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Liquid−Liquid Equilibria for Sulfolane + 2-Methoxyethanol + Octane + Toluene at 293.15 K

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Liquid−liquid equilibrium data were measured at 293.15 K for the quaternary system sulfolane + 2-methoxyethanol + octane + toluene. The Othmer and Tobias method satisfactorily correlated tie-line data. The nonrandom two-liquid (NRTL) equation was used to correlate the experimental data and to predict the phase composition of the systems studied here. The agreement between the correlated and experimental results was good.

Introduction

Liquid−liquid equilibria (LLE) data on a number of ternary mixtures containing sulfolane have been extensively studied.[1−5] Few papers in the literature deal with quaternary liquid−liquid equilibrium data, which include sulfolane.[6,7] In this paper, we present a new experimental quaternary liquid−liquid equilibrium for toluene + octane + sulfolane + 2-methoxyethanol at 293.15 K. This quaternary systems is treated as a pseudoternary system; component 1 is (sulfolane + 2-methoxyethanol). The mass fractions of 2-methoxyethanol in sulfolane were (5 to 75)%. Furthermore, the experimental quaternary results were correlated by fitting the nonrandom two-liquid (NRTL) equation.[8]

Experimental Section

Materials. Sulfolane (>99.5 mol %), 2-methoxyethanol (>99.8 mol %), octane (>99.5 mol %), and toluene (>99.9 mol %) were obtained from Fluka Chemie AG. All solvents were used without further purification but were keeping over freshly activated molecular sieves of type 4A for several days before use. The measured densities and refractive indices of the pure solvents used in this work agreed well with those values published in the literature.[9]

Procedure. The binodal curves were determined using the cloud-point titration technique as described by Hadded and Edmister.[10] The accuracy of this technique was greater than 0.005 mass fraction. Tie lines were determined using the refractive index method described by Briggs and Comings.[11] The accuracy of the technique used to determine the tie lines was better than 0.01 mass fraction. Plait points were determined using the method outlined by Treybal et al.[12] The experimental procedures are described in detail in previous work.[13]

Results and Discussion

Liquid−liquid equilibrium data for the five systems studied here at 293.15 K are presented in Table 1 and illustrated in Figures 1−5. The experimental tie-line data for the systems are given in Table 2 and fit well on the bimodal curves, indicating the accuracy of the experimental tie-line data.

Table 1. Binodal Curve Compositions at 293.15 K for the Mixtures w_1(Sulfolane + 2-Methoxyethanol) + w_2(Octane) + w_3(Toluene)

sulfolane			sulfolane + 5 mass% 2-methoxyethanol			sulfolane + 25 mass% 2-methoxyethanol		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
0.988	0.012	0.000	0.990	0.010	0.000	0.980	0.020	0.000
0.884	0.016	0.100	0.902	0.018	0.080	0.900	0.024	0.076
0.790	0.018	0.192	0.804	0.024	0.172	0.820	0.030	0.150
0.687	0.022	0.291	0.614	0.035	0.351	0.737	0.044	0.219
0.617	0.034	0.349	0.494	0.062	0.444	0.551	0.073	0.376
0.483	0.060	0.457	0.411	0.087	0.502	0.465	0.105	0.430
0.409	0.085	0.506	0.348	0.112	0.540	0.386	0.132	0.482
0.344	0.109	0.547	0.286	0.135	0.579	0.327	0.164	0.509
0.285	0.133	0.582	0.238	0.161	0.601	0.263	0.189	0.548
0.229	0.153	0.618	0.190	0.188	0.622	0.210	0.220	0.570
0.186	0.181	0.633	0.143	0.217	0.640	0.157	0.251	0.592
0.144	0.214	0.642	0.102	0.258	0.640	0.112	0.301	0.587
0.103	0.259	0.638	0.059	0.333	0.608	0.064	0.387	0.549
0.059	0.330	0.611	0.036	0.425	0.539	0.041	0.523	0.436
0.036	0.425	0.539	0.018	0.563	0.419	0.021	0.683	0.296
0.019	0.582	0.399	0.016	0.682	0.302	0.020	0.780	0.200
0.017	0.738	0.245	0.014	0.843	0.143	0.018	0.880	0.102
0.015	0.857	0.128	0.010	0.990	0.000	0.016	0.984	0.000
0.012	0.988	0.000						

sulfolane + 50 mass% 2-methoxyethanol			sulfolane + 75 mass% 2-methoxyethanol		
w_1	w_2	w_3	w_1	w_2	w_3
0.954	0.046	0.000	0.918	0.082	0.000
0.862	0.056	0.082	0.726	0.110	0.164
0.790	0.068	0.142	0.599	0.154	0.247
0.657	0.094	0.249	0.501	0.196	0.303
0.514	0.124	0.362	0.426	0.234	0.340
0.419	0.154	0.427	0.354	0.272	0.374
0.355	0.190	0.455	0.280	0.316	0.404
0.298	0.230	0.472	0.200	0.380	0.420
0.232	0.261	0.507	0.151	0.445	0.404
0.175	0.301	0.524	0.086	0.588	0.326
0.123	0.356	0.521	0.051	0.727	0.222
0.071	0.459	0.470	0.026	0.974	0.000
0.046	0.615	0.339			
0.034	0.750	0.216			
0.025	0.858	0.117			
0.020	0.980	0.000			

