An Equation of State Contribution for Polar Components: Polarizable Dipoles

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The renormalized perturbation theory for polarizable polar fluids of Wertheim is applied in combination with a dipole contribution for non-spherical molecules to account for the non-additive induction interactions due to the polarization of molecules. A comparison to simulation data of pure polarizable dipolar fluids and mixtures reveals a good to excellent agreement between the renormalized perturbation theory and the simulations. The model framework is applied with the Perturbed-Chain SAFT equation of state to model phase equilibria of mixtures containing strongly polar components. The considered values of dipole moments and of average molecular polarizabilities stem from independent sources, and there is thus no additional adjustable parameter introduced along with the polar contributions to the equation of state. It is confirmed that accounting for dipolar interactions not only reduces the value of the binary interaction parameter, but in many cases significantly improves the description of pure-component and mixture phase equilibria. Accounting for molecular polarizability and the dipole induction effects only leads to slightly improved results compared to the case where a permanent dipole moment is considered in the calculations. © 2006 American Institute of Chemical Engineers
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Introduction

Mixtures containing strong polar components often exhibit a nonideal phase behavior (such as azeotropes), which results from the differences in molecular interactions. Fluid theories from statistical mechanics enable a description of such mixtures on a sound physical basis. Based on the perturbation theory of Stell et al.[1,2] and Gubbins and Twu,[3] Gross and Vrabec[4] suggested an equation of state contribution for dipolar interactions of non-spherical molecules. The model is of the form of a third order perturbation theory written in the Padé approximation, where model-constants were adjusted to comprehensive vapor-liquid equilibrium simulation data of pure two-center Lennard-Jones plus pointdipole fluids. The model was applied to real substances with the PC-SAFT equation of state and was found to systematically improve the correlation results for pure components and for mixtures. No additional adjustable parameter was thereby introduced with the dipole-term, since the dipole-moment in vacuo was considered in the calculation, which is independently determined either through experiments or quantum mechanical calculations.

This treatment, however, did not account for the polarizability of molecules. The polarizability allows the induction of a dipolar moment of a molecule such that the effective dipole

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moment of the polarizable substance is increased. The effect is known to be considerable for properties like vapor pressure or liquid densities,[5,6] and several approaches were suggested to account for the dipolar induction. The simplest treatment is the expansion of the Helmholtz energy around the pair-potential of dipoles and induced-dipoles, as worked out in detail by Gubbins and Twu.[3,7] This approach has progressed into engineering-like equations of state for real components.[8-17]

Since, however, the nature of polar induction is a true many-body effect that would actually require the incorporation of fourth- and higher-order correlation functions in conventional perturbation theories, one may state that the above mentioned formalism does not do full justice to the underlying interactions. In 1977 Wertheim[18,19] proposed the renormalized perturbation theory (RPT), which he derived by applying a graphical resummation. The renormalized fluid is one with the effective dipole moment (rather than the value in vacuo) and with no polarizability, and the problem is thus rephrased in terms of two-body and three-body correlations. The theory was extended to mixtures and comprehensively described by Venkatasubramanian et al.,[20] Joslin et al.,[21] and Gray et al.[22] If we restrict our considerations to bulk properties (excluding the dielectric behavior of a fluid), the RPT, despite its elegance, was next applied only a decade later, when Kriebel and Winkelmann[23-25] developed an equation of state for polarizable spherical and polarizable two-center Lennard-Jones molecules with embedded dipole moment. They used a simplified implementation of RPT and compared their model to their own molecular simulation data. Similarly, Kiyohara et al.[26] provided simulation results for the vapor-liquid equilibrium of polarizable Stockmayer (that is, dipolar Lennard-Jones) fluids and compared an implementation of the RPT to the data. Boublik and Winkelmann[27] proposed an equation of state where the RPT was applied to 2CLJ compounds. The RPT also aided in the development of simpler and explicit treatments, where the variation of the effective dipole moment as calculated from RPT was correlated as a function of density and the dependence on temperature and dipole strength were omitted.[28-30]

The ideas and assumptions that lead Wertheim to the RPT are nontrivial to assess, and molecular simulations play an important role in the process of appreciating his original approach. Early simulation results for polarizable polar fluids were delivered by Vesely,[31] by Patey and colleagues,[5,6,32] by Pollock and Alder,[33] and by Mooij et al.[34,35].

In this work, the RPT is used to extend the dipole-dipole expression proposed by Gross and Vrabec to account for the molecule's polarizability. The model is tested against molecular simulation data of pure compounds and mixtures. It is subsequently applied to real substances and their mixtures with the PC-SAFT equation of state. For brevity, the equation of state is here referred to as the Perturbed-Chain Induced-Polar SAFT (PCIP-SAFT).

Equation of State

The PC-SAFT equation of state was derived and described in detail by Gross and Sadowski.[36] In terms of the reduced residual Helmholtz free energy A^{res}/NkT, the PC-SAFT equation of state is given as the sum of different contributions:

$$\frac{A^{\mathrm{res}}}{NkT} = \frac{A^{\mathrm{hc}}}{NkT} + \frac{A^{\mathrm{disp}}}{NkT} + \frac{A^{\mathrm{assoc}}}{NkT} + \frac{A^{\mathrm{multipole}}}{NkT} \tag{1}$$

with N and k denoting the total number of molecules and the Boltzmann constant, respectively, and where A^{hc}/NkT is the expression for the hard-chain fluid as derived by Chapman et al.[37] The contribution due to dispersion is given by A^{disp}/NkT, where the chainlike shape of molecules is accounted for. The short-range interactions due to association are given by A^{assoc}/NkT. For a detailed description of these contributions, the reader is referred to the literature.[36,38] Lastly, the term $A^{\mathrm{multipole}}/NkT$ in Eq. 1 accounts for long range electrostatic interactions due to partial charges. Since in this study we focus on dipolar interactions, the total contribution due to multipolar interaction is simply given as

$$\frac{A^{\mathrm{multipole}}}{NkT} = \frac{A^{DD,eff}}{NkT} \tag{2}$$

and the contributions due to quadrupolar moments (as discussed earlier by one of the authors[39]) and higher-order multipoles as well as the appropriate cross-terms are omitted. The superscript "*eff*" (for effective dipole contribution) indicates that the induction-effect due to the molecular polarizability is taken into account.

