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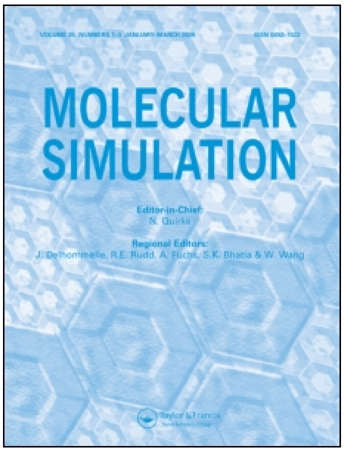

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular models of unlike interactions in fluid mixtures

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To cite this Article Vrabec, Jadran , Stoll, Jürgen and Hasse, Hans(2005) 'Molecular models of unlike interactions in fluid mixtures', Molecular Simulation, 31: 4, 215 — 221

To link to this Article: DOI: 10.1080/08927020412331332776

URL: http://dx.doi.org/10.1080/08927020412331332776

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Molecular Simulation, Vol. 31, No. 4, April 2005, 215–221

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Molecular models of unlike interactions in fluid mixtures

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(Received September 2004; in final form October 2004)

Recently published molecular models of two-centre Lennard–Jones plus pointquadrupole type for pure fluids are used for the quantitative description of vapour–liquid equilibria of 28 binary mixtures. The unlike interactions are described with a modified Lorentz–Berthelot combining rule that contains one binary interaction parameter in the energetic term. A recently published simple and efficient procedure is used to adjust the binary interaction parameter to a single experimental vapour pressure of the binary mixture. Vapour–liquid equilibria from these molecular models for binary mixtures are in good agreement with experimental data also at state points far away from those used for the parameter fit. Vapour–liquid equilibria of ternary mixtures are predicted reliably on that basis.

Keywords: Molecular models; Mixtures; Unlike interactions; Vapour–liquid equilibria

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1. Introduction

Reliable modelling of vapour–liquid equilibria of mixtures is essential for many tasks in process engineering. Conventional approaches to modelling vapour–liquid equilibria of mixtures with empirical equations of state or lattice-based G^{E}-models yield, in many cases, excellent correlations, but often lack in predictive power, especially when the available experimental database for the adjustment of binary parameters is narrow. These models are well developed but hold only little promise for further improvements.

Molecular modelling and simulation is a promising route to a more reliable description and prediction of thermophysical properties of mixtures. The present work deals with molecular simulation of binary and ternary mixtures of 15 small unpolar and quadrupolar molecules, i.e. neon, argon, krypton, xenon, methane, chlorine, nitrogen, oxygen, carbon dioxide, carbon disulfide, ethane, ethene, ethine, perfluoroethane and propylene. Molecular simulations of vapour–liquid equilibria of some mixtures containing these components are available: Potoff and Siepmann [1] (binary and ternary mixtures of nitrogen, carbon dioxide and alkanes), Rivera *et al.*, [2] (nitrogen + butane), Kronome *et al.*, [3] (nitrogen + ethane), Nath *et al.*, [4] (alkane mixtures), Cui *et al.*, [5] (carbon dioxide + (perfluoro)alkane), Potoff *et al.*, [6] (mixtures of various polar and nonpolar components), Delhommelle and Millié [7] (mixtures of neon, argon and krypton), Liu and Beck [8] and Vrabec and Fischer [9,10] (mixtures containing methane, ethane and carbon dioxide).

In a previous work from our group, molecular models for five binary mixtures of nitrogen, oxygen, carbon dioxide and ethane were developed [11]. The pure substance models used in that work were adjusted exclusively to experimental pure substance vapour–liquid equilibria [12]. The unlike interactions in mixtures were described on the basis of the modified Lorentz–Berthelot combining rule containing one binary interaction parameter in the energetic term, that was adjusted to one experimental binary vapour pressure. For that adjustment, a simple and efficient procedure was used [11].