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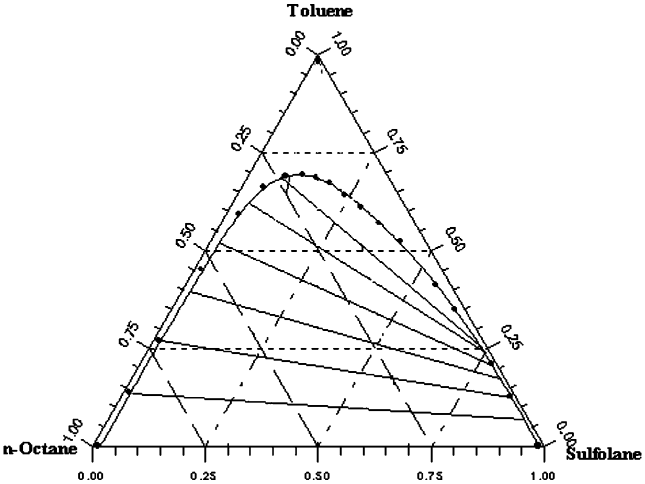

Figure 1. Binodal curve and tie lines for pure sulfolane + octane + toluene at 293.15 K.

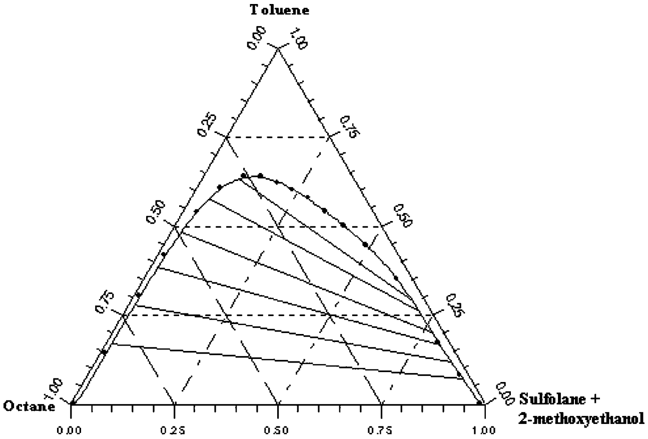

Figure 2. Binodal curve and tie lines for sulfolane + 5 mass % 2-methoxyethanol + octane + toluene at 293.15 K.

The Othmer−Tobias correlation[14] was used to ascertain the reliability of the experimental results for each system. The correlation calls for the tie-line data to have the functional relationship

$$\log\left(\frac{1-w_{22}}{w_{22}}\right) = a\log\left(\frac{1-w_{11}}{w_{11}}\right) + b \tag{1}$$

where w_{11} and w_{22} are the mass fractions of component 1 in the solvent-rich phase and component 2 in the octane-rich phase, respectively. The results of regression analysis are presented in Table 3. The values of the correlation coefficient (r) are close to unity. The goodness of the fit confirms the reliability of the results.

The efficiency of an extracting agent for separating an aromatic compound from alkanes is

$$S = \frac{w_{31}/w_{32}}{w_{21}/w_{22}} \tag{2}$$

where w_{31} and w_{32} represent the toluene mass fraction in

Table 2. Tie-Line Data for w_1(Sulfolane + 2-Methoxyethanol) + w_2(Octane) + w_3(Toluene) at 293.15 K

pure sulfolane						sulfolane + 5% 2-methoxyethanol					
solvent-rich phase			octane-rich phase			solvent-rich phase			octane-rich phase		
w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.918	0.012	0.070	0.014	0.851	0.135	0.915	0.015	0.070	0.010	0.820	0.170
0.861	0.014	0.125	0.016	0.714	0.270	0.860	0.020	0.120	0.014	0.706	0.280
0.810	0.015	0.175	0.018	0.587	0.395	0.810	0.025	0.165	0.015	0.600	0.385
0.774	0.016	0.210	0.020	0.460	0.520	0.765	0.030	0.205	0.025	0.490	0.485
0.748	0.017	0.235	0.030	0.345	0.625	0.705	0.035	0.260	0.050	0.380	0.570
0.730	0.018	0.252	0.070	0.240	0.690	0.670	0.040	0.290	0.085	0.275	0.640

sulfolane + 25% 2-methoxyethanol						sulfolane + 50% 2-methoxyethanol					
solvent-rich phase			octane-rich phase			solvent-rich phase			octane-rich phase		
w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.950	0.020	0.030	0.018	0.932	0.050	0.910	0.050	0.040	0.020	0.930	0. 050
0.886	0.024	0.090	0.020	0.810	0.170	0.830	0.060	0.110	0.030	0.810	0.160
0.815	0.030	0.155	0.020	0.695	0.285	0.755	0.070	0.175	0.040	0.675	0.285
0.735	0.040	0.225	0.030	0.575	0.395	0.670	0.090	0.240	0.055	0.550	0.395
0.675	0.045	0.280	0.045	0.455	0.500	0.575	0.110	0.315	0.090	0.415	0.495
0.570	0.070	0.360	0.090	0.330	0.580						