The dipolar model of Gross and Vrabec was shown to reproduce simulation data of mixtures with good accuracy, and the model was applied to real polar mixtures (of non-spherical molecules) with the PC-SAFT equation of state. The equation of state required three pure component parameters as well as the dipole moment, which, however, can be determined independently through experiments or quantum mechanical calculations. It may be stressed that no additional adjustable parameter was thus introduced with the polar equation of state contribution. The treatment of Gross and Vrabec, however, did not account for the polarizability of molecules and the resulting induction of dipolar interactions. As the induced dipoles have a considerable effect on the thermodynamic behavior of dipolar fluids, the renormalized perturbation theory (RPT) of Wertheim[18,19] is applied in this work in order to extend the dipolar model for polar and polarizable fluids and mixtures.

Renormalized perturbation theory for mixtures

The idea underlying the renormalized perturbation theory of Wertheim is best outlined upon considering a dipolar component with the permanent dipole moment μ_i and polarizability α_i, where the polarizability leads to an additional induction of dipolar moment such that the effective dipole moment is increased to a value of μ_i^{eff}. According to the first level of Wertheim's renormalization (RPT-1), the effective dipole moment μ_i^{eff} is given by

$$\mu_i^{eff} = \mu_i + \alpha_i \cdot E_i' \tag{3}$$

where E_i' is the mean electric field acting on a molecule of fixed orientation. The renormalized fluid is one with the effective dipole moment μ_i^{eff} and with no polarizability, and the theory is of first-order renormalization since the polarizability is assumed constant. In the second-order renormalization (RPT-2), the polarizability α_i is also renormalized. The effect of the second level of renormalization, however, is of subordinate importance, as calculations of Wertheim indicate.[19] Throughout this study we consider the isotropic molecular polarizability, so that the polarizability tensor reduces to an average scalar value α_i. The mean electric field E_i' in Eq. 3 is equal to the derivative of the Helmholtz energy, as

$$E_i' = -\left(\frac{1}{N_i}\frac{\partial A}{\partial \mu_i^{eff}}\right)_{V,T} \tag{4}$$

where N_i is the number of molecules of species i. Combining Eqs. 3 and 4 leads to implicit equations for the effective dipole moment as

$$\mu_i^{*eff} = \mu_i^* - \alpha_i^* T_i^* \left(\frac{1}{x_i}\frac{\partial}{\partial \mu_i^{*eff}}\left(\frac{A'^{DD}}{NkT}\right)\right)_{\rho,T} \tag{5}$$

where x_i denotes the mole fraction and where reduced quantities are introduced as

$$\mu_i^* = \frac{\mu_i}{\sqrt{m_i \varepsilon_i \sigma_i^3}} \tag{6}$$

$$\alpha_i^* = \frac{\alpha_i}{m_i \sigma_i^3} \tag{7}$$

$$T_i^* = \frac{kT}{\varepsilon_i} \tag{8}$$

with the three pure component parameters, namely, the segment number (m_i), the segment diameter (σ_i), and the segment dispersion energy (ε_i/k).

Equation 5 has to be solved iteratively to determine the effective dipole moments. We applied a Newton-scheme and found convergence to compiler-accuracy in three to six steps. The term A'^{DD}/NkT in Eq. 5 is the dipole-expression of Gross and Vrabec[4] written as a Padé approximant, according to

$$\frac{A'^{DD}}{NkT} = \frac{A_2'^{DD}/NkT}{1 - A_3'^{DD}/A_2'^{DD}} \tag{9}$$

where A'_2 and A'_3 are the second order and third order terms of the perturbation expansion (u-expansion), respectively, and where the prime indicates that, first, the dipole–induced dipole interactions are accounted for and, further, that the effective dipole moment μ_i^{*eff} is considered rather than the permanent dipole moment μ_i^*. These conditions are conveniently achieved upon writing the dipole-term in terms of two dimensionless abbreviations z_i^A and z_i^B, such that

$$\frac{A_2'^{DD}}{NkT} = -\pi\rho \sum_i \sum_j x_i x_j \frac{\varepsilon_i}{kT}\frac{\varepsilon_j}{kT}(z_i^A z_j^A - z_i^B z_j^B)\frac{\sigma_i^3 \sigma_j^3}{\sigma_{ij}^3} J_{2,ij}^{DD} \tag{10}$$

$$\frac{A_3'^{DD}}{NkT} = -\frac{4}{3}\pi^2\rho^2 \sum_i \sum_j \sum_k x_i x_j x_k \frac{\varepsilon_i}{kT}\frac{\varepsilon_j}{kT}\frac{\varepsilon_k}{kT} \times (z_i^A z_j^A z_k^A - z_i^B z_j^B z_k^B)\frac{\sigma_i^3 \sigma_i^3 \sigma_k^3}{\sigma_{ij}\sigma_{ik}\sigma_{jk}} J_{3,ijk}^{DD} \tag{11}$$

with z_i^A and z_i^B defined as

$$z_i^A = (\mu_i^{*eff})^2 + 3T_i^* \alpha_i^* \tag{12}$$

and

$$z_i^B = 3T_i^* \alpha_i^* \tag{13}$$

The abbreviations $J_{2,ij}^{DD}$ and $J_{3,ijk}^{DD}$ in Eqs. 10 and 11 denote integrals over the reference-fluid pair correlation function and over three-body correlation functions, respectively. They were adjusted to simulation data of 2CLJ fluids with different chain lengths and are detailed elsewhere.[4]

Once convergence is achieved for Eq. 5 and values for μ_i^{*eff} are determined, the total Helmholtz energy contribution of polar/polarizable mixtures is calculated as[22]

$$\frac{A^{DD,eff}}{NkT} = \frac{A'^{DD}}{NkT} + \frac{1}{2}\sum_i x_i \alpha_i^* T_i^* \left(\frac{1}{x_i}\frac{\partial}{\partial \mu_i^{*eff}}\left(\frac{A'^{DD}}{NkT}\right)\right)^2_{\rho,T} \tag{14}$$

The unrenormalized theory can, of course, be recovered from the above equations by setting the polarizabilities α_i of all components to zero. In this case, z_i^A is equal to the squared (permanent) dipole moment and z_i^B is zero.

