ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/231375782

Application of Infinite Dilution Activity Coefficients for Determining Binary Equation of State Parameters

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JUNE 2010

Impact Factor: 2.59 · DOI: 10.1021/ie100259e

CITATIONS
6

READS
93

4 AUTHORS, INCLUDING:

Lawien F. Zubeir
Technische Universiteit Eindhoven

14 PUBLICATIONS **63** CITATIONS

SEE PROFILE

Joachim Gross
Universität Stuttgart

90 PUBLICATIONS **2,894** CITATIONS

SEE PROFILE

Available from: Lawien F. Zubeir
Retrieved on: 03 February 2016

Application of Infinite Dilution Activity Coefficients for Determining Binary Equation of State Parameters

Christian S. Schacht,[†] Lawien Zubeir,[†] Theo W. de Loos,[†] and Joachim Gross*[,†,‡]

Engineering Thermodynamics, Process & Energy Department, Delft University of Technology, Delft, The Netherlands, and Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, Stuttgart, Germany

Infinite dilution activity coefficients can be determined relatively fast from several experimental techniques. Literature values for the infinite dilution activity coefficients are used to determine a binary interaction parameter of the perturbed-chain polar statistical associating fluid theory (PCP-SAFT) equation of state. The model is, subsequently, applied to the full concentration range of binary mixtures, and the results are compared to experimental data from literature. The applicability of the method is demonstrated for examples involving polar, associating, and polymeric components. It is confirmed that the parametrization allows for extrapolations in temperature. In combination with a group-contribution model for the estimation of infinite dilution activity coefficients (e.g., modified UNIFAC(Do)), the equation of state can be used to predict vapor−liquid equilibria of mixtures.

Introduction

Activity coefficients at infinite dilution (γ^∞) describe the behavior of solute molecules completely surrounded by solvent molecules. Therefore, they are strong indicators of a mixture's nonideality.[1] Measurements of γ^∞ are quickly conducted for a wide range of solutes, for example, by gas chromatographic, ebulliometric, or gas stripping methods.[2−5] However, the full potential of the activity coefficient at infinite dilution can only be harvested if the phase behavior over the complete concentration range can be extracted. Therefore, γ^∞ values were used to determine adjustable parameters of activity coefficient models.[6] Previous studies also applied infinite dilution activity coefficients to determine cubic equation of state parameters.[7−10] More recent physically based equations of state are successfully applied to model a wide range of complex systems, often even allowing for the prediction of thermodynamic properties.[11] The fact that these equations offer precise extrapolations without applying temperature-dependent adjustable parameters suggests an advantageous use of γ^∞ data to determine parameters of physically based equations of state.

This work employs the PCP-SAFT[12−15] equation of state to adjust the binary interaction coefficient k_{ij} to literature data for the solute's activity coefficient at infinite dilution. The method's applicability is shown by applying it to a broad range of mixtures, including symmetric and asymmetric, polar, associating, and macromolecular systems.

Determining the Binary Equation of State Parameters

The PCP-SAFT equation of state requires three pure component parameters for nonassociating fluids. As the dipole and quadropolar moments of small-sized molecules can be taken from literature or from quantum chemical calculations, they are not considered as adjustable parameters. Associating substances are characterized by two additional adjustable pure component parameters. For all but one substances considered here the pure component parameters were available.[13−17] For methyl *tert*-butyl ether (MTBE) these parameters were determined by adjustment to experimental data,[18] as segment number $m = 2.9509$, segment diameter $\sigma = 3.7115$ Å, and dispersive energy $\varepsilon/k_b = 233.06$ K; the dipole moment $\mu = 1.2$ D was taken from literature.[19] For mixtures, the dispersive energy parameter between a pair of substances (i and j) is calculated from a combination rule $\varepsilon_{ij} = (\varepsilon_i\varepsilon_j)^{0.5}(1 - k_{ij})$, where k_{ij} is an adjustable binary parameter.

The solute's infinite dilution activity coefficient, γ_i^∞, in a pure solvent is calculated from the PCP-SAFT equation of state as

$$\gamma_i^\infty = \lim_{x_i\to 0}\left(\frac{\phi_i^{\mathrm{L}}}{\phi_i^{\mathrm{L},0}}\right) \tag{1}$$

where $\phi_i^{\mathrm{L}}(T, p, x_i)$ is the liquid-phase fugacity coefficient of the solute in the mixture and x_i is the mole fraction of the solute. Further, $\phi_i^{\mathrm{L},0}(T, p)$ denotes the fugacity coefficient of the pure solute in real or hypothetical liquid state. The pressure approaches the vapor pressure of the pure solvent ($p \to p_{\mathrm{solv}}^{\mathrm{sat}}$). The binary interaction parameter k_{ij} can be obtained by fitting the calculated to the experimental values of γ_i^∞. This constant binary parameter is subsequently applied to the entire range of compositions.

The pure component liquid fugacity cannot be evaluated for temperatures above a compounds critical temperature. Instead, we applied the solutes Henry's law constant to adjust the binary parameter k_{ij} for systems containing carbon dioxide. The Henry's law constant

$$H_i \equiv \lim_{x_i\to 0}\left(\frac{y_i\phi_i^{\mathrm{V}}p}{x_i}\right) = \lim_{x_i\to 0}(\phi_i^{\mathrm{L}}p) \tag{2}$$

is evaluated approaching the solvent vapor pressure ($p \to p_{\mathrm{solv}}^{\mathrm{sat}}$), with y_i as the solute mole fraction in the vapor and $\phi_i^{\mathrm{V}}(T, p, y_i)$ the vapor phase mixture fugacity coefficient of the solute.

* To whom correspondence should be addressed. E-mail: gross@itt.uni-stuttgart.de.
[†] Delft University of Technology.
[‡] University of Stuttgart.

10.1021/ie100259e © 2010 American Chemical Society
Published on Web 07/01/2010

Table 1. Systems under Investigation, γ^∞, and Their Binary Parameters

solvent	solute	T/K	γ^∞	H_i/bar[a]	data ref[b]	k_{ij}
acetone	hexane	253.15	11.08		21−25	0.033
		268.15	9.23			0.033
		293.15	7.10			0.033
		308.15	6.19			0.033
2-butanone	hexane	333.15	3.40		21, 22, 26	0.026
		338.15	3.29			0.026
heptane	carbon dioxide	310.64		80.6	27	0.028
		352.57		115.3		0.034
		394.23		137.7		0.031
		477.17		153.8		0.027
decane	carbon dioxide	277.59		57.5	27	0.037
		310.93		82.9		0.040
		377.59		136.0		0.051
		444.26		178.5		0.067
		510.93		191.1		0.082
		583.65		155.1		0.076
hexane	MTBE	303.15	1.25		28	0.009
		323.15	1.19			0.008
methanol	hexane	313.15	22.58		21, 22	0.029
ethanol	heptane	313.15	12.36		21, 26, 29−33	0.013
ethyl acetate	chloroform	313.15	0.44		25, 26	$\varepsilon^{A_iB_j}/k = 1684$ K
ethyl acetate	chloroform	323.15	0.46			$\varepsilon^{A_iB_j}/k = 1724$ K
water	pentanol	371.15	168.33		34	$\varepsilon^{A_iB_j}/k = 2483$ K
polystyrene	nonane	448.15	0.00451		35	0.027
polystyrene	benzene	313.15	0.00338		35	−0.020
polystyrene	cyclohexane	413.15	0.00948		36	0.023
polystyrene	cyclohexane	433.15	0.00840		36	0.017
polystyrene	cyclohexane	453.15	0.00754		36	0.011
polystyrene	cyclohexane	413.15	0.00683		36	0.005

