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Liquid−Liquid Equilibria for Binary and Ternary Systems Containing Glycols, Aromatic Hydrocarbons, and Water: Experimental Measurements and Modeling with the CPA EoS

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Liquid−liquid equilibrium data of four binary glycol + aromatic hydrocarbon systems and three ternary systems containing water have been measured at atmospheric pressure. The measured systems are monoethylene glycol (MEG) + benzene or toluene, triethylene glycol (TEG) + benzene or toluene, MEG + water + benzene, MEG + water + toluene, and TEG + water + toluene. The binary systems are correlated with the Cubic-Plus-Association (CPA) equation of state while the ternary systems are predicted from interaction parameters obtained from the binary systems. Very satisfactory liquid−liquid equilibrium correlations are obtained for the binary systems using temperature-independent interaction parameters, while adequate predictions are achieved for multicomponent water + glycol + aromatic hydrocarbons systems when accounting for the solvation between the aromatic hydrocarbons and glycols or water.

Introduction

Mixtures containing associating components, and in particular mixtures of water and glycols with hydrocarbons, are of great interest to the oil−gas and chemical industries. More specifically monoethylene glycol (MEG) is being extensively used for upstream gas hydrate inhibitors because it is more effective as compared to other glycols (smaller amounts for the same temperature depression). Furthermore, triethylene glycol (TEG) is used in approximately 95 % of the glycol dehydration units for natural gas streams due to its chemical stability, low cost, and high affinity to water. The solubility of BTEX compounds (benzene, toluene, ethylbenzene, xylenes) in aqueous glycols is of great importance due to the hydrocarbon emissions from glycol regeneration units, even if they are usually present in low concentrations in natural gas. However, reliable experimental data for the aforementioned glycols with aromatic hydrocarbons, and especially in the presence of water, are very scarce. Extensive data can be found only for the binary mixtures of diethylene glycol (DEG) with benzene or toluene and the ternary mixture DEG + water + benzene,[1] probably due to the fact that DEG was the standard dehydration solvent for many years and therefore more extensively studied. TEG however became more popular as the latter is more favorable with respect to loss and degradation.

From the thermodynamic point of view, accurate description of the phase equilibria of such systems is a challenging problem, usually requiring models that explicitly account for association between like molecules (i.e., two molecules of water) or solvation between unlike molecules, such as the interactions between glycols, water, and aromatic hydrocarbons. Recently the CPA[2] (Cubic-Plus-Association) equation of state (EoS), which combines the well-known Soave−Redlich−Kwong (SRK) EoS for describing the physical interactions with the Wertheim's first-order perturbation theory, applied to different types of hydrogen bonding compounds, was successfully applied to binary and ternary systems containing water, glycols, and aromatic hydrocarbons.[3] A way to account for the interactions between glycols/water and the electronegative aromatic ring was presented. The experimental measurements presented in this work are correlated in the case of binary systems or predicted in the case of ternary systems with the CPA EoS in order to further test the applicability of the model.

Table 1. Specifications of the Chemicals Used in This Work

chemical	specified purity	water content	supplier
ethylene glycol (MEG)	≥99.5 %	≤0.10 %	Merck
triethylene glycol (TEG)	>99 %	≤0.30 %	Merck
toluene	≥99.9 %	≤0.03 %	Merck
benzene	≥99.7 %	≤0.03 %	Merck
acetone	≥99.5 %	≤0.05 %	Merck

Experimental Procedures

The chemicals used in this work are tabulated in Table 1. They were used without further purification.

Mixing and Equilibrium. Mixtures of known mass fraction of glycols, water, and hydrocarbons were vigorously shaken for approximately 24 h in an air-heated oven. For binary systems, the mass fraction was approximately 0.5, while for the ternary systems a mass fraction of 0.5 of the hydrocarbon was added to a mixture of glycol and water; in the latter the mass fraction of glycol in the aqueous phase would vary from 40 % to 90 % since this range of glycol composition is of interest for industrial applications in the North Sea. The temperature of the mixing was in principle the same as the temperature of the equilibrium measurements. However, for the measurements at low temperatures, a higher mixing temperature was chosen in order to achieve an adequate mixing of the components before equilibration.

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Table 2. Characteristics of the Chromatographs Used in This Work

	GC-1	GC-2	GC-3
type	HP 5890, series II	HP 5890, series II	HP 6890
column type	CP-Wax 52 CB polar capillary column	HP-PONA unpolar capillary column	CP-poraplot Q-HT
column length	30 m	50 m	30 m
column i.d.	0.53 mm	0.2 mm	0.32 mm
column film thickness	1 μm	0.5 μm	10 μm
injector type	7673	7673	7683
injection volume	1.0 μL	0.2 μL	1.0 μL
carrier gas	helium	helium	helium
detector type	FID	FID	TCD

[a] FID, flame ionization detector; TCD, thermal conductivity detector.