Determining pure component parameters

Since we are concerned with a physically-based modeling of polar interactions, we don't treat the dipole moment nor the polarizability as adjustable parameters, and the PCIP-SAFT equation of state described in the previous section consequently requires the same three adjustable pure-component parameters as does PC-SAFT for nonpolar fluids. These parameters are the segment number (m_i), the segment diameter (σ_i), and the segment dispersion energy (ε_i/k), and they are usually regressed by fitting pure component vapor pressure and density data. The permanent molecular dipole moment (value in vacuo) and the (isotropic) polarizability are tabulated for a large number of substances[40] and can be determined from experiments or through quantum chemical calculations. Using tabulated values for the dipole moment is, however, only possible for substances with one or only few functional groups; while for larger molecules, either an overall dipole moment may need to be adjusted or a strategy for segmenting the polar sub-groups needs to be adopted, as proposed by Lin and Sandler.[41] In order to avoid considering dipolar-quadrupolar cross-interactions, we neglect the quadrupolar moments (and higher multipoles) of all components in this work.

Mixtures of polar and non-polar substances, both of which are polarizable, are considered in the following section. The non-polar compounds are thereby defined through three pure component parameters and their polarizability α_i. Of course,

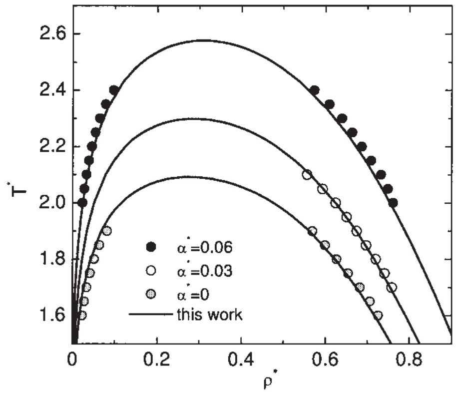

Figure 1. Vapor-liquid equilibrium of the polarizable spherical dipolar LJ fluid (polarizable Stockmayer fluid) with reduced dipole moment μ_i^{*2} = 4 for three polarizabilities α^*.

Comparison of simulation data (symbols: Kiyohara et al.[26]) to the proposed equation of state theory (lines).

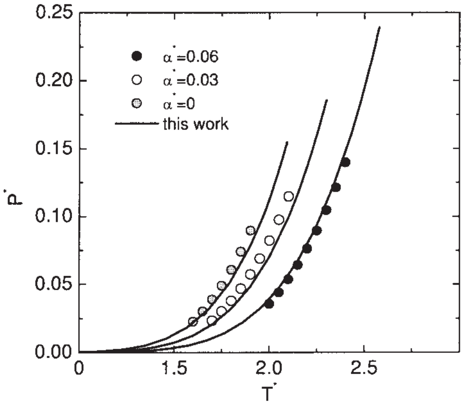

Figure 2. Vapor-pressure curves of the polarizable Stockmayer fluid with reduced dipole moment μ_i^{*2} = 4 for three polarizabilities.

Symbols and lines as defined in Figure 1.

introducing a polarizability has an effect in the equation of state only in the presence of a dipolar substance. Thus, the pure component parameters of nonpolar substances determined, for example, in ref.[36] remain unchanged, and the polarizability α_i can simply be added in the appropriate pure component parameter databank.

Results

This section gives comparisons of the proposed equation of state theory to molecular simulation data from literature and subsequently presents applications of the PCIP-SAFT model to vapor-liquid and liquid-liquid equilibria of real mixtures with strong dipolar components.

Comparison with molecular simulation data

The comparison of an equation of state to molecular simulation data allows a meaningful evaluation of the fluid theory underlying physically based equations of state, since the molecular model adopted in simulations is in full congruence with what is considered in the equation of state and there exists thus no adjustable parameter at all. The molecular model considered here is that of polarizable dipolar Lennard-Jones fluids (termed polarizable Stockmayer fluids). The above proposed dipole-term is for this purpose combined with a Lennard-Jones equation of state.[42] The implementation of the polar term with the Lennard-Jones equation of state is straightforward using dimensionless variables and follows the same logic as described earlier.[4,39]

A comparison between simulation data of Kiyohara et al.[26] and Wertheim's RPT-1 in conjunction with the new dipole-expression is given in Figures 1 and 2. The simulations were performed for the vapor-liquid equilibrium of polarizable Stockmayer fluids, and the diagrams give the coexisting densities over temperature for three values of polarizability α_i as well as the appropriate vapor-pressure curves, respectively. The proposed model is in excellent agreement with the simulation data, confirming the impressive performance of Wertheim's first-order renormalization once it is combined with an appropriate representation of the Stockmayer fluid. One can also conclude that deviations of the RPT-1 observed in previous investigations[26] are due to deviations of the underlying dipole-expressions, rather than Wertheim's theory.

Figure 3 shows the Helmholtz energy of mixing for mixtures of a Stockmayer fluid with polarizable Lennard-Jones fluids for four values of polarizability α_i. The negative curvature of the uppermost curve (for α_i = 0) indicates the existence of a liquid-liquid demixing at the given conditions. For increasing polarizabilities, the Helmholtz energy of mixing decreases and the tendency to form a liquid-liquid phase-split reduces. The predictions of the equation of state theory follow this behavior and are in very satisfying agreement to the simulation data of Mooij et al.[34] The results suggest a good performance of the proposed theoretical framework for describing the phase behavior of mixtures.

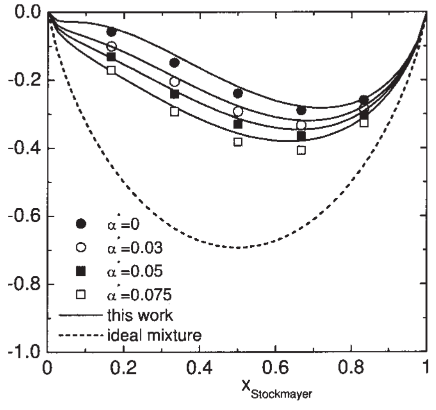

Figure 3. Helmholtz energy of mixing of polarizable Lennard-Jones–Stockmayer mixtures (at T^* = 1.15, ρ^* = 0.822, and μ_i^{*2} = 4 of Stockmayer fluid) for four polarizabilities α^* of the Lennard-Jones fluid.