[a] The Henry constants in ref 27 are extrapolated from experimental vapor−liquid equilibrium data. [b] Data from ref 22−26, 29−34 was take from the collection of activity coefficients of infinite dilution of the DECHEMA Chemistry Data Series.[37]

Table 2. Modeling of Binary Systems

system	T/K	points	k_{ij}	$\Delta p/p \times 100$	data ref[a]
acetone + hexane	293−328	98	0.034	2.1	38−40
2-butanone + hexane	333−338	42	0.026	2.2	41, 42
heptane + carbon dioxide	310−477	118	0.030	2.7	43
decane + carbon dioxide	310−510	46	0.059	4.8	44
MTBE + hexane	313−343	114	0.008	0.4	45−47
hexane + methanol	318−348	144	0.029	2.3	48, 49
heptane + ethanol	303−343	252	0.013	1.1	50, 51
ethyl acetate + chloroform	313−323	21	$\varepsilon^{A_iB_j}/k = 1704$ K	1.7	52
water + pentanol	285−411	34	$\varepsilon^{A_iB_j}/k = 2483$ K	0.17[b]	53, 54
polystyrene + nonane	403−448	19	0.027	1.4	55
polystyrene + benzene	313−353	67	−0.020	1.5	56
polystyrene + cyclohexane	303−333	23	0.014	3.9	57

[a] Data 38−42, 45, 46, 48−53 was taken from the vapor−liquid equilibrium data collection of the DECHEMA Chemistry Data Series.[58] [b] The number corresponds to the deviation for the vapor−liquid equilibrium only.

Often, the data sets for the infinite dilution activity coefficients versus temperature are subject to significant scatter. According to the Gibbs−Helmholtz relation

$$\left(\frac{\partial \ln \gamma_i}{\partial \frac{1}{T}}\right)_{p,x_k} = \frac{h_i^E}{R} \tag{3}$$

where h_i^E is the partial molar excess enthalpy of the solute and R is the gas constant. For subcritical binaries far from the critical temperature, the excess enthalpy h_i^E is often fairly constant. Hence, linear regression can be applied to smooth the scatter of the experimental data. Unless otherwise indicated, the binary interaction parameter has been adjusted to γ_i^∞ data at different temperatures (as given in Table 1). A temperature-independent average value of k_{ij} has been applied to calculate the phase behavior. In the following, this method is applied to binary mixtures of nonpolar, polar, and associating compounds to explore the method's practicability.

Results

The PCP-SAFT equation of state exhibits fair predictive qualities for mixtures of sufficiently similar components.[13,16,20] A meaningful test for the binary k_{ij} parameter determined from the infinite dilution limit involves mixtures of "asymmetric" substances, where asymmetry can prevail as differences in size, polar interactions, or associating bonds. Table 1 gives an overview of the activity coefficients and the parameters adjusted. The results for the modeling at finite concentrations are given in Table 2.

Polar Mixtures. This approach entirely relies on the quality of the experimental infinite dilution data. If binary parameters are adjusted to γ_i^∞ data, one can expect good agreement between the modeling results and the experimental vapor−liquid equilibrium data in the diluted region of the phase diagram ($x_i \rightarrow$

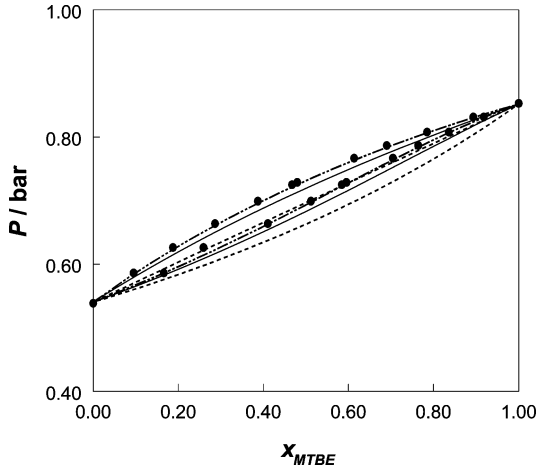

Figure 1. Vapor−liquid equilibrium of methyl *tert*-butyl ether−*n*-hexane mixtures. Comparison of PCP-SAFT correlations to experimental data,[45−47] $T = 323.18$ K (circles). The binary parameter $k_{ij} = 0.008$ was adjusted to γ^{∞} data of MTBE in hexane (dash-dotted line) and $k_{ij} = 0.0056$ was adjusted to γ^{∞} data of hexane in MTBE (solid line). Results for $k_{ij} = 0$ are given for comparison (dashed line).

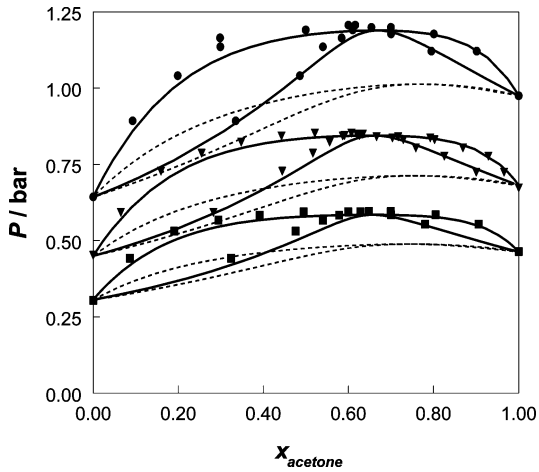

Figure 2. Vapor−liquid equilibrium of acetone−hexane mixtures. Comparison of PCP-SAFT correlations (solid line) to experimental data,[38−40] $T = 328.15$ K (circles), 318.15 K (triangles), and 308.15 K (squares). The binary parameter $k_{ij} = 0.034$ was adjusted to γ^{∞} data of hexane in acetone (solid line). Results for $k_{ij} = 0$ are given for comparison (dashed line).