It was shown in [11] that predictions of vapour–liquid equilibria from molecular simulation, are generally superior to those from the cubic Peng-Robinson equation of state, but also to those from two physically based equations of state (PC-SAFT, BACKONE). Carrero-Mantilla and Llano-Restrepo [13] recently used the pure substance models from our group [12] and calculated vapour–liquid equilibria for several binary mixtures containing methane, ethane, ethylene and propylene with

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2005 Taylor & Francis Group Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020412331332776

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good success from predictive simulations without adjusting binary parameters. Such strictly predictive simulations are often satisfactory, but systematic deviations may be discerned at compositions, where the mole fractions lie in the same order of magnitude. As shown in [11], considerable improvements in the quantitative description of the vapour–liquid equilibria in this region can be achieved in these cases with the introduction of one adjustable binary interaction parameter.

The present work is an extension of the modelling approach reported in [11], using a further 28 models of unlike interactions. The quadrupolar two-centre Lennard–Jones (2CLJQ) model is used to describe the like interactions in pure components [12]. That work was devoted to the development of a set of compatible molecular models for 25 pure fluids based on the 2CLJQ model. These 2CLJQ models allow accurate simulations of vapour–liquid equilibria, as well as thermal and caloric properties of the modelled pure substances [14].

Table 1. Two-centre Lennard–Jones plus pointquadrupole model parameters for 20 pure fluids taken from [12]. The sign of the model parameter Q is undetermined for propylene (cf. table 3).

Fluid	σ Å	ϵ/k_B K	L Å	Q DÅ
Ne	2.8010	33.921	–	0
Ar	3.3952	116.79	–	0
Kr	3.6274	162.58	–	0
Xe	3.9011	227.55	–	0
CH_4	3.7281	148.55	–	0
F_2	2.8258	52.147	1.4129	+0.8920
Cl_2	3.4016	160.86	1.9819	+4.2356
Br_2	3.5546	236.76	2.1777	+4.8954
I_2	3.7200	371.47	2.6784	+5.6556
N_2	3.3211	34.897	1.0464	−1.4397
O_2	3.1062	43.183	0.9699	−0.8081
CO_2	2.9847	133.22	2.4176	−3.7938
CS_2	3.6140	257.68	2.6809	+3.8997
C_2H_6	3.4896	136.99	2.3762	−0.8277
C_2H_4	3.7607	76.950	1.2695	+4.3310
C_2H_2	3.5742	79.890	1.2998	+5.0730
C_2F_6	4.1282	110.19	2.7246	−8.4943
C_2F_4	3.8611	106.32	2.2394	−7.0332
C_2Cl_4	4.6758	211.11	2.6520	−16.143
Propylene	3.8169	150.78	2.5014	5.9387

2. Pure fluid models

In the present work, effective state-independent quadrupolar two-centre Lennard–Jones-based molecular models (2CLJQ) are used, which have recently been developed in our group [12] as a part of a study covering 25 pure substances. The 2CLJQ model is a pairwise additive potential model consisting of two Lennard–Jones sites a distance L apart plus a pointquadrupole of momentum Q placed in the geometric centre of the molecule oriented along the molecular axis connecting the two Lennard–Jones (LJ) sites. The interaction energy of two molecules i and j is

$$u_{ij}^{2CLJQ} = \sum_{a=1}^{2}\sum_{b=1}^{2} 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ab}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ab}}\right)^{6}\right] + \frac{3}{4}\frac{Q_i Q_j}{|\boldsymbol{r}_{ij}|^5} f(\boldsymbol{\omega}_i, \boldsymbol{\omega}_j). \tag{1}$$

Herein, the vector $\boldsymbol{r}_{ij}$ indicates the centre–centre distance of the two molecules, r_{ab} is one of the four LJ site–site distances; a indicates the two sites of molecule i, b counts those of molecule j. The LJ parameters σ and ϵ represent size and energy, respectively. The trigonometric function f $(\boldsymbol{\omega}_i,\boldsymbol{\omega}_j)$, cf. Gray *et al.*, [15], depends only on the orientations $\boldsymbol{\omega}_i$ and $\boldsymbol{\omega}_j$ of the molecules.

The four model parameters σ, ϵ, Q and L were adjusted to experimental pure fluid vapour–liquid equilibrium data using global correlations of the critical temperature, the saturated liquid density and the vapour pressure as functions of these four molecular parameters [16]. The model parameters for the pure fluids used in the present work are given in table 1. Modelling propylene with the 2CLJQ potential is a strong simplification, since its geometric form and dipole are neglected, but the model performs well for the pure fluid [16] and for mixtures, cf. Section 4.