Comparison of simulation data (symbols: Mooij et al.[35]) and predictions of the proposed equation of state (lines).

Table 1. Pure Component Parameters and Correlation Results for Strongly Polar and Polarizable Fluids Obtained for PCIP-SAFT, PCP-SAFT, and PC-SAFT

Substance Equation of state	M [g/mol]	m [−]	σ [Å]	ε/k [K]	$\mu^{\#}$ [D]	$\alpha^{\#}$ [Å^3]	*AAD-%*		Temp. Range [K]	Data Ref.$
							P^{sat}	ρ		
acetone										
PC-SAFT	58.08	2.8287	3.2497	250.26			1.61	2.94	200–508	1, 2
PCP-SAFT	58.08	2.7448	3.2742	232.99	2.88		0.55	1.31	200–508	1, 2
PCIP-SAFT	58.08	2.8473	3.2388	220.88	2.88	6.4	1.02	0.91	200–508	1, 2
butanone										
PC-SAFT	72.107	3.0748	3.3932	252.27			1.52	2.82	186–536	1, 2
PCP-SAFT	72.107	2.9835	3.4239	244.99	2.78		0.7	1.91	186–536	1, 2
PCIP-SAFT	72.107	3.0679	3.3914	236.53	2.78	8.13	0.29	1.53	186–536	1, 2
3-pentanone										
PC-SAFT	86.134	3.3644	3.4877	252.70			0.86	2.02	234–561	1, 2
PCP-SAFT	86.134	3.2786	3.5159	248.69	2.82		0.77	1.53	234–561	1, 2
PCIP-SAFT	86.134	3.3482	3.4890	242.31	2.82	9.93	0.67	1.24	234–561	1, 2
2-pentanone										
PC-SAFT	86.134	3.4304	3.4688	249.83			1.87	1.83	203–430	1, 2
PCP-SAFT	86.134	3.3537	3.4942	246.66	2.7		1.73	1.44	203–430	1, 2
PCIP-SAFT	86.134	3.4222	3.4683	240.90	2.7	9.93	1.63	1.18	203–430	1, 2
propanal										
PC-SAFT	58.08	2.6756	3.2630	251.89			2.43	0.49	193–503	1, 2
PCP-SAFT	58.08	2.6001	3.2872	235.21	2.72		0.75	0.77	193–503	1, 2
PCIP-SAFT	58.08	2.7247	3.2478	221.64	2.72	6.5	0.81	0.47	193–503	1, 2
butanal										
PC-SAFT	72.1066	2.9792	3.4344	253.62			1.53	2.57	248–535	1, 2
PCP-SAFT	72.1066	2.8825	3.4698	247.09	2.72		1.58	2.00	248–535	1, 2
PCIP-SAFT	72.1066	2.9621	3.4376	238.65	2.72	8.2	1.58	1.74	248–535	1, 2
dimethyl sulfoxide (DMSO)										
PC-SAFT	78.13	2.9223	3.2778	355.69			1.45	0.58	291–519	1, 2
PCP-SAFT	78.13	3.0243	3.2427	309.36	3.96		0.46	0.33	291–519	1, 2
PCIP-SAFT	78.13	3.1908	3.1978	286.34	3.96	7.97	0.31	0.33	291–519	1, 2
dimethylformamide (DMF)										
PC-SAFT	73.09	2.388	3.658	363.77			4.77	4.06	320–620	2
PCP-SAFT	73.09	2.269	3.714	331.56	3.82		3.63	3.05	320–620	2
PCIP-SAFT	73.09	2.375	3.667	308.42	3.82	7.81	3.46	3.17	320–620	2
acetonitrile										
PC-SAFT	41.052	2.3290	3.1898	311.31			1.69	6.14	292–529	3, 2
PCP-SAFT	41.052	2.1572	3.2730	216.89	3.9252		1.92	2.32	292–529	3, 2
PCIP-SAFT	41.052	2.1043	3.3940	199.07	3.9252	4.4	3.21	6.66	292–529	3, 2
propionitrile										
PC-SAFT	55.079	2.6621	3.3403	294.08			1.07	4.35	309–564	1, 2, 3
PCP-SAFT	55.079	2.5096	3.3981	239.15	4.05		0.86	1.16	309–564	1, 2, 3
PCIP-SAFT	55.079	2.5468	3.4124	218.30	4.05	6.24	1.34	1.41	309–564	1, 2, 3
butyronitrile										
PC-SAFT	69.11	2.7947	3.5015	298.03			0.80	0.58	293–415	1, 2
PCP-SAFT	69.11	2.9041	3.4585	251.32	4.07		1.06	0.26	293–415	1, 2
PCIP-SAFT	69.11	3.0397	3.4204	232.31	4.07	8.4	1.21	0.27	293–415	1, 2
chloro methane										
PC-SAFT	50.488	1.9902	3.1974	237.27			0.6	1.71	283–416	4, 2
PCP-SAFT	50.488	1.8070	3.3034	229.97	1.8963		0.47	0.46	283–416	4, 2
PCIP-SAFT	50.488	1.8608	3.2752	216.46	1.8963	4.72	0.30	0.57	283–416	4, 2
nitromethane										
PC-SAFT	61.04	2.6547	3.0800	305.98			2.35	4.62	313–588	5, 6
PCP-SAFT	61.04	2.4826	3.1338	259.17	3.46		1.16	1.78	313–588	5, 6
PCIP-SAFT	61.04	2.5159	3.1714	229.09	3.46	7.37	1.85	1.90	313–588	5, 6
nitroethane										
PC-SAFT	75.067	3.0177	3.2136	286.57			7.54	3.09	183–593	1, 2
PCP-SAFT	75.067	2.9490	3.2312	265.96	3.23		3.33	1.67	183–593	1, 2
PCIP-SAFT	75.067	3.0910	3.1936	246.68	3.23	9.63	0.74	1.26	183–593	1, 2
Average deviation										
PC-SAFT							2.15	2.70		
PCP-SAFT							1.36	1.43		
PCIP-SAFT							1.32	1.62		

[#] Dipole moments (1D = $3.33564 \cdot 10^{-30}$ Cm) and polarizabilities from literature: Lide DR. *CRC Handbook of Chemistry and Physics.* Table "Dipole Moments" and Table "Molecular Polarizabilities." Cleveland: CRC Press, 2004. For dimensionless dipole moments from parameters in units as specified, it is $\mu_i^{*2} = \mu_i^2/(m_i \sigma_{ii}^3 \varepsilon_{ii}/k) \cdot 10^4/1.3807$ Å^3 $\cdot$ K/D^2.