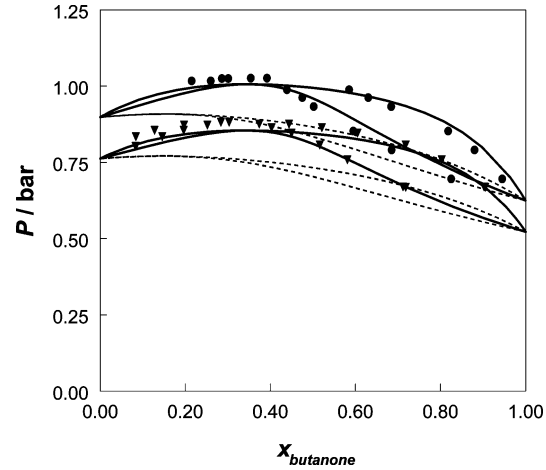

Figure 3. Vapor−liquid equilibrium of 2-butanone−*n*-hexane mixtures. Comparison of PCP-SAFT correlations to experimental data,[41,42] $T = 338.15$ K (circles) and 333.15 K (triangles). The binary parameter $k_{ij} = 0.026$ was adjusted to γ^{∞} data of hexane in butanone (solid line). Results for $k_{ij} = 0$ are given for comparison (dashed line).

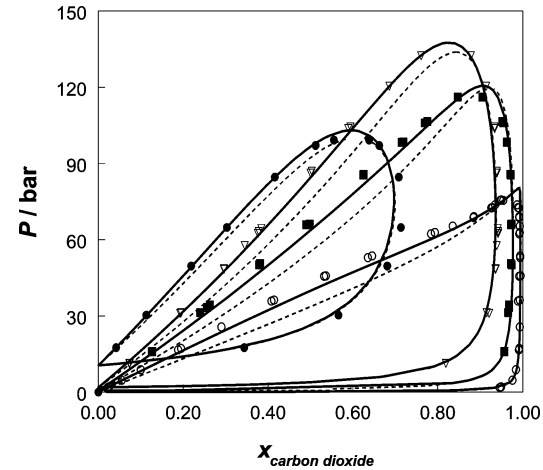

Figure 4. Vapor−liquid equilibrium of carbon dioxide−*n*-heptane mixtures. Comparison of PCP-SAFT correlations to experimental data,[43] $T = 477.17$ K (solid circles), 394.32 K (triangles), 352.57 K (squares), and 310.64 K (open circles). The binary parameter $k_{ij} = 0.030$ was adjusted to Henry's constants of carbon dioxide in heptane (solid line). Results for $k_{ij} = 0$ are given for comparison (dashed line).

0). Deviations of the modeling from experimental data within the diluted region suggest inconsistencies between the experimental vapor−liquid equilibrium and the γ_i^{∞} data, leading to a poor description of the data at finite concentrations. Figure 1 demonstrates this effect. It shows the phase behavior of the MTBE−hexane system at 323.15 K. The binary parameter $k_{ij} = 0.0080$ has been adjusted to the activity coefficient of hexane infinitely diluted in MTBE (solid line) and $k_{ij} = 0.0056$ to MTBE infinitely diluted in hexane (dash-dotted line). The parameter adjusted to infinitely diluted MTBE results in an insufficient description of the hexane-rich phase ($x_{\mathrm{MTBE}} \rightarrow 0$) and, in fact, deviates for the entire concentration range. Consequently, we will only apply data sets that allow for accurate modeling results in the region for $x_i \rightarrow 0$.

The vapor−liquid equilibrium of acetone and hexane in the temperature range from 293.15 to 328.15 K is shown in Figure 2. The azeotropic behavior as well as the azeotropic concentrations are described well. The binary parameter has been adjusted to the activity coefficient of hexane infinitely diluted in acetone. Accordingly, the model is in excellent agreement with the experimental data at acetone mole fractions above the azeotropic concentration. For higher hexane concentrations, some underprediction of the pressures can be noticed. Similar deviations have been shown by Gross and Vrabec[15] and might be caused by the fact that the polar contribution of the PCP-SAFT equation of state has been developed for dipoles oriented along the molecular axis. Nonetheless, a comparison with a PCP-SAFT prediction without the application of a binary interaction parameter shows a strong improvement in reproducing the experimental data. This finding can also be seen for the system butanone−hexane (Figure 3).

To explore the applicability of this method for substances above their critical point, we applied the Henry's law constant of carbon dioxide in heptane and decane to adjust the binary interaction coefficients k_{ij}. Figures 4 and 5 demonstrate the excellent agreement of the model with literature data, including the critical region.

The binary interaction within the PCP-SAFT equation of state usually shows a fairly constant behavior with temperature. It is then sufficient to adjust only one k_{ij} for data sets of varying temperature. Figure 6 illustrates this advantage for the system MTBE−hexane. The data can be well-described with a nonzero

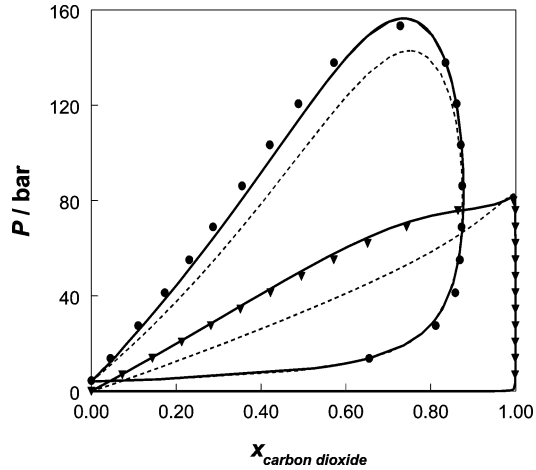

Figure 5. Vapor−liquid equilibrium of carbon dioxide−*n*-decane mixtures. Comparison of PCP-SAFT correlations to experimental data,[44] $T = 510.93$ K (circles) and 310.77 K (triangles). The binary parameter $k_{ij} = 0.059$ was adjusted to Henry's constants of carbon dioxide in decane (solid line). Results for $k_{ij} = 0$ are given for comparison (dashed line).

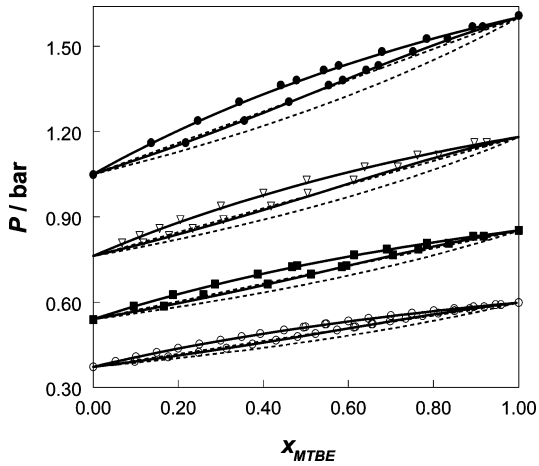

Figure 6. Vapor−liquid equilibrium of methyl *tert*-butyl ether−*n*-hexane mixtures. Comparison of PCP-SAFT correlations to experimental data,[45−47] $T = 343.11$ K (solid circles), 333.15 K (triangles), 323.18 K (squares), and 313.15 K (open circles). The binary parameter $k_{ij} = 0.008$ was adjusted to γ^{∞} data of MTBE in hexane (solid line). Results for $k_{ij} = 0$ are given for comparison (dashed line).

k_{ij}. The parameter has been determined by adjusting it to the γ^{∞} of MTBE in hexane at 323.15 K. Only one data point was required to predict the mixtures $p-x$ behavior over the given temperature range. The stability of the binary coefficient k_{ij} with respect to temperature is demonstrated by the $T-x$ diagram for MTBE−hexane system in Figure 7.