As discussed in Appendix B, quadrupole momenta have signed values. While the sign of the model parameter Q in table 1 is irrelevant for the simulation of pure fluids, it plays a role in the simulation of mixtures, cf. equation (1). Appendix B outlines the physical meaning of the sign of the parameter Q and describes, which approach was chosen here in order to determine it.

The advantages of these pure substance molecular models are their simplicity, which reduces simulation time considerably, and their accuracy: typically, the relative deviations between simulation and experiment are below 1% for the saturated liquid density, below 3% for the vapour pressure, and below 2% for the enthalpy of vapourization [12]. The compatibility of these models allows to use them for modelling of mixtures.

3. Mixture models

On the basis of existing molecular models for pure fluids, molecular modelling of binary mixtures reduces to modelling the interactions between unlike molecules. Two 2CLJQ molecules of different species A and B show one quadrupole–quadrupole interaction and four Lennard–Jones interactions. While the first can be treated physically in a straightforward way

$$u_{ij}^{Q} = \frac{3}{4}\frac{Q_i Q_j}{|\boldsymbol{r}_{ij}|^5} f(\boldsymbol{\omega}_i, \boldsymbol{\omega}_j), \tag{2}$$

the description of the unlike Lennard–Jones interactions requires the knowledge of the unlike Lennard–Jones parameters σ_{AB} and ϵ_{AB}. For their determination, the broadly used Lorentz–Berthelot combining rule is a good

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starting point [17]

$$\sigma_{\mathrm{AB}} = \frac{(\sigma_{\mathrm{A}} + \sigma_{\mathrm{B}})}{2}, \tag{3}$$

$$\epsilon_{\mathrm{AB}} = \sqrt{\epsilon_{\mathrm{A}}\epsilon_{\mathrm{B}}}. \tag{4}$$

Applying σ_{AB} and ϵ_{AB} as given by equations (3) and (4) in molecular simulation allows the prediction of mixture properties from pure fluid data alone. In many cases, these predictions are already in good agreement with experimental data [11,13]. But as shown in [11], a considerable further improvement can generally be achieved by introducing one state independent, binary interaction parameter ξ in equation (4), so that

$$\epsilon_{\mathrm{AB}} = \xi\sqrt{\epsilon_{\mathrm{A}}\epsilon_{\mathrm{B}}}. \tag{5}$$

A simple and efficient procedure to adjust ξ has been proposed in a previous work [11] and shall be outlined here briefly. It was found that the vapour pressure, P of a binary mixture model decreases almost linearly with increasing ξ, whereas the vapour mole fraction, y shows little sensitivity to variations of ξ. This behaviour is exploited to determine the value of ξ. For this purpose, at one selected experimental bubble point (temperature T^{exp}, pressure p^{exp}, liquid mole fraction x^{exp}) the saturated vapour pressure for three different values of ξ close to unity, i.e. ξ_1, ξ_2, ξ_3, are calculated by simulation: p_1, p_2, p_3. A linear fit $p(\xi) = a \cdot \xi + b$ proves to be sufficient to describe the results. The binary interaction parameter ξ is obtained from equating that $p(\xi)$ to the experimental value of the pressure p^{exp}. The information on the vapour phase composition is not used in the fit.

The experimental bubble points T^{exp}, p^{exp}, x^{exp} for the fit of ξ are chosen preferably so that the liquid mole fraction is about equimolar, cf. tables 2 and 3. This assures a maximal occurence of unlike interactions in the dense phase, where the molecules interact intensively with each other. Furthermore, an intermediate temperature is chosen for the fit to avoid, on one hand, the critical region and, on the other hand, very cold liquids, where the calculation of chemical potentials by molecular simulation shows higher statistical uncertainties.

For each binary mixture, the correct description of the state point that was used for the fit, was verified by molecular simulation using the value of ξ resulting from the adjustment. The pressure p^{sim} and the vapour mole fraction y_1^{sim} obtained from this validation are given in tables 2 and 3. It should be pointed out that the vapour compostion y_1^{sim} is fully predictive.

