether with Carbon Dioxide, Propane, and Nitrogen	511
	<i>Eckhard Weidner and Veronika Wiesmet</i>	
23.1	Abstract	511
23.2	Introduction	512
23.3	Experimental Equipment, Methods, and Substances	512
23.3.1	Polymers	512
23.3.2	Determination of Melting Point	512
23.3.3	Determination of Solubility	513
23.3.4	Correlation of the Experimental Results with SAFT	514
23.4	Results and Discussion	514
23.4.1	PEG + Carbon Dioxide	515
23.4.1.1	Liquid + Gas Systems	515
23.4.1.2	Solid-Liquid Transition	517
23.4.2	PEG + Nitrogen	519
23.4.2.1	Liquid + Gas Systems	519
23.4.2.2	Solid-Liquid Transition	520
23.4.3	PEG + Propane	520
23.4.3.1	Liquid + Gas Systems	520
23.4.3.2	Solid-Liquid Transition	523
23.4.4	Comparison of the Phase Behavior of Liquid and Solid PEGs With Different Gases	524
23.4.5	Influence of Functional Groups	525
23.4.5.1	Short Polymer Chains	526

23.4.5.2	Longer Polymer Chains	528
23.4.6	Classification of Phase Behavior for (Solid and Liquid) PEGs and Pressurized Gases	529
23.5	Application	530
23.5.1	Powder Generation from Poly(ethylene glycols)	531
23.5.2	Polyglycols as Lubricants in Climatisation Systems	531
23.6	Conclusion	532
	Acknowledgements	533
	References	533
	Nomenclature	534
24	Measurements and Modeling of High-Pressure Fluid Phase Equilibrium of Systems Containing Benzene Derivatives and CO₂	535
	<i>Gerd Brunner, Oliver Pföhl, and Stanimir Petkov</i>	
24.1	Abstract	535
24.2	Introduction	536
24.3	Experimental/ Methods	536
24.3.1	Apparatus	536
24.3.2	Procedure	537
24.3.3	Analysis	538
24.3.4	Materials	539
24.4	Results and Discussion	539
24.4.1	Binary Systems: Benzene Derivative + Carbon Dioxide	539
24.4.2	Ternary Systems	543
24.4.3	Discussion of Experimental Results	550
24.4.3.1	Binary Systems Benzene Derivative + Carbon Dioxide	550
24.4.3.2	Ternary System <i>o</i> -Cresol + <i>p</i> -Cresol + Carbon Dioxide	550
24.4.3.3	Ternary Systems Benzene Derivative + Water + Carbon Dioxide	551
24.4.3.4	Ternary Systems Cresol Isomer + Ethanol + Carbon Dioxide	552
24.5	Theory/Methods	552
24.5.1	Equations of State	552
24.5.1.1	Cubic EoS	552
24.5.1.2	Association EoS	554
24.5.1.3	Mixing Rules	555
24.5.2	Parameter Estimation	556
24.5.2.1	Pure Component Parameters	556
24.5.2.2	Binary Systems: Determining Binary Interaction Parameters	559
24.5.2.3	Ternary Systems	559
24.6	Results and Discussion	563
24.7	Conclusion	565
	References	566
	Nomenclature	567