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Measurement and Modeling of Liquid−Liquid Equilibrium for Ternary and Quaternary Mixtures of Water, Methanol, 2-Propanol, and 2,2,4-Trimethylpentane at 293.2 K

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Liquid−liquid equilibrium (LLE) phase compositions for ternary and quaternary mixtures of water, methanol, 2-propanol, and 2,2,4-trimethylpentane were measured at 293.2 K. The universal quasichemical activity coefficient (UNIQUAC) model was used to model the experimental observations. Binary interaction parameters were estimated from the experimental equilibrium phase compositions. The agreement between calculations and experimental observations was very good with an overall root-mean-square deviation (rmsd) of 0.53 %.

Introduction

Mixtures of alcohols, water, and hydrocarbons have served successfully as analogue fluid systems in experimental investigations of two-phase displacement dynamics in porous materials.[1−3] In particular the study of gas injection processes for enhanced oil recovery purposes, where phase behavior plays a central role, has gained greatly from the use of these analogue systems. In addition, the partitioning of methanol between hydrocarbon and aqueous phases is an area of active research given the popular application of methanol as a gas-hydrate inhibitor in oil and gas operations.[4]

In this paper, we present a combined experimental and modeling study of the liquid−liquid phase equilibrium (LLE) of 31 ternary and quaternary mixtures of water, methanol (MeOH), 2-propanol (IPA), and 2,2,4-trimethylpentane (iC_8). The objectives of this work were (a) to generate a consistent set of measurements for the water−MeOH−IPA−iC_8 system and (b) to estimate model parameters for the universal quasichemical activity coefficient (UNIQUAC) model to allow for predictions of the phase behavior of these mixtures. We report measurements of equilibrium phase compositions at 293.2 K and a new set of parameters for the UNIQUAC model that represents accurately the observed equilibrium phase compositions.

Experimental Section

Materials. The chemicals used in this experimental effort were: iC_8 (99.93 %) from OmniSolv, distilled water, dried MeOH (99.9 %) from VWR, IPA (99.9 %) from Burdick and Jackson, and ACS/USP grade ethanol from Pharmco-Aaper (> 99.5 %). Ethanol was used to dilute all samples prior to analysis by gas chromatography (GC). To ensure that MeOH, IPA, and ethanol remained dry throughout the experimental work, a molecular sieve (type 3A from EMD Chemicals) was added to all storage containers.

Procedure. All of the mixture compositions that were investigated in this study were created and maintained at 293.2 K (at atmospheric pressure). To secure an accurate two-phase sampling procedure, two GC glass vials were cut and connected at the bottom to create containers with sample caps at both ends. This design allowed us to withdraw samples by syringe from each of the equilibrium phases without interrupting the interface and hence reduce the potential contamination of the needle. The volume of the two-phase sample vials was 4 mL.

A Varian CP3800 GC was calibrated (by external standard) for the relevant pure solvents to ensure separate and timely peaks while providing for a reasonable and repeatable accuracy (± 0.001) for all components. Samples from the two-phase equilibrium cells were subsequently analyzed using the thermal conductivity detector (TCD). A Megabore capillary column (WCOT fused silica 50MX 0.53 MM ID coating CP-SIL 5CB) was used in this work. Helium served as the carrier gas for the TCD analysis with a flow rate of 5 $mL \cdot min^{-1}$. A portion of 1 μL of the diluted equilibrium samples was injected automatically in split/split less injector mode with a split ratio of 10. The injector temperature was set at 220 °C, and the GC oven temperature was programmed to initiate at 60 °C for 6 min, followed by a gradual increase in temperature to 150 °C at a rate of 20 $°C \cdot min^{-1}$. The above procedure provided for a good separation of ethanol, water, MeOH, IPA, and iC_8.

To characterize the quaternary system of water, MeOH, IPA, and iC_8, we initially studied the associated ternary systems. Three of these exhibit two-phase liquid−liquid equilibrium (LLE) at 293.2 K (water−MeOH−IPA mixtures are fully miscible at 293.2 K).

For the iC_8−water−IPA ternary system, mixture samples were prepared by adding a constant amount of IPA to an initial mixture of 1 mL of iC_8 and 1 mL of water in the two-phase sample cells. The samples were mixed for 5 min and left to equilibrate for 24 h. Samples from the equilibrated phases were withdrawn by 500 μL syringes and mixed with 1 mL of ethanol in separate GC vials. A similar sample preparation procedure was applied for the ternary systems of iC_8−water−MeOH and iC_8−MeOH−IPA.