An alternative approach, which can be used if no experimental vapour–liquid equilibria are available, is the adjustment to experimental Henry's law constants or excess enthalpies [9]. But if no experimental binary data is available at all, it has to be relied on combination rules.

Altogether, models for 28 unlike interactions were developed in the present work, cf. tables 2 and 3. Additionally, binary interaction parameters ξ for the five mixtures $N_2 + O_2$, $CO_2 + C_2H_6$, $O_2 + CO_2$, $N_2 + CO_2$ and $N_2 + C_2H_6$ of the 2CLJQ fluids studied in the present work are given in table 2 that were taken from [11].

Table 2. Binary interaction parameters ξ. Experimental bubble points used for the determination of ξ and simulation results with adjusted ξ.

Mixture (1+2)	ξ	T *K*	x_1 *mol/mol*	p^{exp} *MPa*	p^{sim} *MPa*	y_1^{exp} *mol/mol*	y_1^{sim} *mol/mol*	*Ref.*
Ne + Ar	0.854	110.78	0.145	12.2	12.1	0.828	0.836	[18]
Ne + N_2	0.945	82.70	0.122	4.05	3.90	0.923	0.916	[19]
Ne + O_2	0.921	110.39	0.159	14.0	14.2	0.848	0.855	[20]
Ne + CO_2	1.124	273.15	0.038	8.84	8.84	0.445	0.466	[21]
Ar + Kr	0.989	88.06	0.647	0.083	0.075	0.978	0.995	[22]
Ar + CH_4	0.964	123.05	0.448	0.811	0.833	0.808	0.793	[23]
Ar + N_2	1.008	84.50	0.521	0.150	0.144	0.280	0.287	[24]
Ar + O_2	0.988	104.95	0.500	0.440	0.436	0.546	0.549	[25]
Ar + CO_2	0.999	253.15	0.095	6.14	5.96	0.548	0.572	[26]
Kr + Xe	0.989	200.64	0.463	2.07	2.11	0.787	0.813	[27]
Kr + CH_4	1.005	115.77	0.532	0.107	0.108	0.375	0.367	[28]
Kr + O_2	0.979	109.80	0.500	0.297	0.293	0.076	0.084	[29]
$CH_4 + CO_2$	0.962	230.00	0.318	5.57	5.61	0.764	0.769	[30]
$CH_4 + C_2H_6$	0.997	172.04	0.504	1.24	1.16	0.966	0.985	[31]
$CH_4 + C_2H_4$	1.022	160.00	0.476	0.851	0.853	0.954	0.955	[32]
$N_2 + CH_4$	0.958	140.00	0.301	2.19	2.24	0.685	0.702	[33]
$N_2 + O_2$	1.007	105.00	0.500	0.743	0.734	0.702	0.707	[34]
$N_2 + CO_2$	1.041	270.00	0.132	9.29	9.19	0.417	0.457	[35]
$N_2 + C_2H_6$	0.974	260.00	0.165	7.11	6.96	0.558	0.590	[36]
$N_2 + C_2H_4$	0.962	200.00	0.274	8.18	7.72	0.816	0.845	[36]
$O_2 + CO_2$	0.979	253.15	0.141	8.11	8.24	0.574	0.616	[37]
$CO_2 + C_2H_6$	0.954	263.15	0.425	2.90	2.95	0.514	0.517	[38]
$CO_2 + CS_2$	0.918	360.01	0.477	11.5	10.8	0.875	0.924	[39]
$CO_2 + Cl_2$	0.936	233.15	0.228	4.86	4.68	0.880	0.862	[40]
$C_2H_4 + C_2H_6$	1.037	208.40	0.556	0.497	0.490	0.684	0.700	[41]
$C_2H_4 + C_2H_2$	0.975	235.93	0.818	1.56	1.53	0.842	0.849	[42]
$C_2H_6 + C_2H_2$	0.968	277.59	0.859	3.20	3.11	0.789	0.785	[43]
$C_2H_4 + CO_2$	0.944	243.15	0.459	1.93	1.95	0.515	0.524	[44]
$C_2F_6 + CO_2$	0.867	227.60	0.511	0.911	0.923	0.344	0.341	[45]

Table 3. Binary interaction parameters ξ for mixtures containing propylene (P). Experimental bubble points used for the determination of ξ and simulation results with adjusted ξ. Superscript +/−: sign of model quadrupole.