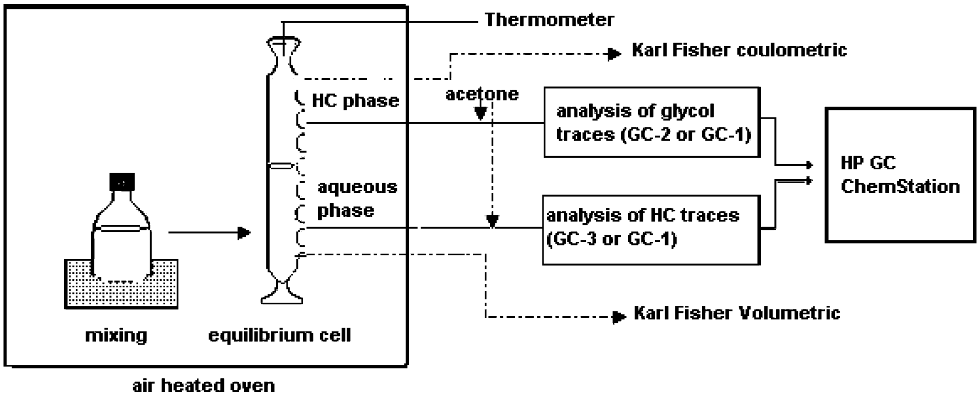

Figure 1. Sketch of the experimental procedure.

The solutions, after mixing, were transferred in equilibrium cells to obtain phase equilibria at the desired temperature. The cells were made of glass, and sampling was possible from each phase since the cells were equipped with several orifices sealed with Teflon-coated septa. Two experiments were carried out in parallel in order to check the reproducibility of the data; for the binary systems, the reproducibility was in all cases within the uncertainty of the measured values. For the ternary systems, the reproducibility can be up to 3 % in the worst case. The solutions were left at the desired temperature for 24 h in order to obtain equilibrium. When the mixture was transferred to the equilibrium cells for separation, both phases were cloudy while after 24 h the phases were completely transparent, indicating that the mixture reached the equilibrium state. A DOSTMANN P500 thermometer (± 0.1 °C) was used for the temperature measurements.

Sampling and Analysis. Samples from the two phases were withdrawn manually with a preheated syringe and needle after equilibration in order to avoid phase separation during sampling. For the same reason, acetone was added to the sample before the analysis. After sampling and mixing with acetone, the amounts of the desired components were analyzed using gas chromatography (GC). The GC apparatus was calibrated based on external standards of mixtures of acetone with a known composition of the component that was going to be determined; the calibrating standards covered a limited concentration range, which was close to the concentration range of the actual samples, to increase the accuracy of the measurements. The composition is determined with an uncertainty of 2 %. The uncertainty of the water content in the polar phase is estimated to be 1 %.

Three different GC apparatus, equipped with different columns and detectors were used to analyze the trace amounts of the components involved in this study. The characteristics of the chromatographs are tabulated in Table 2. More specifically, GC-2 was used to obtain the amount of glycol in the hydrocarbon phase. GC-3 was used to analyze the trace amounts of hydrocarbons in the glycol or polar phase. Water concentration in the polar phase was also analyzed using GC-3. However, in the case of benzene + MEG and water + MEG + benzene systems, the peak of benzene was very close (in time) to the peak of MEG both when GC-2 or GC-3 were used. Therefore both the glycol or polar (for the ternary system) and the hydrocarbon phase were analyzed using GC-1.

The water content in the hydrocarbon phase was obtained using Karl−Fisher (KF) titration, which is a method extensively used in chemical industry, providing very reliable results, especially for systems where the solubility of water in the hydrocarbon phase is very low such as the systems involved in this work. For comparison purposes the water content in the polar phase was obtained using KF titration in parallel with gas chromatography. Two different KF titration apparatus were used: Mettler Toledo DL37 coulometric titrator for determining the amount of water in the HC phase and Mettler Toledo DL38 volumetric titrator for determining the amount of water in the polar phase. Prior to analysis, external standards were analyzed in order to test the reliability of the measurements. The uncertainty of the water content measurements is estimated to be 4 % for the coulometric titrator and 1 % for the volumetric titrator. Regarding the polar phase, the results obtained using gas chromatography are in good agreement to those obtained with KF titration (deviation within the experimental uncertainty of each method). The values of the water content in the polar phase are those obtained using GC analysis. The experimental procedure is illustrated in Figure 1.

Results

Tables 3 and 4 present mutual solubility measurements for the binary and ternary systems studied, respectively. All the experimental measurements presented here contribute new data, for the following reasons: (a) experimental data for the binary systems MEG + benzene are scarce; in most cases over a limited temperature range (b) there are no measurements performed at low temperatures for the binary system MEG + toluene; (c) very few or no data for the binary systems TEG + benzene or toluene; (d) there are no experimental data at all for the ternary systems presented in this work.