Associating Mixtures. Similar results are obtained for the ethanol−*n*-heptane system in Figure 8. The system contains a self-associating compound and shows azeotropic behavior. A binary interaction parameter of $k_{ij} = 0.013$ was found by adjusting the γ^{∞} values of heptane in ethanol at 303.15 *K*. This value allows an accurate description of the experimental data up to $T = 343.15$ K. In order to assess the role of the equation of state model in our approach, we have also applied the Peng−Robinson equation of state using van der Waals mixing rules. A description of the slope at $x_i \rightarrow 0$ is for this model only possible with adjusting a binary parameter for each temperature. The values are $k_{ij} = 0.010$, $k_{ij} = 0.025$, and $k_{ij} = 0.033$ for 313.15, 333.15, and 343.15 K, respectively. Although the Peng−Robinson equation of state describes the region around $x_i \rightarrow 0$ well, it entirely fails to extrapolate to the

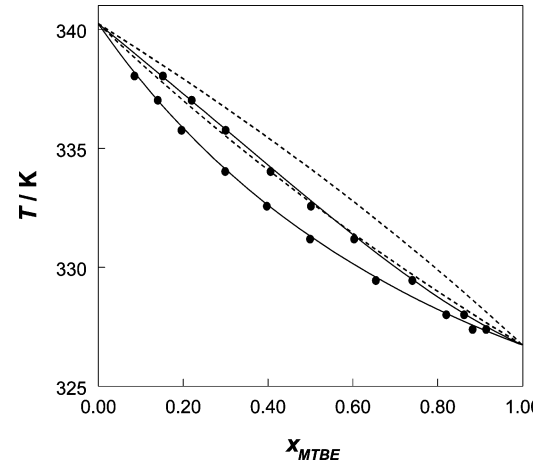

Figure 7. Vapor−liquid equilibrium of a methyl *tert*-butyl ether−*n*-hexane mixture. Comparison of PCP-SAFT correlations to experimental data[59] at $P = 0.96$ bar (solid circles). The binary parameter $k_{ij} = 0.008$ was adjusted to γ^{∞} data of MTBE in hexane (solid line). Results for $k_{ij} = 0$ are given as comparison (dashed line).

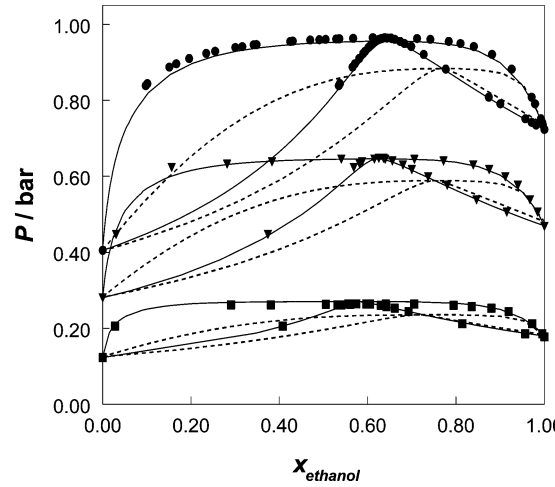

Figure 8. Vapor−liquid equilibrium of ethanol−*n*-heptane mixtures. Comparison of PCP-SAFT correlations to experimental data,[50,51] $T = 343.15$ K (circles), 333.15 K (triangles), and 313.15 K (squares). The binary parameter $k_{ij} = 0.013$ was adjusted to γ^{∞} data of heptane in ethanol (solid line). Results of the Peng−Robinson model (dashed line) are given for comparison ($k_{ij} = 0.010$, $k_{ij} = 0.025$, $k_{ij} = 0.033$ with increasing temperature).

experimental data at finite concentrations. In this light the PC-SAFT equation of state is confirmed to be a suitable model, because each isotherm is well-described over the whole concentration range and because the binary parameters are independent of temperature.

Cross-associating interactions are determined by orbital overlaps and are, thus, quantum mechanically determined. Although these interactions can be modeled classically, it is clear that cross-association parameters can not be well estimated from combining rules. Combining rules are particularly suitable for repulsive and dispersive interactions, where geometric arguments and the hypothesis of a universal frequency dependence of the dynamic polarizability can be applied. Therefore, it is, usually, for cross-associating systems that we find the largest deviations between modeled and experimental data.[60] The use of γ^{∞} data to model the vapor−liquid equilibria is of particular benefit for these mixtures. Ohta et al.[52] have studied the vapor−liquid equilibria of the system ethyl acetate + chloroform to show that this mixture exhibits strong associative interactions. Figure 9 compares the experimental isotherms to modeling results

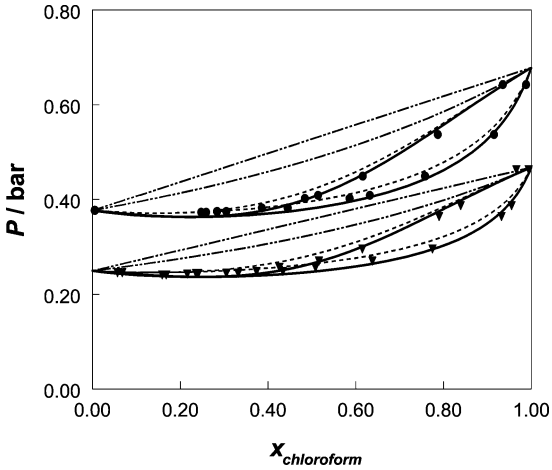

Figure 9. Vapor−liquid equilibrium of ethyl acetate−chloroform mixtures. Comparison of PCP-SAFT correlations to experimental data,[52] $T = 323.15$ K (circles) and 313.15 K (triangles). The association parameter $\varepsilon^{A_iB_j}/k = 1704$ K was adjusted to γ^∞ data of chloroform in ethyl acetate (solid line). Similar results are obtained by fitting $k_{ij} = -0.036$ to γ^∞ data without association parameters (dashed line). Results for $k_{ij} = 0$ with the association parameter from a combining rule are given for comparison (dash-dotted line).