Mixture (1+2)	*ξ*	*T* *K*	x_1 *mol/mol*	p^{exp} *MPa*	p^{sim} *MPa*	y_1^{exp} *mol/mol*	y_1^{sim} *mol/mol*	*Ref.*
$N_2 + P^+$	0.958	260.00	0.220	11.9	12.4	0.879	0.879	[36]
$N_2 + P^-$	0.959				11.7	n.a.	0.898	
$CO_2 + P^+$	0.920	273.15	0.539	2.42	2.35	0.821	0.826	[46]
$CO_2 + P^-$	0.915				2.34	n.a.	0.821	
$C_2H_6 + P^+$	1.019	277.59	0.568	1.72	1.72	0.775	0.785	[47]
$C_2H_6 + P^-$	1.015				1.77	n.a.	0.785	
$C_2H_4 + P^+$	1.018	258.15	0.794	2.23	2.18	n.a.	0.954	[48]
$C_2H_4 + P^-$	1.021				2.21	n.a.	0.952	

Mixtures where no experimental data was available were not considered in the present work. The same holds for mixtures, for which the experimental data is very spotty, poor, or contradictive.

Among the pure substance molecular models used in the present work are models for non-polar fluids (Ne, Ar, Kr, Xe, CH_4 (the octupole of CH_4 is neglected)), for fluids with positive quadrupole momentum (F_2, Cl_2, Br_2, I_2, CS_2, C_2H_2, C_2H_4), and for fluids with negative quadrupole momentum (N_2, O_2, CO_2, C_2H_6, C_2F_6, C_2F_4, C_2Cl_4), cf. Appendix B. These models can be applied straightforwardly to modelling of mixtures.

The sign of the model quadrupole of the multipolar molecule propylene was not determined, cf. Appendix B. However, it was attempted to study the influence of the sign of the model quadrupole of propylene empirically using the description of vapour–liquid equilibria of mixtures as a criterion. For that purpose the binary interaction parameter ξ was adjusted for both signs of the model quadrupole of propylene. Table 3 shows, that the adjustment yielded very similar values of ξ for all studied mixtures (with N_2, CO_2, C_2H_6 and C_2H_4). The sign of the model quadrupole has practically no influence on the description of macroscopic thermodynamic properties of the mixtures.

No additional parameters have to be introduced in models for ternary mixtures, nor were any pure fluid model parameters altered.

4. Discussion of results

Vapour–liquid equilibria of mixtures at different state points were calculated with the molecular models developed and described above. The results are compared to vapour–liquid equilibria from experiment and to results from the Peng-Robinson equation of state [49].

The Peng-Robinson equation of state requires the acentric factor ω, the critical temperature T_c and the critical pressure p_c of the pure fluids. That data was taken from Reid *et al.*, [50]. The binary parameter k_{ij} of the Peng-Robinson equation of state was adjusted to the same mixture data points (cf. tables 2 and 3) that were used for the determination of the binary interaction parameter ξ.

Figures 1–5 show that results from molecular simulation are in good agreement with the experimental data. Molecular simulation predicts correctly the azeotropic behaviour of the mixture $C_2H_2 + C_2H_6$ from pure substance data alone, i.e. with $\xi = 1$, whereas the Peng-Robinson equation of state fails in prediction and only yields a correct description of the vapour–liquid equilibria of this mixture when the binary parameter k_{ij} is adjusted, cf. figure 1. In the case of the mixtures N_2 + propylene and $CO_2 + CS_2$, cf. figures 2 and 3, a considerable overestimation of the critical points is obtained from the Peng-Robinson equation of state, whereas molecular simulation yields more reliable results in both cases. This overestimation is mainly due to the poor description of the bubble lines by the Peng-Robinson equation of state, which is particularly poor in the case of $CO_2 + CS_2$. The molecular model describes the bubble lines essentially better than the Peng-Robinson equation of state. In the work of Stoll *et al.*, [11] an analogous finding is discussed for the mixtures $N_2 + C_2H_6$ and $O_2 + CO_2$. For the mixture C_2H_6 + propylene, cf. figure 4, both the results from molecular simulation and those from the Peng-Robinson equation of state are in good agreement with experimental data.