Table 3. Mutual Solubility Measurements for the Binary System Glycol (1) + Aromatic Hydrocarbon, HC (2)

T/K	100 x_2 in glycol phase	100 x_1 in HC phase
	Monoethylene Glycol + Benzene	
279.2	4.664	0.106
288.5	4.878	0.155
303.3	5.005	0.299
318.1	5.105	0.463
332.6	5.530	0.753
342.1	5.569	0.982
	Monoethylene Glycol + Toluene	
279.1	1.879	0.104
297.9	2.014	0.211
302.1	2.085	0.254
312.1	2.188	0.320
316.3	2.265	0.379
323.2	2.382	0.470
331.2	2.547	0.603
345.1	2.808	0.957
357.1	3.052	1.471
361.0	3.170	1.671
	Triethylene Glycol + Benzene	
279.6	63.422	7.062
281.6	64.375	7.222
283.0	64.881	7.703
284.3	65.926	8.045
287.6	67.324	10.952
	Triethylene Glycol + Toluene	
279.0	30.839	1.074
293.0	32.960	1.858
302.0	34.780	2.265
312.8	35.893	3.162
321.2	38.138	4.159
331.5	41.952	5.662
344.2	46.375	8.366
345.4	48.498	8.661

Table 4. Mutual Solubility Measurements for the Ternary Systems of Glycol (1) + Water (2) + Aromatic Hydrocarbon, HC (3) at Two Different Temperatures

	polar phase			HC phase		
T/K	100 x_1	100 x_2	100 x_3	100 x_1	100 x_2	100 x_3
			MEG + Water + Benzene			
298.2	16.615	83.223	0.162	0.033	0.263	99.705
	23.125	76.673	0.202	0.046	0.240	99.715
	30.397	69.318	0.285	0.060	0.217	99.723
	39.270	60.314	0.417	0.078	0.190	99.733
	70.065	28.360	1.575	0.143	0.096	99.761
323.2	16.416	83.423	0.161	0.076	0.514	99.410
	22.487	77.279	0.235	0.106	0.478	99.416
	29.470	70.211	0.319	0.142	0.457	99.401
	39.293	60.208	0.499	0.191	0.392	99.418
	70.572	27.666	1.763	0.352	0.187	99.461
			MEG + Water + Toluene			
298.2	64.746	34.555	0.700	0.134	0.094	99.772
	41.494	58.272	0.234	0.080	0.159	99.761
	22.455	77.494	0.051	0.038	0.220	99.742
	15.167	84.807	0.027	0.023	0.245	99.732
323.2	64.438	34.696	0.866	0.330	0.197	99.474
	42.687	57.013	0.300	0.214	0.320	99.466
	21.672	78.255	0.073	0.105	0.438	99.457
	15.942	84.019	0.038	0.069	0.472	99.460
			TEG + Water + Toluene			
298.2	48.877	42.490	8.633	0.670	0.208	99.122
	28.549	69.939	1.513	0.212	0.237	99.551
	12.033	87.825	0.142	0.048	0.283	99.670
	8.047	91.886	0.067	0.024	0.308	99.668
323.2	47.967	42.055	9.978	1.162	0.458	98.380
	26.942	71.271	1.787	0.395	0.488	99.117
	11.123	88.688	0.189	0.107	0.543	99.351
	7.256	92.657	0.088	0.056	0.579	99.365

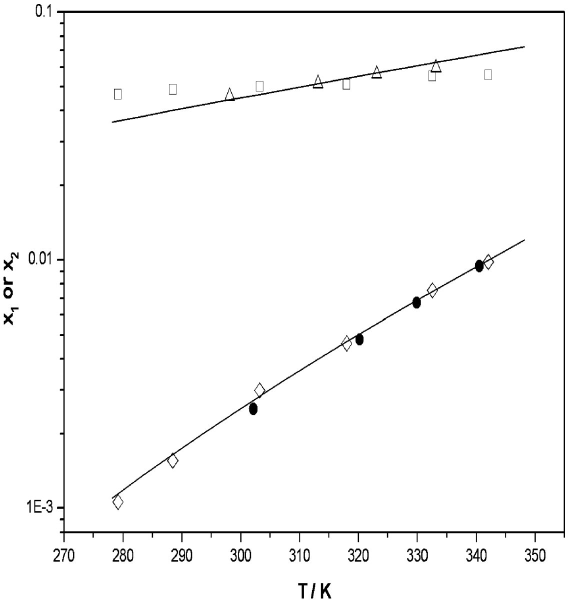

Figure 2. LLE correlation of the system MEG (1) + benzene (2) with the CPA EoS: □, x_2 in MEG, this work; ◇, x_1 in benzene, this work; ●, x_1 in benzene, Staveley and Milward;[4] △, x_2 in MEG, Kugo et al.;[5] —, CPA EoS using $k_{12} = 0.049$ and BETCR = 0.04.