[$] References: (1) Korea Thermophysical Properties Data Bank, 2004, http://www.cheric.org/kdb/. (2) Daubert TE, Danner RP, Sibul HM, Stebbins CC. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation,* Washington: Taylor & Francis, 1989. (3) Antosik M, Gałka M, Malanowski SK. Vapor liquid equilibrium for acetonitrile + propanenitrile and 1-pentanamine + 1-methoxy-2-propanol. J Chem Eng Data. 2004;49:11–17. (4) Hsu CC, McKetta JJ. Pressure volume-temperature properties of methyl chloride. J Chem Eng Data. 1964;9:45–51. (5) Berman HA, West ED. Density and vapor pressure of nitromethane 26 to 200C. J Chem Eng Data. 1967;12:197–199. (6) McCullough JP, Scott DW, Pennington RE, Hossenlopp IA, Waddington G. Nitromethane: The vapor heat capacity, heat of vaporization, vapor pressure and gas imperfection. J Am Chem Soc. 1954;76:4791–4796.

Table 2. Pure Component Parameters and Correlation Results of the PCIP-SAFT Equation of State for Weakly Dipolar and Polarizable Fluids

Substance	M [g/mol]	m [−]	σ [Å]	ε/k [K]	$\mu^{\#}$ [D]	$\alpha^{\#}$ [Å^3]	AAD-%		Temp. Range [K]	Data Ref.$
							P^{sat}	ρ		
halogenated hydrocarbons										
HCl	36.461	1.6335	2.9066	190.17	1.1086	2.63	0.63	0.94	150–324	1
dichloromethane	84.932	2.3435	3.2987	260.66	1.6	6.48	2.18	1.37	220–510	1
chloroform	119.377	2.5957	3.4299	264.66	1.04	8.23	2.24	0.40	207–536	1
chloroethane	64.514	2.3274	3.3773	225.64	2.05	6.4	2.03	1.16	135–460	1
11difluoroethane	66.05	2.6955	3.1064	171.46	2.27	4.43	1.03	0.33	173–386	1
1-chlorobutane	92.568	2.8874	3.6282	251.20	2.05	11.3	1.60	0.81	150–537	1
chlorobenzene	112.558	2.6816	3.7352	308.82	1.69	14.1	2.54	0.47	228–632	1
bromobenzene	157.01	2.6723	3.8205	328.98	1.7	13.62	1.30	1.23	242–670	1
esters										
methyl methanoate	60.053	2.6979	3.0785	232.18	1.77	5.05	1.65	0.79	174–487	1
ethyl methanoate	74.079	2.9064	3.3011	238.13	1.93	6.94	0.68	1.27	193–508	1
propyl methanoate	88.106	3.2207	3.4093	241.85	1.89	8.97	0.91	0.70	270–538	1
ethyl ethanoate	88.106	3.5481	3.3021	227.50	1.78	8.62	1.26	2.01	190–523	1
propyl ethanoate	102.133	3.8001	3.4166	233.32	1.78	10.41*	1.16	0.90	260–549	1
n-butyl ethanoate	116.16	3.9984	3.5358	240.15	1.87	14.2*	2.04	1.01	200–579	1
methyl propanoate	88.106	3.4916	3.3079	231.04	1.85*	8.97	1.20	1.61	186–530	1
ethyl propanoate	102.133	3.8286	3.4050	231.10	1.74	10.41	1.20	1.05	240–546	1
propyl propanoate	116.16	4.1328	3.4807	233.50	1.8*	14.2*	3.60	0.59	220–568	1
methyl butanoate	102.133	3.6854	3.4373	237.13	2.03	10.41	1.04	0.76	240–554	1
ethers										
dimethyl ether	46.069	2.3188	3.2421	205.28	1.3	5.29	0.26	0.37	200–400	1, 2
methyl ethyl ether	60.096	2.6791	3.3611	212.87	1.17	7.93	1.95	0.58	270–437	1, 2
methyl n-propyl ether	74.123	3.0236	3.4496	221.02	1.107	8.86	1.98	1.16	220–476	1
diethyl ether	74.123	2.9956	3.5017	217.89	1.15	8.73	0.66	0.94	220–466	1

[#] Dipole moments from literature: Lide DR. *CRC Handbook of Chemistry and Physics.* Table "Dipole Moments" and Table "Molecular Polarizabilities." Cleveland: CRC Press, 2004.

*Values estimated based on similar compounds.

[$] References: (1) Daubert TE, Danner RP, Sibul HM, Stebbins CC. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation.* Washington: Taylor & Francis, 1989. (2) *VDI-Wärmeatlas*, VDI-Gesellschaft Verfahrenstechnik und Chemieingenieurwesen (GVC), Düsseldorf, 1994.

Real components and mixtures

The PCIP-SAFT model is applied to vapor-liquid and liquid-liquid equilibria of mixtures with strongly dipolar components. In order to assess the effect of polarizability, the PCIP-SAFT model is thereby compared to the PCP-SAFT equation of state, which accounts for a molecular dipole moment (here we also use the value in vacuo) but not for the polarizability. Comparisons to the PC-SAFT model where electrostatic interactions are not explicitly accounted for are also given.