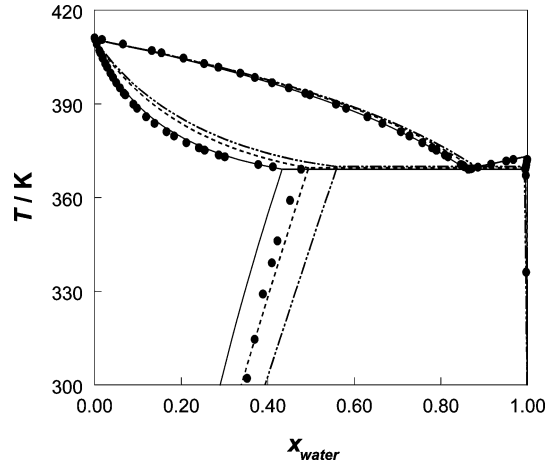

Figure 10. Phase equilibrium of the water−pentanol mixture. Comparison of PCP-SAFT correlations to experimental data[53,54] at $P = 1.013$ bar (circles). The association parameter $\varepsilon^{A_iB_j}/k = 2483$ K was adjusted to γ^∞ data of pentanol in water (solid line). Similar results are obtained by fitting $k_{ij} = 0.012$ to γ^∞ data with the association parameter from a combining rule (dashed line). Results for $k_{ij} = 0$ are given for comparison (dash-dotted line).

obtained by the proposed method. The cross-associating interaction is in PCP-SAFT described by the association volume $\kappa^{A_iB_j}$ and energy $\varepsilon^{A_iB_j}$. For this mixture, we assign one cross-association site for each component, which does not allow self-association. The association volume is fixed (with a typical value[16]) to $\kappa^{A_iB_j} = 0.01$. The interaction energy was determined as $\varepsilon^{A_iB_j}/k = 1704$ K by adjusting to experimental γ^∞ data, while k_{ij} was set to zero. For comparison, the same system was modeled without cross-associating interactions, but instead, the binary interaction parameter $k_{ij} = -0.0365$ was adjusted to γ^∞ data at 313.15 and 323.15 K (see the dashed line in Figure 9). Both approaches (solid line and dashed line) lead to satisfying agreement with the experimental data. The example suggests robustness with respect to the choice of the parameter that is used for correlating the infinite dilution limit.

The system water−pentanol shows liquid−liquid demixing. The compounds exhibit self- and cross- associating interactions and its phase equilibrium is modeled using the same approach as for the system ethyl acetate−chloroform. With a fixed association volume of $\kappa^{A_iB_j} = 0.01$, the interaction energy $\varepsilon^{A_iB_j}/k = 2483$ K was adjusted to γ^∞ data of pentanol in water at 371.15 K. A binary interaction coefficient of $k_{ij} = 0.012$ can be adjusted, when the cross-association is approximated from combination rules [$\varepsilon^{A_iD_j} = (\varepsilon^{A_iB_i}\varepsilon^{C_iD_j})^{0.5}$, $\kappa^{A_iD_j} = (\kappa^{A_iB_j} + \kappa^{C_iD_j})/2$]. The results are shown in a $T-x$ diagram in Figure 10. The system is characterized by an heteroazeotropic vapor−liquid equilibrium with the formation of a liquid−liquid equilibrium at lower temperatures. Considering that only the infinite dilution limit has gone into the correlation, both results lead to reasonable agreement for the liquid−liquid demixing as a function of temperature.

Experimental data for activity coefficients at infinite dilution is often scattered and it is interesting to evaluate the sensitivity of the calculation results concerning such uncertainties. If the Poynting factor and the ratio of the fugacity coefficients is assumed to be unity, a mixture's liquid phase activity coefficient is given by

$$\gamma_i = \frac{y_i p}{x_i p_i^{\mathrm{sat}}} \tag{4}$$

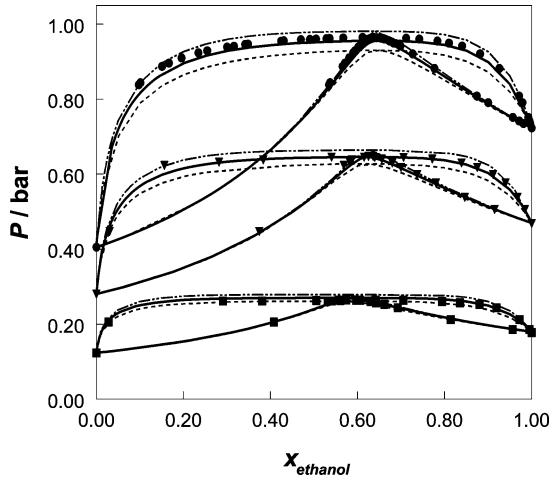

Figure 11. Vapor−liquid equilibrium of ethanol−n-heptane mixtures. Comparison of PCP-SAFT correlations to experimental data,[50,51] $T = 343.15$ K (circles), 333.15 K (triangles), and 313.15 K (squares). The binary parameter $k_{ij} = 0.013$ was adjusted to γ^∞ data of heptane in ethanol (solid line). A 20% increase of the experimental γ^∞ values leads to an increased $k_{ij} = 0.019$ (dash-dotted line). The dashed line is the result of a 20% decrease of the experimental γ^∞ with $k_{ij} = 0.007$.

with p_i^{sat} as the vapor pressure. Upon approaching the infinite dilution limit, $x_i \to 0$, $y_i \to 0$, minor uncertainties within the concentrations of the liquid or vapor phase will lead to large errors in the composition ratio y_i/x_i and, thus, in the infinite dilution activity coefficient. Extrapolations toward infinite dilution are highly sensitive toward the quality of the finite data. Eckert et al.[2] explain that phase equilibria in concentrated solutions, on the other hand, are rather insensitive toward modest errors in the diluted limit, when extrapolated to the finite region. In order to confirm their argument, we analyze a system where the experimental activity coefficient γ^∞ is varied by ±20%. Figure 11 displays the resulting deviations in the phase equilibrium calculation for the example ethanol−n-heptane. Although, the γ^∞ data varies by 20%, the finite concentration pressures stay within a 3.5% band. Consequently, the scatter often found in the experimental data does not necessarily disqualify the proposed approach.

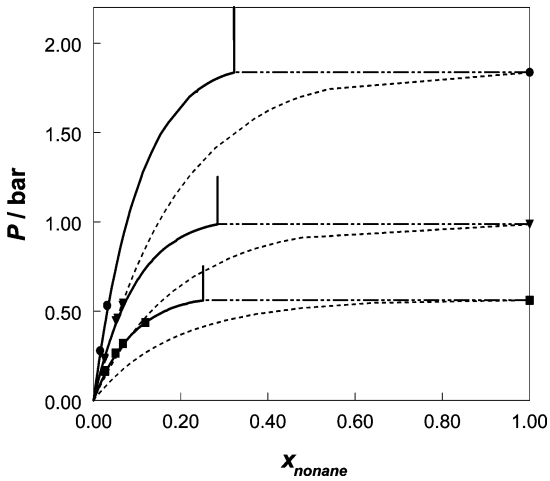

Figure 12. Vapor−liquid equilibrium of PS−*n*-nonane mixtures with $M_{n,ps}$ = 218 000 g/mol. Comparison of PCP-SAFT correlations to experimental data,[55] T = 448.15 K (circles), 423.15 K (triangles), and 403.15 K (squares). The binary parameter k_{ij} = 0.027 was adjusted to γ^{∞} data of nonane in polystyrene (solid line). The dash dotted line indicates a three-phase equilibrium. Results for k_{ij} = 0 are given for comparison (dashed line).