The results obtained in this work for the binary system of MEG + benzene are in excellent agreement with the solubility measurements of Staveley and Milward,[4] who measured the solubility of ethylene glycol in benzene using a synthetic method; however, the solubility of benzene in MEG was not measured in their work. Kugo et al. [5] on the other hand measured the solubility of benzene in MEG over a temperature range of 50 K, and their measurements are in very good agreement with the results obtained in this work. There is some disagreement regarding the reported solubility of benzene in MEG at the lower temperature measured by Kugo et al. The work of Kugo et al. indicates the formation of a closed loop at low temperatures, which was not observed in this work, even though solubility measurements were performed almost 30 K lower than the lowest temperature measurement of Kugo et al. Finally equilibrium measurements for the same system were performed by Zaretskii et al.[6] using the isothermal titration method. Their results are in disagreement with all the other experimental works (including this one), especially regarding the solubility of MEG in benzene which is 2 orders of magnitude higher as compared to the aforementioned studies.

Regarding the binary system of MEG + toluene, this work is in good agreement with the results obtained by Mandik and Lesek,[7] as demonstrated in Figure 3. We have emphasized at low-temperature measurements, which combined with the work of Mandik and Lesek provide solubility data for a temperature range of more than 100 K.

Hughes and Haoran[8] measured the system TEG + toluene using a synthetic method over a very limited temperature range, which is less than 15 K. Good agreement is obtained regarding the solubility of toluene in TEG, while the measured solubility of TEG in toluene at low temperatures is systematically lower than the one obtained in this work.

Modeling Results with the CPA EoS

The extension of the CPA EoS to systems containing glycols, water, and aromatic hydrocarbons was recently presented by Folas et al.[3] The details of the model are presented in Appendix A. To account for the solvation between the associating and

Table 5. LLE Correlation Results for the Binary Systems of Glycol (1) + Aromatic HC (2) with CPA EoS, Expressed as % AAD of Mole Fraction (x) of the Compound i[a]

					% AAD	
system	exp T range/K	exp ref	k_{12}	BETCR	x_2 in I	x_1 in II
MEG + benzene	279.15−342.05	4, 5, this work	0.049	0.04	9.7	4.3
MEG + toluene	279.05−381.65	7, this work	0.051	0.042	9.7	11.5
TEG + benzene	279.55−287.55	this work	0.032	0.083	0.9	16.3
TEG + toluene	278.95−345.4	This work	0.038	0.048	7.5	3.6

[a] I = glycol-rich phase. II = hydrocarbon-rich phase.

Table 6. LLE Prediction Results for the Ternary Systems of Glycol (1) + Water (2) + Aromatic Hydrocarbon (3) with the CPA EoS, Expressed as % AAD of Mole Fraction (x) of the Compound i in Each Phase

		% AAD in polar phase			% AAD in HC phase		
T/K	interaction parameters	x_1	x_2	x_3	x_1	x_2	x_3
	MEG + Water + Benzene						
298.2	$k_{12} = -0.115$ & ECR, $k_{13} = 0.049$ & BETCR = 0.04, $k_{23} = 0.0355$ & BETCR = 0.079	1.9	1.5	19.4	17.5	11.9	0.01
323.2	$k_{12} = -0.115$ & ECR, $k_{13} = 0.049$ & BETCR = 0.04, $k_{23} = 0.0355$ & BETCR = 0.079	1.3	1.1	24.8	16.1	5.2	0.01
	MEG + Water + Toluene						
298.2	$k_{12} = -0.115$ & ECR, $k_{13} = 0.051$ & BETCR = 0.042, $k_{23} = 0.0095$ & BETCR = 0.06	2.5	1.1	20.6	22.5	19.3	0.03
323.2	$k_{12} = -0.115$ & ECR, $k_{13} = 0.051$ & BETCR = 0.042, $k_{23} = 0.0095$ & BETCR = 0.06	1.8	0.7	13.3	7.5	11.0	0.03
	TEG + Water + Toluene						
298.2	$k_{12} = -0.211$ & CR-1, $k_{13} = 0.038$ & BETCR = 0.048, $k_{23} = 0.0095$ & BETCR = 0.06	5.3	2.3	23.6	59.0	29.9	0.06
323.2	$k_{12} = -0.211$ & CR-1, $k_{13} = 0.038$ & BETCR = 0.048, $k_{23} = 0.0095$ & BETCR = 0.06	2.6	1. 8	11.4	50.6	17.6	0.04
298.2	$k_{12} = -0.372$ & ECR, $k_{13} = 0.038$ & BETCR = 0.048, $k_{23} = 0.0095$ & BETCR = 0.06	5.4	3.2	66.6	75.7	41.3	0.2
323.2	$k_{12} = -0.372$ & ECR, $k_{13} = 0.038$ & BETCR = 0.048, $k_{23} = 0.0095$ & BETCR = 0.06	2.8	3.0	58.5	82.8	28.6	0.4

the aromatic compounds, an extra fitted parameter (BETCR) of the association term is used in addition to the binary interaction parameter (k_{12}) in the physical term (SRK term). Table 5 presents the correlation of the LLE of the binary systems involved in this study, while the prediction of phase equilibria of the ternary systems, based solely on binary parameters, is elucidated in Table 6.