Results and Discussion

Mixtures of Water, MeOH, and iC_8. The LLE region of the water−MeOH−iC_8 ternary system occupies the majority of the

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Table 1. Equilibrium Data (Mass Fractions) for Water−MeOH−iC$_8$ Mixtures at T = 293.2 K

hydrocarbon-rich phase			aqueous phase		
water	MeOH	iC$_8$	water	MeOH	iC$_8$
0.0000	0.0000	1.0000	1.0000	0.0000	0.0000
0.0000	0.0000	1.0000	0.7389	0.2611	0.0000
0.0000	0.0000	1.0000	0.4209	0.5791	0.0000
0.0000	0.0050	0.9950	0.2602	0.7322	0.0077
0.0000	0.0112	0.9888	0.1359	0.8283	0.0358
0.0000	0.0170	0.9830	0.0818	0.8495	0.0687
0.0000	0.0569	0.9431	0.0000	0.7772	0.2228

Table 2. Equilibrium Data (Mass Fractions) for Water−IPA−iC$_8$ Mixtures at T = 293.2 K

hydrocarbon-rich phase			aqueous phase		
water	IPA	iC$_8$	water	IPA	iC$_8$
0.0000	0.0000	1.0000	1.0000	0.0000	0.0000
0.0010	0.0185	0.9805	0.7941	0.2058	0.0001
0.0027	0.0298	0.9675	0.7572	0.2424	0.0004
0.0046	0.0923	0.9032	0.5532	0.4389	0.0079
0.0119	0.1640	0.8241	0.4090	0.5563	0.0348
0.0452	0.3038	0.6510	0.2176	0.5948	0.1876

compositional space. To validate the experimental ternary data reported by Budantseva et al.[5] and Buchowski and Teperek,[6] samples were created starting from the binary mixtures of iC$_8$ and water by adding known amounts of MeOH to the original two-phase samples. After equilibration of the sample vials (24 h), samples were taken from each phase and analyzed by GC. The measured equilibrium phase compositions (mass fractions) are reported in Table 1. Our measurements of the equilibrium phase compositions are in excellent agreement with the work of Budantseva et al.,[5] whereas deviations are observed between our measurements and the measurements of Buchowski and Teperek[6] (the current National Institute of Standards and Technology (NIST) reference), particularly for the aqueous phase at high MeOH concentrations.

Mixtures of Water, IPA, and iC$_8$. Next, the ternary system of water, IPA, and iC$_8$ was analyzed. Two-phase equilibrium data for this ternary are available in the literature, for example, Arda and Sayer[7] at 293.2 K and Otero et al.[8] at 298.2 K. However, in the interest of creating a consistent set of experimental data for the quaternary system under investigation as well as to validate the previously published experimental data, two-phase samples were created at 293.2 K, and the equilibrium phase compositions were analyzed. Table 2 reports our experimental data for this ternary system. The experimental observations of Table 2 are in good agreement with the measurements of Arda and Sayer[7] (current NIST reference). We note that the solubility of iC$_8$ in the aqueous phase reported by Arda and Sayer[7] is slightly larger than for our measurements at moderate concentrations of IPA.

Mixtures of MeOH, IPA, and iC$_8$. The ternary system of MeOH−IPA−iC$_8$ exhibits a small LLE region at 293.2 K that develops from the MeOH−iC$_8$ binary system. To our best knowledge, no experimental data for this ternary exist in the literature. Three samples were prepared starting from the binary system of iC$_8$−MeOH by adding a fixed amount of IPA. After sample preparation, the vials were allowed to equilibrate for 24 h. Samples were then taken from the top and bottom phases of each vial and analyzed with the GC to determine the equilibrium phase compositions. The equilibrium phase compositions are reported in Table 3.

Quaternary Mixtures. In addition to the LLE measurements for the above ternaries, 15 two-phase LLE samples containing all four components were prepared to delineate the two-phase region inside the quaternary composition space. The first four samples were created by adding water to an initial composition of MeOH, IPA, and iC8. The next five samples were created by adding MeOH to an initial mixture of water, IPA, and iC8. Finally, six samples were created by gradually adding IPA to an initial mixture of water, IPA, and MeOH. All of the equilibrated phase compositions were subsequently analyzed by GC and are reported in Table 4.