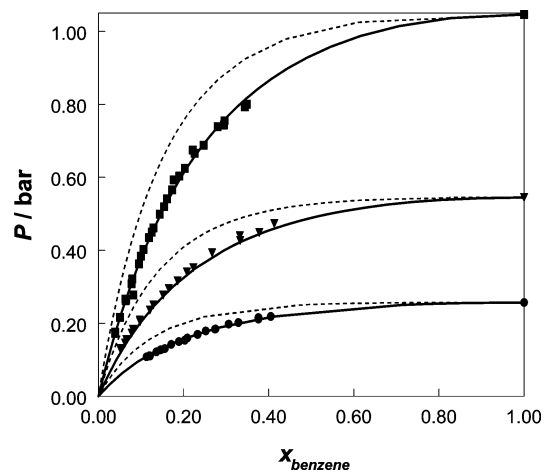

Figure 13. Vapor−liquid equilibrium of PS−benzene mixtures (with $M_{n,ps}$ = 218 000 g/mol). Comparison of PCP-SAFT correlations to experimental data,[56] T = 353.2 K (circles), 333.2 K (triangles), and 313.2 K (squares). The binary parameter k_{ij} = −0.020 was adjusted to γ^{∞} data of benzene in polystyrene (solid line). Results for k_{ij} = 0 are given for comparison (dashed line).

Polymer−Solvent Systems. Experimental vapor−liquid equilibrium measurements are elaborate and might become difficult, particularly for macromolecular systems. It is an appealing prospect to conduct gas chromatographic experiments for the infinite dilution limit in combination with an equation of state instead of performing phase equilibrium measurements at finite concentrations. Although polymeric γ^{∞} data usually show large scatter,[61] we illustrate the advantageous application of experimental infinite dilution activity coefficients to model vapor−liquid equilibria. The phase behavior of polystyrene with benzene as well as with nonane are shown in Figures 12 and 13, respectively. In both cases, polystyrene (PS) is assumed to be monodisperse with a molar mass of M_n = 218 000 g/mol. The temperature independent binary parameter k_{ij} = −0.02 is determined by adjustment to γ^{∞} values at M_n = 110 000 g/mol (at 298 K) for the system polystyrene−benzene. For the polystyrene−nonane system, k_{ij} = 0.027 is found by adjustment to γ^{∞} values at M_n = 309 000 g/mol (at 448 K), leading to a liquid−liquid split within the phase diagram. Imre et al.[62] confirm that polystyrene−alkane systems exhibit a liquid−liquid split, even at moderate temperatures. The upper solution temperature (UST) behavior shown in Figure 12 is, thus, in accordance with experimental findings.

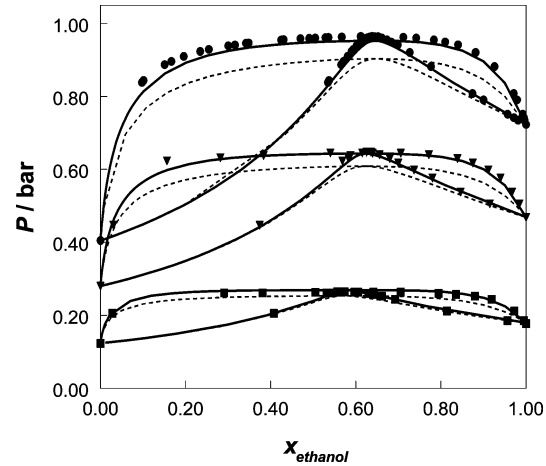

Figure 14. Vapor−liquid equilibrium of ethanol−*n*-heptane mixtures. Comparison of PCP-SAFT correlations to experimental data,[50,51] T = 343.15 K (circles), 333.15 K (triangles), and 313.15 K (squares). The binary parameter k_{ij} = 0.0132 was adjusted to γ^{∞} values of heptane in ethanol, which were calculated from the mod-UNIFAC(Do) model[64] (solid line). Results for k_{ij} = 0 are given for comparison (dashed line).

Application with mod-UNIFAC(Do) for Predicting γ^{∞}. According to Voutsas and Tassios,[63] the activity coefficients at infinite dilution of many systems can be predicted by the modified UNIFAC (Dortmund) model of Gmehling et al.[64] This model lends itself to combination with the proposed modeling approach in order to get a predictive method. Figure 14 shows the results of the PCP-SAFT modeling approach combined with mod-UNIFAC(Do) for the system heptane−ethanol. The average deviation increases only mildly as compared to the earlier results (Figure 8). One receives a significantly improved description of the system's vapor−liquid equilibrium compared to modeling the system with k_{ij} = 0.

Conclusion

Vapor−liquid equilibria of associating, polar, and macromolecular systems are described well by the PCP-SAFT equation of state with binary parameters determined from infinite dilution activity coefficients. The major advantage of this method is that the γ^{∞} values can be measured conveniently and are readily available in comprehensive databases[37] that have been compiled over the years. Furthermore, a constant binary parameter can usually be applied for large ranges of temperature. Extrapolations from infinite dilution to finite concentrations are fairly insensitive toward the values of the limiting activity coefficient. It is possible to gain full predictions by applying the mod-UNIFAC(Do) model to approximate the activity coefficient at infinite dilution. This study confirms that measurements at infinite dilution are meaningful for estimating the full phase behavior of mixtures.

Acknowledgment

We appreciate the financial support by Shell Global Solutions (Amsterdam).

Note Added after ASAP Publication: The version of this paper that was published online July 1, 2010 was missing several minor text changes. The corrected version was reposted July 6, 2010.

Literature Cited

(1) Gautreaux, M. F.; Coates, J. Activity coefficients at infinite dilution. *AIChE J.* **1955**, *1*, 496–500.

(2) Eckert, C. A.; Newman, B. A.; Nicolaides, G. L.; Long, T. C. Measurement and application of limiting activity-coefficients. *AIChE J.* **1981**, *27*, 33–40.

(3) Sandler, S. I. Infinite dilution activity coefficients in chemical, environmental and biochemical engineering. *Fluid Phase Equilib.* **1996**, *116*, 343–353.

(4) Richon, D.; Antoine, P.; Renon, H. Infinite dilution activity-coefficients of linear and branched alkanes from C1 to C9 in *n*-hexadecane by inert-gas stripping. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 144–147.

(5) Gruber, D.; Krummen, M.; Gmehling, J. The determination of activity coefficients at infinite dilution with the help of the dilutor technique (inert gas stripping). *Chem. Eng. Technol.* **1999**, *22*, 827–831.