For the correlation of the systems MEG + benzene and MEG + toluene, all experimental data are considered, using only temperature-independent interaction parameters. The LLE correlation of the systems TEG + benzene and TEG + toluene is based on the experimental measurements obtained in this work. The performance of the model is further tested to VLE data using the interaction parameters obtained from LLE.

The correlation of the systems MEG + benzene and MEG + toluene is presented in Figures 2 and 3, respectively, providing very good results for the mutual solubilities of both compounds (per binary system) in both phases, as Table 5 illustrates. The correlation of the MEG + toluene system was previously presented by Folas et al.[3] using $k_{12} = 0.055$ and BETCR = 0.045 (solid line in Figure 3), which were the optimized parameters based on the data of Mandik and Lesek.[7] The dashed line presents the correlation of the system using new parameters, optimized based on both this work and Mandik and Lesek,[7] covering a temperature range of more than 100 K. The performance of the model is very similar with both sets, as shown in Figure 3. This fact demonstrates the reliability of the model for extrapolations when the parameters are obtained over an extended temperature range.

CPA satisfactorily correlates the LLE of TEG + benzene and TEG + toluene binary systems, as presented in Table 5. New parameters for both systems are obtained in this work (compared to the ones presented by Folas et al.[3]), which are explicitly fitted to the experimental solubilities presented in this work. Gupta et al.[9] performed VLE measurements for both systems at atmospheric pressure and over a temperature range of almost 80 K. Prediction of VLE using the binary interaction parameters (k_{12} and BETCR in the case of systems with aromatic hydrocarbons) obtained from LLE is a demanding test of the model. CPA provides very satisfactory results, as elucidated by Figures

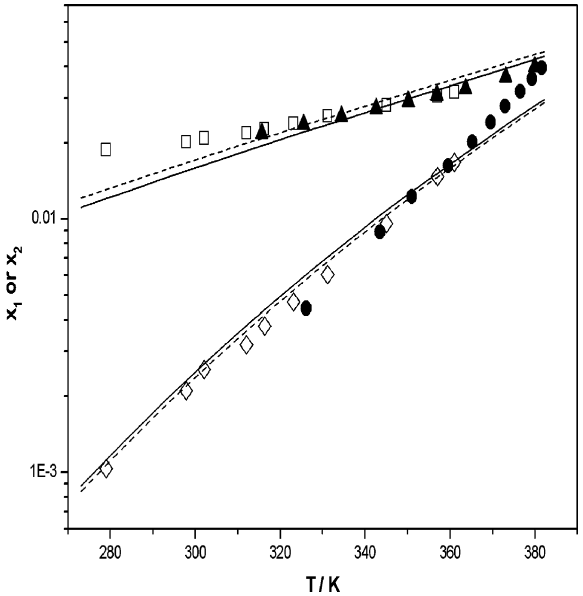

Figure 3. LLE of MEG (1) + toluene (2) system with the CPA EoS: □, x_2 in MEG, this work; ◇, x_1 in toluene, this work; ●, x_1 in toluene, Mandik and Lesek;[7] ▲, x_2 in MEG, Mandik and Lesek;[7] - - -, CPA EoS using k_{12} = 0.051 and BETCR = 0.042 (parameters based also on the data of this work); —, CPA EoS based on parameters proposed by Folas et al.[3] (k_{12} = 0.055 and BETCR = 0.045).

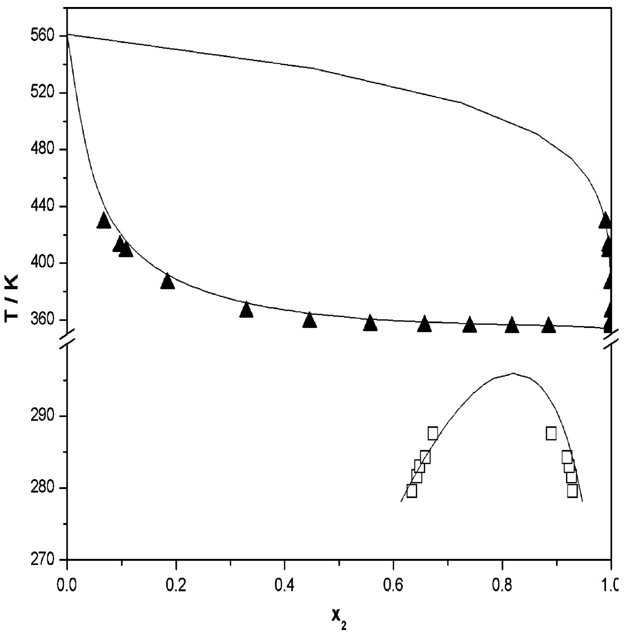

Figure 4. LLE and VLE correlation of the system TEG + benzene with the CPA EoS: □, LLE measurements, this work; ▲, VLE measurements, Gupta et al.;[9] —, CPA EoS using $k_{12} = 0.032$ and BETCR = 0.083.