For the two mixtures containing propylene shown in figures 2 (with N_2) and 4 (with C_2H_6), the molecular simulations with positive and negative model quadrupole momentum for propylene perform equally well, also for isotherms far away from the state point chosen for

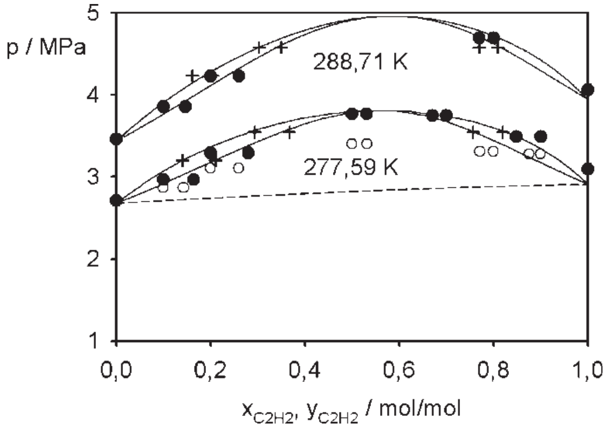

Figure 1. Vapour–liquid equilibria of the mixture $C_2H_2 + C_2H_6$. • Simulation with adjusted $\xi = 0.968$, o simulation with $\xi = 1$, — Peng-Robinson equation of state with adjusted $k_{ij} = 0.15579$, - - - Peng-Robinson equation of state with $k_{ij} = 0$, + experiment [43].

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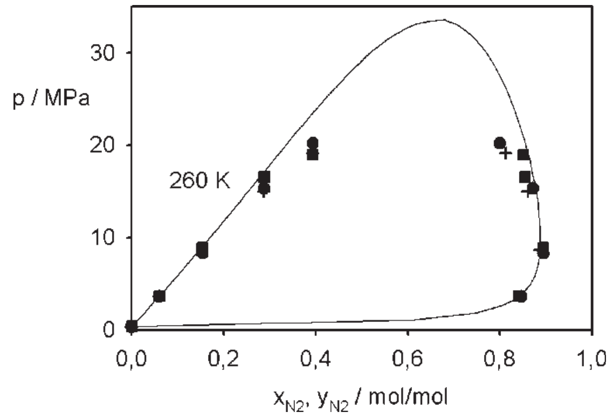

Figure 2. Vapour–liquid equilibria of the mixture N_2 + propylene. Simulation: • same quadrupole signs, ■ opposite quadrupole signs. — Peng-Robinson equation of state ($k_{ij} = 0.08844$), + experiment [36].

the adjustment of ξ. Similar results were obtained for other mixtures of this type not shown here. This finding supports the negligible influence of the sign of the model quadrupole on the description of vapour–liquid equilibria.

Similar agreement of simulation and experimental data as that shown in figures 1–4 was also obtained for all remaining binary mixtures.

The present molecular models for the binary mixtures $C_2H_6 + C_2H_4$, $C_2H_6 + C_2H_2$ and $C_2H_4 + C_2H_2$ were used unaltered for the prediction of vapour–liquid equilibria of the ternary mixture $C_2H_6 + C_2H_4 + C_2H_2$, cf. figure 5. The results from molecular simulation are in excellent agreement with experimental data, whereas for the Peng-Robinson equation of state deviations occur, which are mainly due to deficiencies in the description of the binary subsystems. Similar results were obtained for vapour–liquid equilibria of two other ternary mixtures in a recent work of our group [11].

5. Conclusions

In the present work the approach of Stoll *et al.*, [11], who developed molecular models for five binary mixtures containing nitrogen, oxygen, carbon dioxide and ethane, is used for modeling 28 further binary systems. The molecular models of the pure fluids are of two-centre Lennard–Jones plus pointquadrupole type. They were taken from Vrabec *et al.*, [12] and allow accurate simulations of the pure component properties.