Table 3. Equilibrium Data (Mass Fractions) for MeOH−IPA−iC$_8$ Mixtures at T = 293.2 K

hydrocarbon-rich phase			MeOH-rich phase		
MeOH	IPA	iC$_8$	MeOH	IPA	iC$_8$
0.0569	0.0000	0.9431	0.7772	0.0000	0.2228
0.0724	0.0062	0.9215	0.6806	0.0342	0.2853
0.1013	0.0165	0.8822	0.5911	0.0621	0.3468

Table 4. Equilibrium Data (Mass Fractions) for Water−MeOH−IPA−iC$_8$ Mixtures at T = 293.2 K

hydrocarbon-rich phase				aqueous phase			
water	MeOH	IPA	iC$_8$	water	MeOH	IPA	iC$_8$
0.0003	0.0055	0.0019	0.9923	0.2354	0.6967	0.0617	0.0063
0.0007	0.0037	0.0015	0.9942	0.3600	0.5891	0.0496	0.0013
0.0011	0.0029	0.0014	0.9946	0.4607	0.4960	0.0427	0.0006
0.0011	0.0020	0.0010	0.9959	0.5061	0.4550	0.0384	0.0005
0.0027	0.0000	0.0298	0.9675	0.7572	0.0000	0.2424	0.0004
0.0023	0.0010	0.0255	0.9712	0.7168	0.0493	0.2320	0.0019
0.0010	0.0017	0.0246	0.9726	0.6792	0.0956	0.2243	0.0009
0.0027	0.0020	0.0193	0.9760	0.6278	0.1437	0.2281	0.0004
0.0017	0.0025	0.0184	0.9775	0.6216	0.1765	0.2014	0.0004
0.0025	0.0010	0.0000	0.9966	0.8410	0.1585	0.0000	0.0005
0.0029	0.0010	0.0038	0.9922	0.7696	0.1265	0.1034	0.0005
0.0025	0.0015	0.0119	0.9841	0.6792	0.1248	0.1957	0.0003
0.0035	0.0022	0.0263	0.9679	0.6217	0.1133	0.2640	0.0009
0.0035	0.0025	0.0375	0.9566	0.5982	0.0975	0.3029	0.0014
0.0043	0.0029	0.0499	0.9430	0.5002	0.1001	0.3944	0.0053

Table 5. Structural Q and R Parameters Used in This Work

parameters	water	MeOH	IPA	iC$_8$
Q_i	1.4000	1.4320	3.1240	5.0080
R_i	0.9200	1.4311	3.2491	5.8463

Modeling and Correlation of LLE Data

The UNIQUAC model[9] was used in this study to model the phase behavior of the ternary and quaternary mixtures. In the UNIQUAC model, the activity coefficient of a component in a mixture is derived from the molar excess Gibbs energy of the mixture. Intermolecular forces are related to the surface areas, Q_i, and relative van der Waals volumes, R_i, of the pure components. Q and R parameters were calculated from the molecular structures[10] and are reported in Table 5.

The UNIQUAC model includes two adjustable binary interaction coefficients for each pair of components in a given mixture. Accordingly, 12 interaction parameters are required to model the quaternary system. Optimally, the interaction parameters should be determined from regression of data for the individual binary mixtures at various temperatures. In this work, however, only the water−iC$_8$ and the MeOH−iC$_8$ binary systems form two phases at the experimental conditions, and

Table 6. UNIQUAC Interaction Coefficients: Water (1)−MeOH (2)−IPA (3)−iC$_8$ (4)

a_{ij} [K]	1	2	3	4
1	0.0	−760.7	301.2	429.0
2	2175.8	0.0	146.3	11.5
3	−241.1	−143.2	0.0	−83.2
4	2512.6	598.5	169.0	0.0

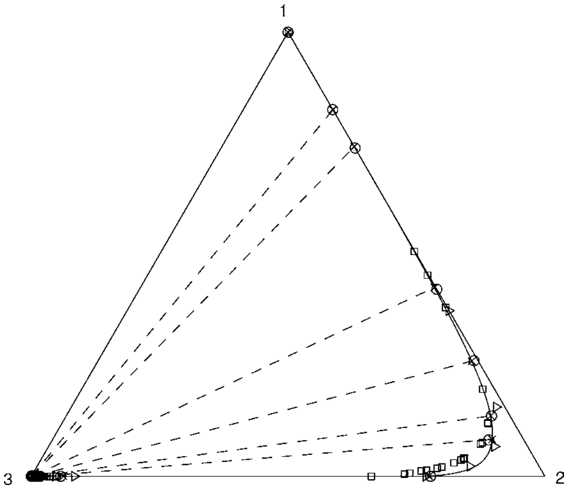

Figure 1. Ternary system of water (1)−MeOH (2)−iC$_8$ (3) at 293.2 K. Experimental data (mass fractions) are shown with circles, the calculated phase boundaries with solid lines, and the dashed lines show the calculated tie-lines. ○, our measurements; △, ref 5; □, ref 6.