(6) Schreiber, L. B.; Eckert, C. A. Use of infinite dilution activity coefficients with wilsons equation. *Ind. Eng. Chem. Process Des. Dev.* **1971**, *10*, 572–576.

(7) Feroiu, V.; Geana, D. Prediction of vapor−liquid equilibria at high pressures using activity coefficients at infinite dilution. *Fluid Phase Equilib.* **1996**, *120*, 1–10.

(8) Soave, G. S.; Betucco, A.; Vecchiato, L. Equation-of-state group contributions from infinite-dilution activity-coefficients. *Ind. Eng. Chem. Res.* **1994**, *33*, 975–980.

(9) Twu, C. H.; Bluck, D.; Cunningham, J. R.; Coon, J. E. A cubic equation of state relation between binary interaction parameters and infinite dilution activity-coefficients. *Fluid Phase Equilib.* **1992**, *72*, 25–39.

(10) Constantinescu, D.; Klamt, A.; Geana, D. Vapor−liquid equilibrium prediction at high pressures using activity coefficients at infinite dilution from COSMO-type methods. *Fluid Phase Equilib.* **2005**, *231*, 231–238.

(11) Tan, S. P.; Adidharma, H.; Radosz, M. Recent advances and applications of statistical associating fluid theory. *Ind. Eng. Chem. Res.* **2008**, *47*, 8063–8082.

(12) Gross, J.; Sadowski, G. Application of perturbation theory to a hard-chain reference fluid: An equation of state for square-well chains. *Fluid Phase Equilib.* **2000**, *168*, 183–199.

(13) Gross, J.; Sadowski, G. Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260.

(14) Gross, J. An equation-of-state contribution for polar components: Quadrupolar molecules. *AIChE J.* **2005**, *51*, 2556–2568.

(15) Gross, J.; Vrabec, J. An equation-of-state contribution for polar components: Dipolar molecules. *AIChE J.* **2006**, *52*, 1194–1204.

(16) Gross, J.; Sadowski, G. Application of the perturbed-chain SAFT equation of state to associating systems. *Ind. Eng. Chem. Res.* **2002**, *41*, 5510–5515.

(17) Kleiner, M.; Gross, J. An equation of state contribution for polar components: Polarizable dipoles. *AIChE J.* **2006**, *52*, 1951–1961.

(18) Yaws, C. L. *Chemical Properties Handbook: Physical, Thermodynamics, Environmental Transport, Safety, and Health Related Properties for Organic and Inorganic Chemicals*; McGraw-Hill: New York, 1 ed.; 1999.

(19) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(20) Gross, J.; Sadowski, G. Modeling polymer systems using the perturbed-chain statistical associating fluid theory equation of state. *Ind. Eng. Chem. Res.* **2002**, *41*, 1084–1093.

(21) Dallinga, L.; Schiller, M.; Gmehling, J. Measurement of activity-coefficients at infinite dilution using differential ebulliometry and non-steady-state gas−liquid-chromatography. *J. Chem. Eng. Data* **1993**, *38*, 147–155.

(22) Deal, C. H.; Derr, E. L. Selectivity and solvency in aromatics recovery. *Ind. Eng. Chem. Process Des. Dev.* **1964**, *3*, 394–399.

(23) Dohnal, V.; Horakova, I. A new variant of the rayleigh distillation method for the determination of limiting activity-coefficients. *Fluid Phase Equilib.* **1991**, *68*, 173–185.

(24) Magiera, B.; Brostow, W. Vapor−liquid equilibria of binary mixtures of carbon-14-labeled hexane with aliphatic ketones. *J. Phys. Chem.* **1971**, *75*, 4041–4047.

(25) Trampe, D. M.; Eckert, C. A. Limiting activity-coefficients from an improved differential boiling-point technique. *J. Chem. Eng. Data* **1990**, *35*, 156–162.

(26) Thomas, E. R.; Newman, B. A.; Nicolaides, G. L.; Eckert, C. A. Limiting activity-coefficients from differential ebulliometry. *J. Chem. Eng. Data* **1982**, *27*, 233–240.

(27) Yau, J. S.; Tsai, F. N. Solubilities of carbon-dioxide in normal-paraffins. *Chem. Eng. J.* **1993**, *52*, 55–62.

(28) Pividal, K. A.; Sterner, C.; Sandler, S. I.; Orbey, H. Vapor−liquid-equilibrium from infinite dilution activity-coefficients—Measurement and prediction of oxygenated fuel additives with alkanes. *Fluid Phase Equilib.* **1992**, *72*, 227–249.

(29) Asprion, N.; Hasse, H.; Maurer, G. Limiting activity coefficients in alcohol-containing organic solutions from headspace gas chromatography. *J. Chem. Eng. Data* **1998**, *43*, 74–80.

(30) Bao, J.; Liu, W.; Han, S. The measurement of infinite dilution activity coefficients of alcohol−*n*-alkane systems by gas stripping method. *Zhejiang-Daxue-Xuebao Ziran Kexue Ban (J. Zhejiang Univ., Nat. Sci. Ed.)* **1990**, *24*, 374–382.

(31) Castells, C. B.; Carr, P. W.; Eikens, D. I.; Bush, D.; Eckert, C. A. Comparative study of semitheoretical models for predicting infinite dilution activity coefficients of alkanes in organic solvents. *Ind. Eng. Chem. Res.* **1999**, *38*, 4104–4109.

(32) Cori, L.; Delogu, P. Infinite dilution activity-coefficients of ethanol−alkane mixtures. *Fluid Phase Equilib.* **1986**, *27*, 103–118.

(33) Tochigi, K.; Kojima, K. The determination of group wilson parameters to activity coefficients by ebulliometer. *J. Chem. Eng. Data Jpn.* **1976**, *9*, 267–273.

(34) Vrbka, P.; Fenclova, D.; Lastovka, V.; Dohnal, V. Measurement of infinite dilution activity coefficients of 1-alkanols (C1-C5) in water as a function of temperature (273−373 K). *Fluid Phase Equilib.* **2005**, *237*, 123–129.

(35) Schuster, R. H.; Grater, H.; Cantow, H. J. Thermodynamic studies on polystyrene-solvent systems by gas-chromatography. *Macromolecules* **1984**, *17*, 619–625.

(36) Galin, M.; Rupprecht, M. C. Study by gas−liquid-chromatography of interactions between linear or branched polystyrenes and solvents in tempertature-range 60-degrees-200-degrees-C. *Polymer* **1978**, *19*, 506–512.

(37) Gmehling, J.; Tiegs, D.; Medina, A.; Soares, M.; Bastos, J.; Alessi, P.; Kikic, I.; Schiller, M.; Menke, J. *DECHEMA Chemistry Data Series, Vol. 9: Activity Coefficients at Infinite Dilution*; DECHEMA: Frankfurt, Germany, 1986−2007.