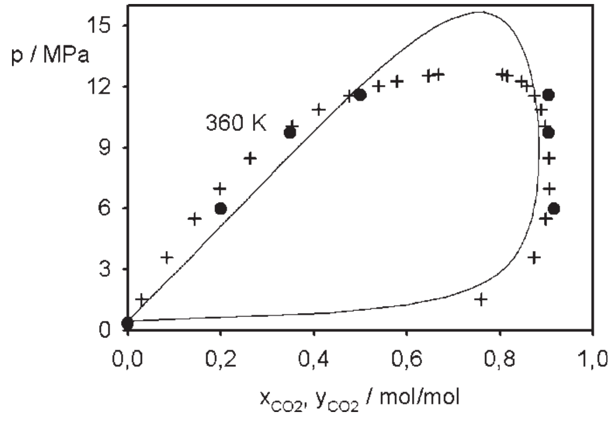

Figure 3. Vapour–liquid equilibria of the mixture $CO_2 + CS_2$. • Simulation, — Peng-Robinson equation of state ($k_{ij} = -0.00227$), + experiment [39].

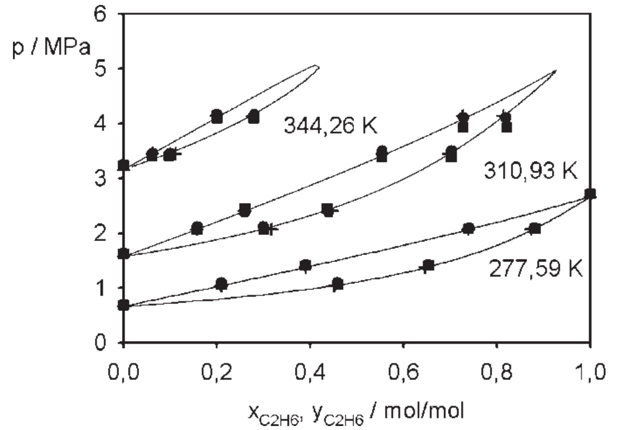

Figure 4. Vapour–liquid equilibria of the mixture C_2H_6 + propylene. Simulation: • same quadrupole signs, ■ opposite quadrupole signs. — Peng-Robinson equation of state ($k_{ij} = 0.00701$), + experiment [47].

A modified Lorentz–Berthelot combining rule with one binary interaction parameter in the energetic term is used for the description of unlike interactions in mixtures. An efficient procedure for the adjustment of this binary interaction parameter to a single experimental vapour pressure of the mixture is applied. In this way, good agreement of vapour–liquid equilibria from molecular simulation and experimental data is obtained for all binary mixtures modeled here. The present binary interaction parameter data base can be used for the verification of other combinig rules.

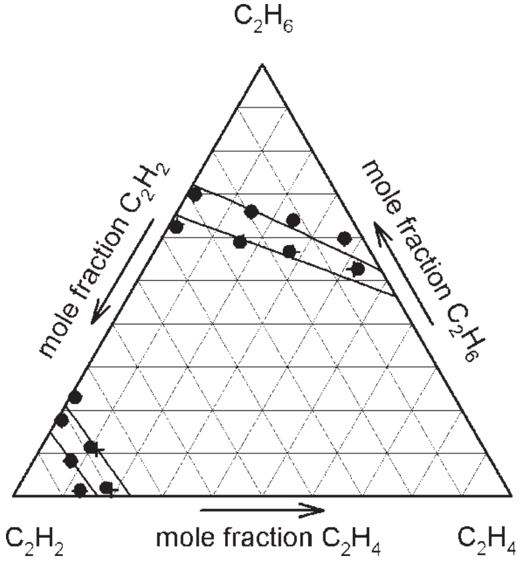

Figure 5. Vapour–liquid equilibria of the ternary mixture $C_2H_6 + C_2H_4 + C_2H_2$ at $T = 277.79\,K$ and $p = 3.547\,MPa$. • Simulation, — Peng-Robinson equation of state, + experiment [43].

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It is shown that results from the Peng-Robinson equation of state, if adjusted to the same binary data, can deviate considerably from the experiment.

Finally, it is shown that the binary molecular models developed here can be applied directly for the successful prediction of vapour–liquid equilibria of ternary mixtures.

Acknowledgements

The authors thank Tobias Günther for his literature and simulation work. We gratefully acknowledge financial support by Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 412, University of Stuttgart.