The pure component parameters of the PCIP-SAFT model as well as correlation results for vapor pressure and liquid density data of pure strongly polar substances are reported in Table 1. Correlation results of all considered equations of state are given in terms of the average absolute deviations (AAD) over the considered temperature range. The correlation results in Table 1 demonstrate a good performance of the proposed PCIP-SAFT equation of state for wide temperature intervals. The unweighted average of all individual AAD-values for vapor pressure data are 1.32, 1.36, and 2.15% for the PCIP-SAFT, PCP-SAFT, and PC-SAFT models, respectively. Since the dipole moments and polarizabilities are taken from independent literature sources, this confirms the physical soundness of the proposed PCIP-SAFT equation of state. Table 2 gives pure component parameters of moderately and weakly dipolar substances.

A mixture of 3-pentanone with heptane, as an example for a system containing a moderately dipolar substance, is depicted in Figure 4. It is seen that all three equations of state can be brought to good agreement with the experimental data.[43] The binary correction parameter, however, differs in a pattern, where the highest value is required for the nonpolar PC-SAFT model, whereas lower values are needed for PCP-SAFT and PCIP-SAFT.

As opposed to mixtures of moderately dipolar substances, one finds that for mixtures containing a strongly dipolar and a nonpolar component, it is often not possible to describe the phase behavior accurately without accounting for the dipolar

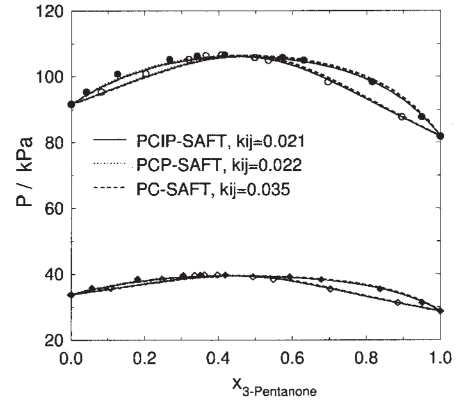

Figure 4. Vapor-liquid equilibrium of the mixture 3-pentanone–n-heptane at two temperatures.

Comparison of experimental data[43] to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT.

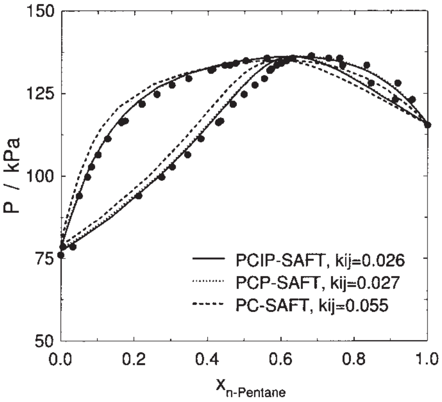

Figure 5. Vapor-liquid equilibrium of the mixture propanal–n-pentane at T = 40°C.

Comparison of experimental data (Eng and Sandler[44]) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT.

interactions in the equation of state. Those systems show a strong deviation from ideality. Calculation results for mixtures of propanal with n-pentane[44] and with cyclohexane[45] are shown in Figures 5 and 6, respectively, and the vapor-liquid equilibrium of acetone and n-heptane[46] is displayed in Figure 7. It becomes obvious that the PC-SAFT model does not properly represent the vapor-liquid equilibria of these systems even if a relatively high binary interaction parameter is introduced. When the dipolar interactions are considered explicitly, the results are improved, while at the same time, a smaller k_{ij}-value is required.

The vapor-liquid equilibrium of the mixture acetone and hexadecane in Figure 8 challenges the suitability of an equation of state to describe strongly asymmetric mixtures. The PCIP-SAFT model is in good agreement to the experimental data,[47] while PC-SAFT predicts a liquid-liquid demixing, which is known to not exist at the given temperature. Although the problem of overpredicting liquid-liquid phase separations is generally not eliminated when polar interactions are accounted for, it is at least considerably reduced.

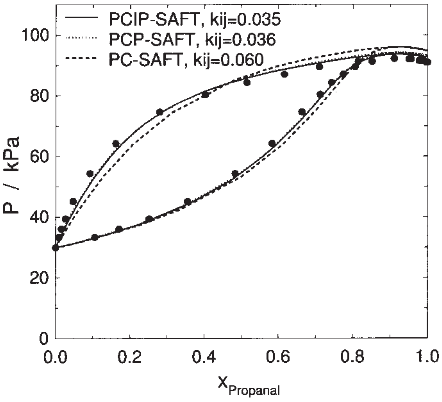

Figure 6. Vapor-liquid equilibrium of the mixture propanal–cyclohexane at T = 45°C.

Comparison of experimental data (Matsunaga and Katayama[45]) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT.

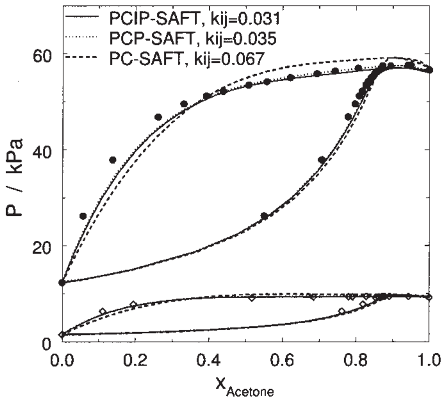

Figure 7. Vapor-liquid equilibrium of the mixture acetone–n-heptane at two temperatures.

Comparison of experimental data[46] (spheres for T = 40°C; diamonds for T = 0°C) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT.

This assessment is substantiated in Figure 9, where the vapor-liquid equilibrium of a DMF–1-butene mixture[48] is presented for two temperatures. The nonpolar PC-SAFT model reveals a false temperature-behavior in describing a liquid-liquid demixing at too high temperatures. The vapor-liquid equilibrium is well represented only when the polar interactions of DMF are accounted for.

The phase behavior of a mixture of DMF and cyclohexane at atmospheric pressure[49-51] is shown in Figure 10. The system exhibits an azeotropic vapor-liquid equilibrium at higher temperatures and shows a liquid-liquid equilibrium at lower temperatures. The binary interaction parameters for all models were adjusted to the upper liquid-liquid demixing temperature. The results of the vapor-liquid and liquid-liquid equilibrium of this system confirm that the value of the binary interaction parameter is small if induction forces due to polarizability are taken into account.