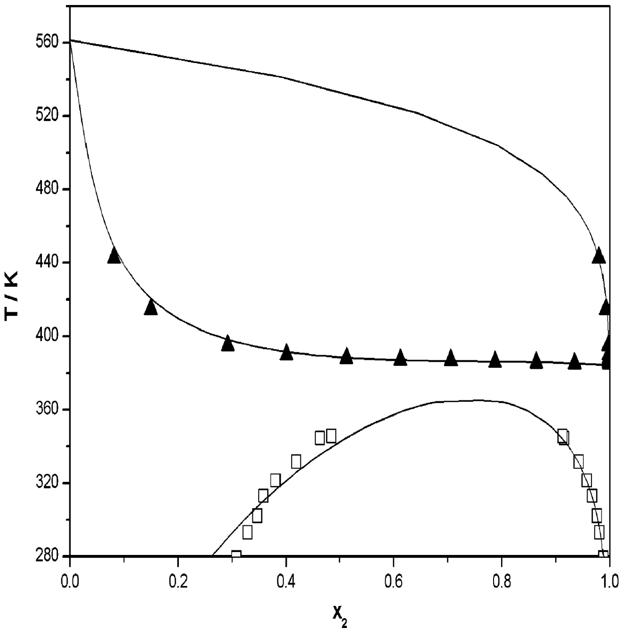

Figure 5. LLE and VLE correlation of the system TEG + toluene with the CPA EoS: □, LLE measurements, this work; ▲, VLE measurements, Gupta et al.;[9] $\Delta^{A_iB_j}$, CPA EoS using $k_{12} = 0.038$ and BETCR = 0.048.

4 and 5, enabling phase equilibria calculations (both VLE and the very demanding LLE) over a temperature range of more than 200 K.

The predictive performance of CPA for the ternary systems measured in this work is presented in Table 6. All calculations were performed based solely on interaction parameters obtained from the binary systems. For the binary systems of water + aromatic hydrocarbons and glycols + aromatic hydrocarbons, the two adjustable parameters are temperature independent, as demonstrated by Folas et al.[3] and this work. For the MEG + water system, the Elliott combining rule (ECR) with a binary interaction parameter $k_{12} = -0.115$ was used since this was shown[10] to provide adequate results (both solid−liquid and vapor−liquid equilibrium) over an extended temperature range.

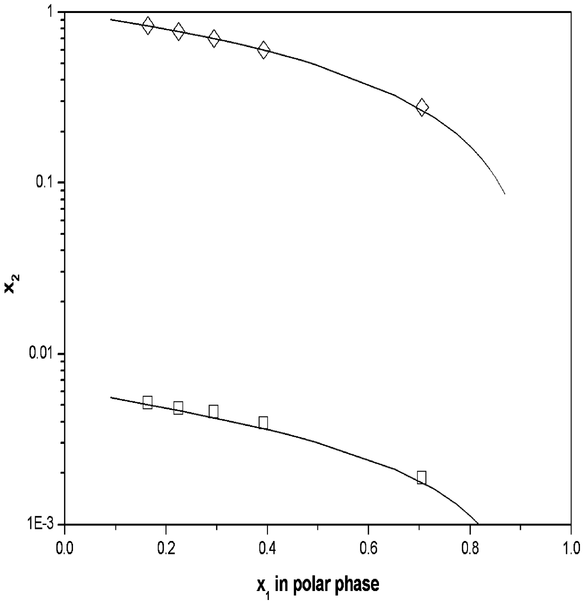

Figure 6. Prediction of water solubility in the polar and the hydrocarbon phase for the ternary system MEG (1) + water (2) + benzene (3) at 323.2 K with the CPA EoS; □, x_2 in hydrocarbon phase; ◇, x_2 in polar phase. —, CPA EoS.