A. Appendix A, Simulation Details

Technical details of the molecular simulations in the present work are identical to those published in [11]. A center–center cut-off radius was used for the evaluation of the molecular interaction. The Lennard–Jones tail corrections for the internal energy, the pressure and the chemical potential were calculated with angle averaging proposed by Lustig [51]. Tail corrections for the quadrupolar term in equation (1) vanish beyond the cut-off radius.

For the adjustment of the binary interaction parameter ξ, $N = 864$ particles were used for liquid simulations and about $N = 300$ particles for vapour simulations; the cut-off radius was 5σ. Liquid simulation runs were carried out using molecular dynamics with 100,000 time steps, vapour simulation runs were performed using the Monte Carlo technique with 100,000 cycles. Within one cycle, N attempts to translate or rotate, and two attempts to insert or delete particles were performed. The low percentage of insertions and deletions is sufficient, as the acceptance rate is high due to the low density in the vapor phase. For the simulations of the binary systems in figures 1–4, $N = 500$ particles were used in the liquid phase and about $N = 200$ particles in the vapour phase. The cut-off radii were 4σ in both phases. Ternary simulations were carried out with 864 particles in the liquid phase and about 300 particles in the vapour phase, the cut-off radii were 5σ in both phases. Vapour–liquid equilibria were obtained with the recently published Grand Equilibrium method [52].

B. Appendix B, sign of quadrupolar momentum

The type of quadrupole considered in this work consists of the charges q, $-2q$, q at distances a along the z-axis, with the x,y-plane perpendicular to the z-axis. With the origin of the (x, y, z)-coordinate system located in the central $-2q$ charge, the charge density $\rho(x,y,z)$ of that quadrupole is given by

$$\rho(x,y,z) = q \cdot \delta(x) \cdot \delta(y) \cdot [\delta(z-a) - 2\delta(z) + \delta(z+a)], \quad (6)$$

wherein Dirac δ functions are used. The quadrupole tensor is

$$\boldsymbol{Q} = \begin{pmatrix} -\frac{1}{2}Q_{\mathrm{zz}} & 0 & 0 \\ 0 & -\frac{1}{2}Q_{\mathrm{zz}} & 0 \\ 0 & 0 & Q_{\mathrm{zz}} \end{pmatrix}, \quad (7)$$

cf. [53,54], wherein

$$Q_{\mathrm{zz}} = 4qa^2. \quad (8)$$

The momentum Q of a symmetric elongated quadrupole with the quadrupole tensor $\boldsymbol{Q}$ is the component Q_{zz}. Equations (6) and (8) show, that $Q_{\mathrm{zz}} > 0$ for $q > 0$, i.e. charge arrangement $+ \; - \; - \; +$, and $Q_{\mathrm{zz}} < 0$ for $q < 0$, i.e. inverse arrangement $- + + \; -$. Consequently, the sign of the molecular model parameter Q is determined when signed values for Q_{zz} are available from experiment, calculation, or estimation.

Signed values of Q_{zz} from experiment are available from Gray and Gubbins [15] and from Stogryn and Stogryn [55] for the symmetric molecules F_2, Cl_2, Br_2, I_2, N_2, O_2, CO_2, CS_2, C_2H_6, C_2H_4 and C_2H_2. These signs have been adopted here as signs of the model parameter Q for these fluids, cf. table 1.

For the perhalogenated molecules C_2F_4, C_2Cl_4 and C_2F_6 the signs of Q_{zz} were determined here with the bond dipole method suggested by Eubank [56] for molecules with cylindrically symmetric charge distribution, like ethane (C_2H_6) or ethine (C_2H_2). Eubank applied his method also to ethene (C_2H_4). The bond dipole method yields $Q_{\mathrm{zz}} < 0$, and thus $Q < 0$ for these three molecules, which is physically reasonable due to the high electronegativity of fluorine and chlorine atoms.

In the case of propylene, which is a multipolar molecule with asymmetric charge distribution, the bond dipole method yields a squared effective quadrupole momentum, which is useless for the determination of the sign of Q. Therefore, the influence of the sign inversion on vapour–liquid equilibria was empirically tested as described in section 3 (cf. also table 3).

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