The vapor-liquid equilibrium of the system butyronitrile and heptane is displayed in Figure 11. Butyronitrile with a dipole

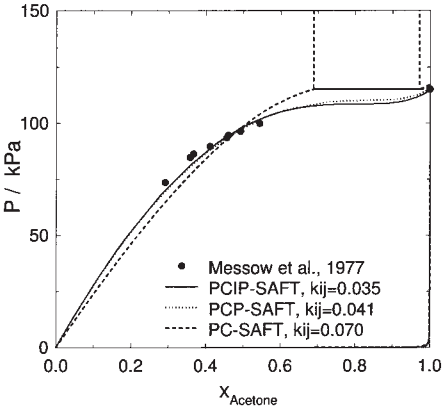

Figure 8. Vapor-liquid equilibrium of the mixture acetone–n-hexadecane at T = 60°C.

Comparison of experimental data (Messow et al.[47]) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT. A liquid-liquid demixing as predicted by PC-SAFT occurs at lower temperatures only.

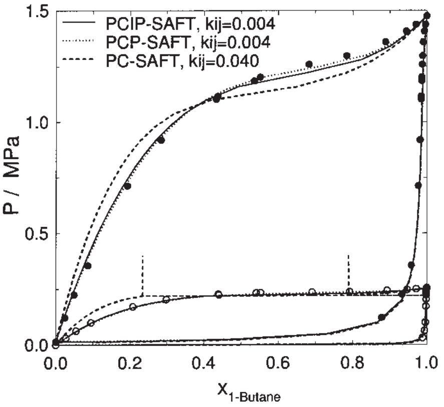

Figure 9. Vapor-liquid equilibrium of the mixture N,N-dimethyl formamide–1-butene at two temperatures ("●" for $T = 90°C$, "○" for $T = 20°C$).

Comparison of experimental data (Wilding et al.[48]) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT. A liquid-liquid demixing as predicted by PC-SAFT does not occur at the considered temperature.

moment of 4.05 D is a strongly polar compound. The binary interaction parameter of the non-polar PC-SAFT model was adjusted to suppress an artificial liquid-liquid demixing, and the model is incapable of reflecting the actual vapor-liquid equilibrium. The PCIP-SAFT, in contrast, gives a good representation of the experimental data,[52] while a binary correction factor is almost zero. Although the binary interaction parameter is somewhat higher for the PCP-SAFT model, it is in almost as good agreement to the data. The closeness of correlation results between the two polar equations of state was unexpected to the authors. The surprise is not only due to personal intuition, along with the fact that the effective dipole moments in the RPT are calculated to be in the order of 20% higher than the value in vacuo, but it is also due to the observation that when the polarizability of the non-polar compound is neglected, the results of PCIP-SAFT are far off reality. The fact that the model is relatively sensitive to the considered values of all polarities, in turn, indicates that tabulated (experimental) polarities lead to a consistent interplay also in the RPT framework. This finding can be regarded as complaisant considering the simplicity of the adopted molecular model, where an orientational resolution of the polar interactions through spherical harmonics is avoided and isotropic mean values for the polarizability are applied.

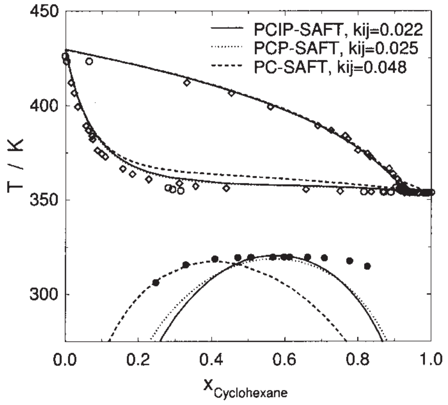

Figure 10. Liquid-liquid and vapor-liquid equilibrium of the mixture N,N-dimethylformamide–cyclohexane at $P = 1.013$ bar.

Comparison of experimental data ("○"Blanco et al.[49]; "◇" Dechema[50]; "●" Hradetzky et al.[51]) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT.

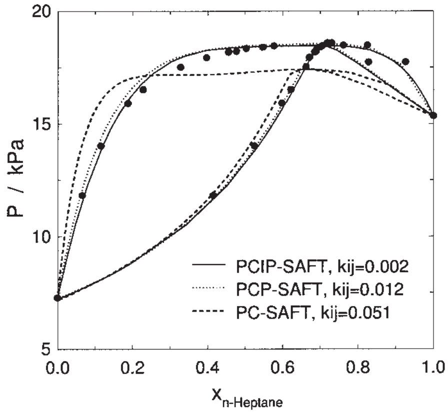

Figure 11. Vapor-liquid equilibrium of the mixture butyronitrile–n-heptane at $T = 45°C$.

Comparison of experimental data (Artal et al.[52]) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT.

A limitation of the angle-averaged approach may surface for the compound acetonitrile (and was studied earlier by Hloucha and Deiters[53]). Upon reviewing the deviations of the PCIP-SAFT model for pure components in Table 1, one finds those of acetonitrile to be in contrast to the general pattern. As opposed to an improved or approximately equal representation of pure component data, one finds that for acetonitrile the PCIP-SAFT gives considerably poorer results than the PC-SAFT. It has been found that the preferential orientation of two acetonitrile molecules is the head-to-tail (anti-parallel) configuration,[54,55] in which the dipoles are oppositely aligned. On the one hand, this leads to a canceling of the dipole moment to a certain extent and, on the other hand, lower values of the polarizability tensor[56] in the molecular x- and y-axis are effective. We have adjusted the dipole moment for acetonitrile in order to test whether a still sensible value for the dipole moment for the PCIP-SAFT would be adjusted. The resulting value of 3.4315 D is in quite good agreement to the tabulated value of 3.925 D, and the errors (AAD) for vapor pressure and density data, respectively, are 0.66% and 3.31% ($m_i = 2.3627$, $\sigma_I = 3.1855$Å, $\varepsilon_I/k = 225.14$K, $\alpha_I = 4.4$ Å ^{3}).