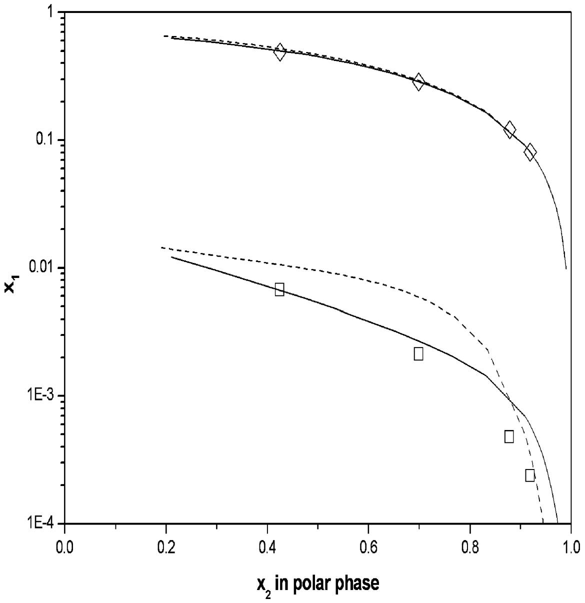

Figure 7. Prediction of TEG solubility in the polar and the hydrocarbon phase for the ternary system TEG (1) + water (2) + toluene (3) at 298.2 K: □, x_1 in hydrocarbon phase; ◇, x_1 in polar phase; —, CPA EoS, using the CR-1 combining rule and $k_{12} = -0.211$ for the water + TEG binary system; - - -, CPA EoS, using ECR and $k_{12} = -0.372$ for the water + TEG binary system.

Derawi et al.[11] correlated the VLE of the binary system TEG + water, using both CR-1 and ECR. It was shown that CR-1 combining rule performs better than ECR, providing in the temperatures tested an error of about 5 % in the vapor pressure. In the case of ECR, a much higher value of an interaction parameter is required and the error in vapor pressure is over 10 %. In this work both combining rules are tested for the TEG + water system, using the binary interaction parameters optimized at 297.6 K (i.e., CR-1 with $k_{12} = -0.211$ and ECR with $k_{12} = -0.372$, respectively). In all cases the binary parameters used are presented in Table 6, together with the percentage deviation (% AAD) of each compound of the ternary system in both phases.

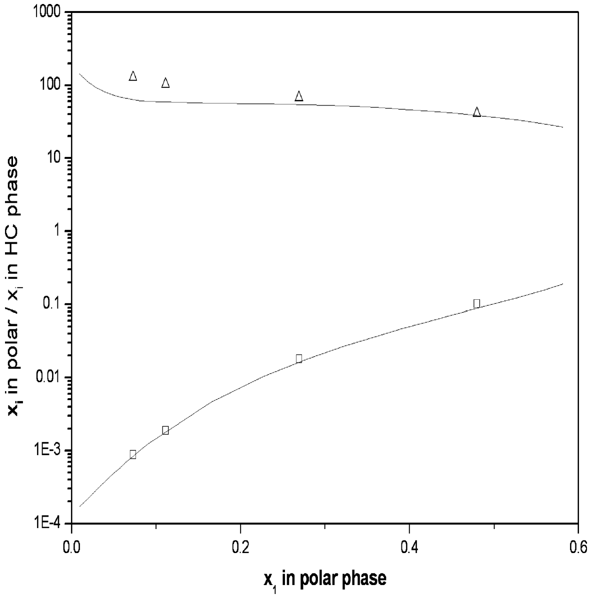

Figure 8. Prediction of the partition coefficients of TEG and toluene for the ternary system TEG (1) + water + toluene at 323.2 K: □, x_3 partition coefficient; △, x_1 partition coefficient; —, CPA EoS, using CR-1 combining rule and $k_{12} = -0.211$ for the water + TEG binary system.

As can be seen from Table 6, satisfactory predictions are achieved for all systems with the CPA EoS at both temperatures. CPA adequately predicts even the "difficult" solubility of the hydrocarbon in the polar phase and the polar compounds in the hydrocarbon phase. The average deviations are 19 % for the prediction of the solubility of the aromatic hydrocarbon in the polar phase, 29 % for the solubility of glycol, and 16 % for the solubility of water in the hydrocarbon phase, respectively. For the ternary system of TEG + water + toluene, the results obtained with ECR are inferior to those with CR1 combining rule, which is probably a result of the inferior correlation of the TEG + water binary system with ECR. Typical results are presented in Figures 6 to 8.

Conclusions

In this work experimental measurements of binary and ternary systems containing glycols, aromatic hydrocarbons, and water are presented. Gas chromatography and KF titration were used to analyze the traces of the components in each phase. The results obtained in this work are in good agreement with other experimental works for the temperature range that comparison was possible, demonstrating the reliability and validity of the measurements.

The CPA EoS was used to correlate the binary systems and predict the ternary based solely on temperature-independent binary parameters. The LLE correlative performance of the model is very satisfactory over extensive temperature ranges, while the same parameters can be used for VLE predictions. Adequate predictions can be achieved in the case of the ternary systems at different temperatures, based on the same binary parameters.

Acknowledgment

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Appendix A

The CPA EoS, proposed by Kontogeorgis et al.,[2,12] can be expressed for mixtures in terms of pressure P, as:

$$P = \frac{RT}{V_m - b} - \frac{\alpha(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad \text{(A.1)}$$

The key element of the association term is X_{A_i}, which represents the fraction of A sites on molecule i that do not form bonds with other active sites, while x_i is the mole fraction of component i. X_{A_i} is related to the association strength $\Delta^{A_iB_j}$ between two sites belonging to two different molecules (e.g., site A on molecule i and site B on molecule j) determined from

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_i} \Delta^{A_iB_j}} \quad \text{(A.2)}$$

where the association strength $\Delta^{A_iB_j}$ in CPA is expressed as:

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\epsilon^{A_iB_j}}{RT}\right) - 1\right] b_{ij} \beta^{A_iB_j} \quad \text{(A.3)}$$

with the radial distribution function:

$$g(\rho) = \frac{1}{1 - 1.9\eta}$$

the reduced density $\eta = (1/4)b\rho$ while

$$b_{ij} = \frac{b_i + b_j}{2}$$

b_i is the co-volume parameter of the component i, and ρ is the molar density.