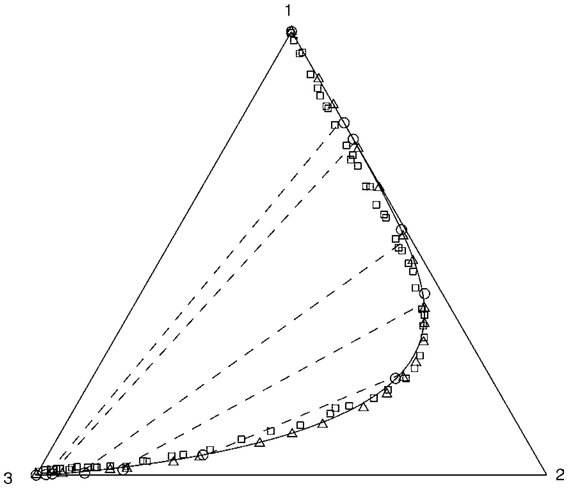

Figure 2. Ternary system of water (1)−IPA (2) and iC$_8$ (3) at 293.2 K. Experimental data (mass fractions) are shown with circles, the calculated phase boundaries with a solid line, and the dashed lines show the calculated tie-lines. ○, our measurements; □, ref 7; △, ref 8.

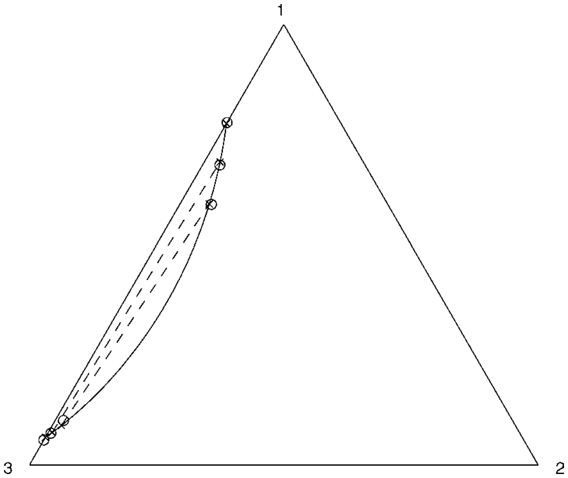

Figure 3. Ternary system of MeOH (1)−IPA (2)−iC$_8$ (3) at 293.2 K. Experimental data (mass fractions) are shown with circles, the calculated phase boundaries with a solid line, and the dashed lines show the calculated tie-lines.

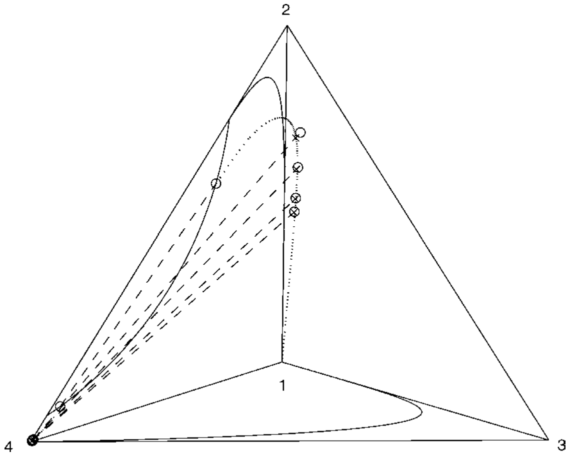

Figure 4. Quaternary mixtures of water (1)−MeOH (2)−IPA (3)−iC$_8$ (4) at 293.2 K. Experimental data (mass fractions) are shown by circles, and the dashed lines show the predicted tie-lines. The calculated phase boundaries are shown (solid line) for the three relevant ternaries. The boundaries of the surface associated with the samples are also shown (dotted line).