We used this set of pure component parameters for a mixture of acetonitrile and methylcyclohexane. In Figure 12, the PCIP-SAFT equation of state is found to be in fair agreement to the experimental data,[57] while neither the PC-SAFT nor the PCP-SAFT can reproduce the actual phase equilibrium. This suggests that the adjusted dipole moment is not only reasonably close to the actual value, but it is also suitable to describe mixture phase equilibria. This hypothesis is tested for a cross-dipolar mixture of acetonitrile and 1-chlorobutane in Figure 13, and a good agreement to the experimental data[58] is found. The cross-polar interactions are best tested in mixtures of a light and a strong polar component (here, chlorobutane and acetonitrile), because it is the difference in dipolar strength that

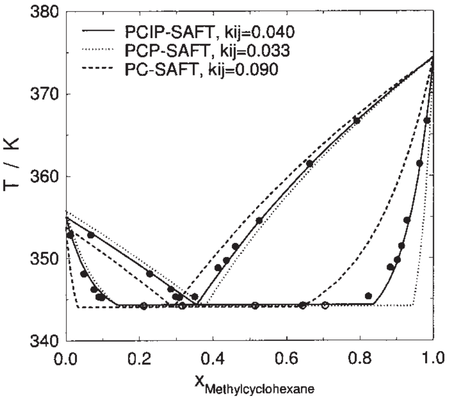

Figure 12. Vapor-liquid equilibrium of the mixture acetonitrile–methylcyclohexane at P = 1.013 bar.

Comparison of experimental data (Krishna et al.[57]) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT.

introduces difficulties for many equations of state rather than the absolute values.

This study aims at dipolar interactions of polarizable molecules and in order to isolate these interactions we have so far avoided associating substances. In a last example, it is interesting, however, to show that associating components, of course, can also be considered. Pure component parameters of methanol were determined (PCIP-SAFT: m_i = 2.0693, σ_i = 2.9547Å, ε_i/k = 174.51K, ε_i^{assoc}/k = 2418.5K, κ_i^{assoc} = 0.06319, μ_i = 1.7D, α_i = 3.29 Å ^{3}) and better agreement for vapor pressure and liquid densities was found compared to PC-SAFT. The vapor-liquid and liquid-liquid equilibrium of methanol with n-decane is displayed in Figure 14, and a good agreement between experimental data[59,60] and the PCIP-SAFT model is found. Although one can attribute a higher predictive ability to the PCIP-SAFT, it seems to some extent coincidental for this particular case that a value of k_{ij} = 0 is optimal for describing the phase behavior over a wide temperature range.

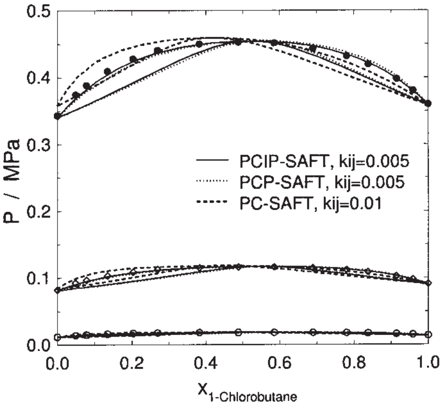

Figure 13. Vapor-liquid equilibrium of the mixture acetonitrile–1-chlorobutane at three temperatures (“●” for T = 398.89K, “◇” T=348.18K, “○” for T = 298.69°C).

Comparison of experimental data (Khurma et al.[58]) to correlation results of PCIP-SAFT, of PCP-SAFT, and of PC-SAFT.

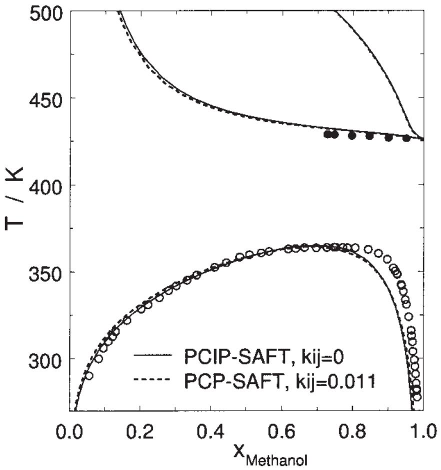

Figure 14. Vapor-liquid and liquid-liquid equilibrium of the mixture methanol–n-decane (“●” for P = 1.5MPa).

Comparison of experimental data (Matsuda and Ochi[59] and de Loos et al.[60]) to correlation results of PCIP-SAFT and of PCP-SAFT.

Conclusions

The renormalized perturbation theory (RPT-1) of Wertheim allows accounting for the molecular polarizability and, thus, the induction effect of polar interactions. The first-order renormalization theory in conjunction with a new dipole-expression for nonspherical molecules was compared to molecular simulation data. The theory was found to be in very good agreement with the simulation data for polarizable dipolar fluids and mixtures.

The theory was applied to real substances with the PC-SAFT equation of state, and we refer to the proposed model as the Perturbed-Chain Induced-Polar SAFT (PCIP-SAFT) equation of state. Independently determined values for dipole moments and for molecular polarizabilities were here considered and, thus, no additional adjustable parameter has to be introduced with the polar contributions to the equation of state. The average isotropic polarizability is considered in the theory, so that a detailed orientational resolution of molecular interactions is not required. Despite its simplicity, this approach leads to a good description of real substances, with clear improvements when compared to the non-polar equation of state. The pure component parameters of 36 substances, ranging from moderately dipolar to strongly dipolar, were adjusted to vapor-pressure data and liquid density data.

When considering mixtures, the inclusion of dipolar interaction and induced dipolar interactions due to molecules' polarizability usually leads to lower (absolute) values of the required binary interaction parameter, and the proposed model shows thus more predictive abilities than the nonpolar model. More importantly, the PCIP-SAFT equation of state significantly improves the representation of the mixture phase behavior of strongly dipolar substances when compared to the PC-SAFT. When the dipole moment is accounted for but the polarizability is omitted, as done in the PCP-SAFT, one obtains very similar results for the phase behavior of mixtures as with the PCIP-SAFT. This is despite the fact that the pure component parameters are very different for both cases and in spite of the sensitivity to the polarizability values.

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