Finally, the energy parameter of the EoS is given by a Soave-type temperature dependency, while b is temperature independent:

$$\alpha(T) = \alpha_0[1 + c_1(1 - \sqrt{T_r})]^2 \quad \text{(A.4)}$$

$T_r = (T/T_c)$ is the reduced temperature, while T_c is the

Table A.1. CPA Parameters for the Compounds Considered in This Work[a]

component	ref	b (L/mol)	a_0 (bar·L^2/mol^2)	c_1	ϵ^{AB}/K	$\beta^{AB}\cdot 10^3$	% AAD ΔP^S	% AAD $\Delta\rho$
water	12	0.0145	1.2277	0.67359	2003.25	69.2	0.8	0.5
MEG	11	0.0514	10.8190	0.67440	2375.75	14.1	0.9	1.6
TEG	11	0.1321	39.126	1.1692	1724.44	18.8	3.0	1.4
benzene	13	0.0749	17.876	0.75766			0.9	1.0
toluene	13	0.0921	23.375	0.80372			0.2	0.6

[a] The last two columns provide the percentage average absolute deviations between experimental and calculated vapor pressures and liquid densities.

experimental critical temperature. Finally c_1 is a CPA parameter in the energy term (eq A.4).

In the expression for the association strength $\Delta^{A_iB_j}$, the parameters $\epsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ are called the association energy and the association volume, respectively. These two parameters are only used for associating components, and the three additional parameters of the SRK term (a_0, b, c_1) are the five pure compound parameters of the model. They are obtained by fitting vapor pressure and liquid density data. For inert components (e.g., hydrocarbons), only the three parameters of the SRK term are required, which can be obtained either from vapor pressures and liquid densities or calculated in the conventional manner (critical data, acentric factor). In this work, the former approach is adopted. The CPA parameters for the compounds considered in this work are presented in Table A.1. When the CPA EoS is used for mixtures, the conventional mixing rules are employed in the physical term (SRK) for the energy and co-volume parameters. The geometric mean rule is used for the energy parameter α_{ij}. The interaction parameter k_{ij} is, for applications only with aliphatic hydrocarbons, the only adjustable binary parameter of CPA:

$$\alpha = \sum_i \sum_i x_i x_j \alpha_{ij}, \text{ where } \alpha_{ij} = \sqrt{\alpha_i \alpha_j}(1 - k_{ij}) \qquad \text{(A.5)}$$

$$b = \sum_i x_i b_i$$

For extending the CPA EoS to mixtures of two associating compounds (e.g., alcohols or glycols with water), combining rules for the association energy ($\epsilon^{A_iB_j}$) and the association volume ($\beta^{A_iB_j}$) are required. The CR-1 and the Elliott combining rule (ECR), described below, have been found successful in previous applications.

The expressions of the cross-association energy and cross-association volume parameters with CR-1 are

$$\epsilon^{A_iB_j} = \frac{\epsilon^{A_iB_i} + \epsilon^{A_jB_j}}{2} \text{ and } \beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} \qquad \text{(A.6)}$$

The expression of the cross-association strength ($\Delta^{A_iB_j}$) with ECR is

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}}$$

To account for solvation, Folas et al.[3] used:

$$\epsilon^{A_iB_j} = \frac{\epsilon_{\text{associating}}}{2} \text{ and } \beta^{A_iB_j} = \text{BETCR (fitted)} \qquad \text{(A.7)}$$

Then, the association strength will be estimated by eq 3, and in this way the in-built temperature dependency of the cross-association strength is retained for solvating systems. Previous calculations[3] have showed that this is important in order to obtain satisfactory results (e.g., for water−aromatic hydrocarbons over large temperature ranges).

Abbreviations

AAD	average absolute deviation (AAD = $(1/NP)\sum_{i=1}^{\mathrm{NP}} \mathrm{ABS}(x_{\mathrm{exp},i} - x_{\mathrm{calc},i}/x_{\mathrm{exp},i})$)
calc	calculated
CPA	Cubic-Plus-Association equation of state
ECR	Elliott combining rule
EoS	equation of state
exp	experimental
GC	gas chromatography
KF	Karl−Fisher titration
LLE	liquid−liquid equilibria
MEG	(mono)ethylene glycol
SRK	Soave−Redlich−Kwong equation of state
VLE	vapor−liquid equilibria
TEG	triethylene glycol

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