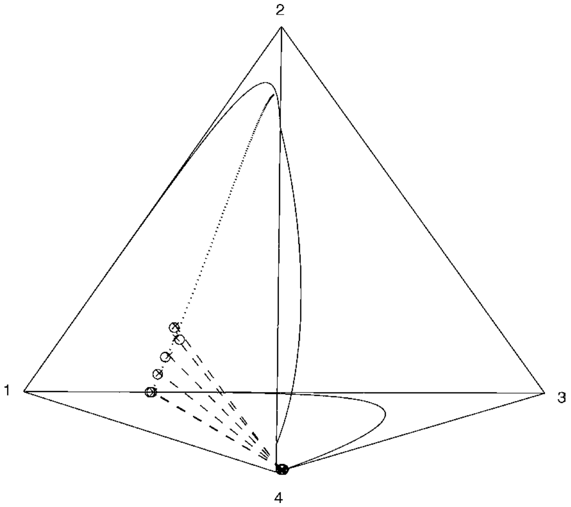

Figure 5. Quaternary mixtures of water (1)−MeOH (2)−IPA (3)−iC$_8$ (4) at 293.2 K. Experimental data (mass fractions) are shown by circles, and the dashed lines show the predicted tie-lines. The calculated phase boundaries are shown (solid line) for the three relevant ternaries. The boundaries of the surface associated with the samples are also shown (dotted line).

the optimal approach is hence not feasible. Instead, all binary interaction coefficients were estimated simultaneously from the experimental data reported above. This amounts to estimating 12 parameters from 150 independent mass fractions. We applied the following objective function and a Levenberg−Marqardt algorithm[11] to estimate the binary interaction parameters

$$\text{obj} = \sum_{i=1}^{N} \sum_{j=1}^{m-1} (w_{ij,\text{exp}} - w_{ij,\text{calc}})^2 \tag{1}$$

where $w_{ij,\text{exp}}$ is the experimental and $w_{ij,\text{calc}}$ is the calculated mass fraction, respectively. m is the number of components in the mixture, and N is the total number of equilibrium phases. Table 6 reports the estimated values of the interaction parameters. We note that a consistent set of Q, R, and interaction parameters should always be used in predictive applications as the values of the interaction parameters depend strongly on the values of Q and R.[12]

On the basis of the estimated interaction parameters, a good agreement was obtained between measured and calculated

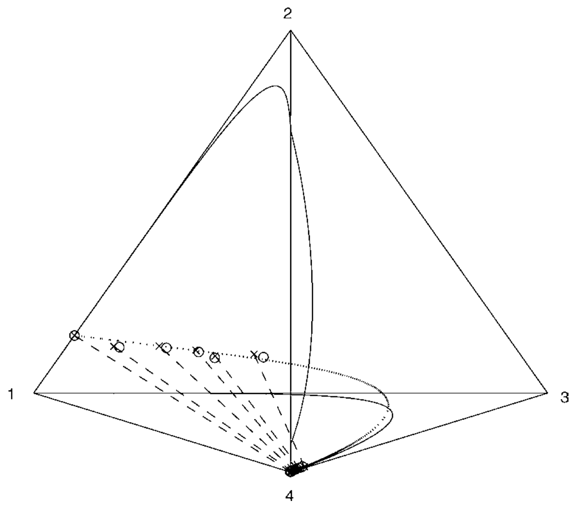

Figure 6. Quaternary mixtures of water (1)−MeOH (2)−IPA (3)−iC_8 (4) at 293.2 K. Experimental data (mass fractions) are shown by circles, and the dashed lines show the predicted tie-lines. The calculated phase boundaries are shown (solid line) for the three relevant ternaries. The boundaries of the surface associated with the samples are also shown (dotted line).

equilibrium phase compositions. The overall root-mean-square deviation (rmsd) was 0.53 % with a slightly better agreement between measurements and calculations for the quaternary mixtures (rmsd of 0.50 %) than for the ternary mixtures (rmsd of 0.56 %). Figures 1 to 3 compare our UNIQUAC LLE calculations with the experimental observation for the three ternaries that exhibit a two-phase region. In Figure 1, we compare our measurements (water−MeOH−iC_8) to the experimental observations of Budantseva et al.[5] and Buchowski and Teperek[6] In addition, we compare our measurements (water−IPA−iC_8) with those of Arda and Sayer[7] and Otero et al.[8] in Figure 2.

Figures 4 to 6 compare calculations and experimental observations for the four-component LLE samples.

Conclusions

In this work, the LLE for mixture compositions of water, MeOH, IPA, and iC_8 has been characterized experimentally at 293.2 K and successfully modeled with the UNIQUAC activity coefficient model. A new set of parameters for the UNIQUAC model is presented that provides for a good agreement between calculations the presented experimental LLE observations. The accuracy of the calculations corresponds to an overall rmsd of 0.53 %.

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