(38) Kudryavtseva, L. S.; Susarev, M. P. Liquid−vapor equilibriums in the systems acetone−hexane and hexane−ethyl alcohol at 35, 45, and 55° and 760mmHg. *Zh. Prikl. Khim.* **1963**, *36*, 1471–1477.

(39) Rall, W.; Schafer, K. Thermodynamische untersuchungen an flussigen mischsystemen von aceton und normal-pentan sowie von aceton und normal-hexan. *Z. Elektrochem.* **1959**, *63*, 1019–1024.

(40) Schafer, K. L.; Rall, W. Dampfdruckuntersuchungen und aktivitatskoeffizienten des systems aceton-n-hexan. *Z. Elektrochem.* **1958**, *62*, 1090–1092.

(41) Hanson, D. O.; Vanwinkl, M. Alteration of relative volatility of *n*-hexane−1-hexene by oxygenated and chlorinated solvents. *J. Chem. Eng. Data* **1967**, *12*, 319–325.

(42) Maripuri, V. C.; Ratcliff, G. A. Isothermal vapor−liquid equilibria in binary-mixtures of ketones and alkanes. *J. Appl. Chem. Biotechnol.* **1972**, *22*, 899–903.

(43) Kalra, H.; Kubota, H.; Robinson, D. B.; Ng, H. J. Equilibrium phase properties of carbon dioxide normal-heptane system. *J. Chem. Eng. Data* **1978**, *23*, 317–321.

(44) Reamer, H. H.; Sage, B. H. Phase equilibria in hydrocarbon systems. Volumetric and phase behavior of the n-decane-co2 system. *J. Chem. Eng. Data* **1963**, *8*, 508–513.

(45) Jin, Z. L.; Lin, H. M.; Greenkorn, R. A.; Chao, K. C. Vapor-liquid equilibrium in binary miztures of *tert*-butyl methyl ether plus *n*-hexane and plus benzene. *AIChE Symp. Ser.* **1985**, *81*, 155–160.

(46) Lozano, L. M.; Montero, E. A.; Martin, M. C.; Villamanan, M. A. Vapor−liquid-equilibria of binary-mixtures containing methyl *tert*-butyl ether (MTBE) and/or substitution hydrocarbons at 298.15 and 313.15 K. *Fluid Phase Equilib.* **1995**, *110*, 219–230.

(47) Plura, J.; Matous, J.; Novak, J.; Sobr, J. Vapor−liquid equilibrium in the methyl *tert*-butyl ether−*n*-hexane and methyl *tert*-butyl ether−toluene systems. *Collect. Czech. Chem. Commun.* **2009**, *44*, 3627–3631.

(48) Ferguson, J. B. The system methyl alcohol−*n*-hexane at 45 degrees. *J. Phys. Chem.* **1932**, *36*, 1123–1128.

(49) Wolff, H.; Hoeppel, H.-E. Die wasserstoffbruecken-sssoziation von methanol in *n*-hexan nach dampfdruck-messungen. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 710–721.

(50) Berro, C.; Rogalski, M.; Peneloux, A. A new ebulliometric technique—Vapor−liquid-equilibria in the binary-systems ethanol normal-heptane and ethanol normal-nonane. *Fluid Phase Equilib.* **1982**, *8*, 55–73.

(51) Pena, M. D.; Cheda, D. R. Equilibrio liquido−vapor. II. El sistema etanol + *n*-heptano a 40 y 60 C. *An. Quim.* **1970**, *66*, 737–745.

(52) Ohta, T.; Asano, H.; Nagata, I. Thermodynamic study of complex-formation in 4 binary-liquid mixtures containing chloroform. *Fluid Phase Equilib.* **1980**, *4*, 105–114.

(53) Cho, T. H.; Ochi, K.; Kojima, K. Isobaric vapor−liquid-equilibria for binary s-systems with limited miscibility, water−normal-amyl alcohol and water−isoamyl alcohol. *Kagaku Kogaku Ronbunshu* **1984**, *10*, 181–183.

(54) Zhuravleva, I. K.; Zhuravlev, E. F. *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.* **1970**, *13*, 480.

(55) Iwai, Y.; Arai, Y. Measurement and prediction of solubilities of hydrocarbon vapors in molten polymers. *J. Chem. Eng. Jpn.* **1989**, *22*, 155–161.

(56) Wang, N. H.; Takishima, S.; Masuoka, H. Solubility of benzene, toluene and cyclohexane in polystyrene below its gas-transition temperature. *Kagaku Kogaku Ronbunshu* **1989**, *15*, 795–803.

(57) Bae, Y. C.; Shim, J. J.; Soane, D. S.; Prausnitz, J. M. Representation of vapor liquid and liquid liquid equilibria for binary systems containing polymers−Applicability of an extended Flory Huggins equation. *J. Appl. Polym. Sci.* **1993**, *47*, 1193–1206.

(58) Gmehling, J.; Onken, U.; Arlt, W.; Grenzheuser, P.; Weidlich, U.; Kolbe, B.; Rarey, J. *DECHEMA Chemistry Data Series, Vol. 1: Vapor−liquid equilibrium data collection*; DECHEMA: Frankfurt, Germany, 1991−2009.

(59) Plura, J.; Matous, J.; Novak, J. P.; Sobr, J. Liquid−vapor-equilibrium. 88. Vapor−liquid-equilibrium in the methyl *tert*-butyl ether *n*-hexane and methyl *tert*-butyl ether toluene systems. *Collect. Czech. Chem. Commun.* **1979**, *44*, 3627–3631.

(60) Grenner, A.; Tsivintzelis, I.; Economou, I. G.; Panayiotou, C.; Kontogeorgis, G. M. Evaluation of the nonrandom hydrogen bonding (NRHB) theory and the simplified perturbed-chain-statistical associating fluid theory (sPC-SAFT). 1. Vapor−liquid equilibria. *Ind. Eng. Chem. Res.* **2008**, *47*, 5636–5650.

(61) Lee, B. C.; Danner, R. P. Prediction of infinite dilution solvent activity coefficients in polymer solutions: Comparison of prediction models. *Fluid Phase Equilib.* **1997**, *128*, 97–114.

(62) Imre, A. R.; Van Hook, W. A.; Chang, B. H.; Bae, Y. C. The effect of alkane chain length on the liquid−liquid critical temperatures of oligostyrene/linear-alkane mixtures. *Monatsh. Chem.* **2003**, *134*, 1529–1539.

(63) Voutsas, E. C.; Tassios, D. P. Prediction of infinite-dilution activity coefficients in binary mixtures with UNIFAC. A critical evaluation. *Ind. Eng. Chem. Res.* **1996**, *35*, 1438–1445.

(64) Gmehling, J.; Li, J. D.; Schiller, M. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178–193.

Received for review February 2, 2010
Revised manuscript received May 26, 2010
Accepted June 10, 2010

IE100259E