sulfolane + 75% 2-methoxyethanol					
solvent-rich phase			octane-rich phase		
w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.875	0.090	0.035	0.030	0.930	0.040
0.820	0.095	0.085	0.030	0.870	0.100
0.775	0.100	0.125	0.035	0.805	0.160
0.720	0.115	0.165	0.050	0.730	0.220
0.640	0.140	0.220	0.065	0.660	0.275
0.540	0.180	0.280	0.090	0.575	0.335

Table 3. Composition of Plait Points, Selectivity (S), Correlation Parameters (a and b) and Regression Factor (r) for the Mixtures w_1(Sulfolane + 2-Methoxyethanol) + w_2(Octane) + w_3(Toluene) at 293.15 K

solvent	w_1	w_2	S	a	b	r
pure sulfolane	0.391	0.076	37	0.5050	−0.6252	0.9970
sulfolane + 5% 2-methoxyethanol	0.397	0.086	23	0.7097	−0.5284	0.9966
sulfolane + 25% 2-methoxyethanol	0.322	0.163	29	0.8160	−0.3665	0.9975
sulfolane + 50% 2-methoxyethanol	0.307	0.223	15	0.6840	−0.2494	0.9978
sulfolane + 75% 2-methoxyethanol	0.283	0.318	9	0.7390	−0.0385	0.9957

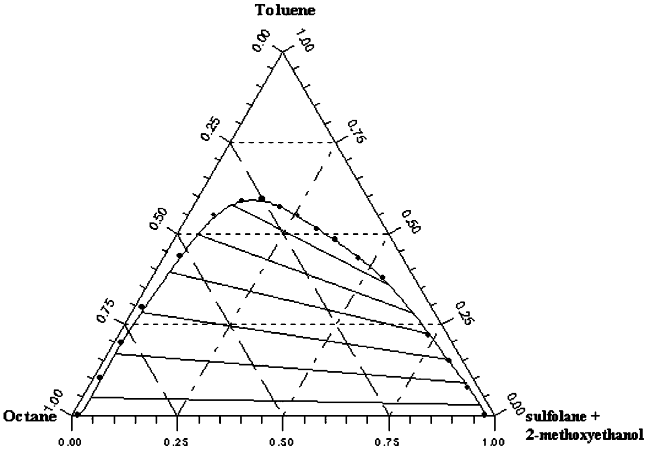

Figure 3. Binodal curve and tie lines for sulfolane + 25 mass % 2-methoxyethanol + octane + toluene at 293.15 K.

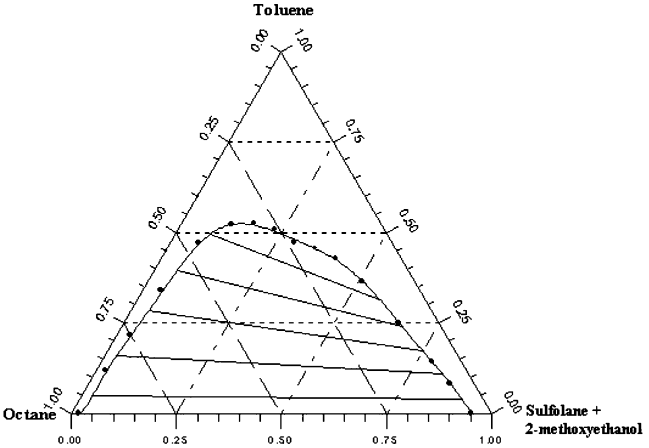

Figure 4. Binodal curve and tie lines for sulfolane + 50 mass % 2-methoxyethanol + octane + toluene at 293.15 K.

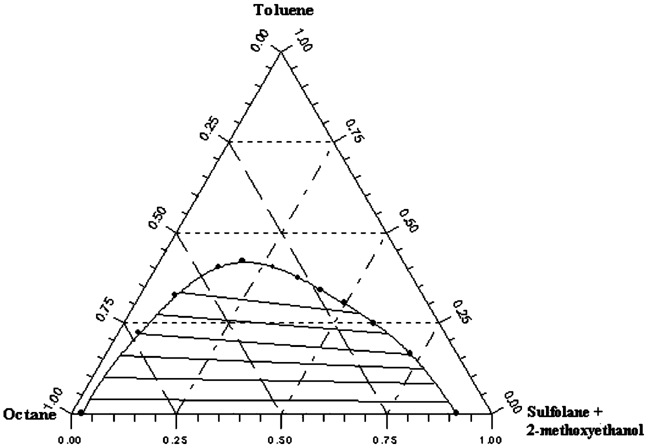

Figure 5. Binodal curve and tie lines for sulfolane + 75 mass % 2-methoxyethanol + octane + toluene at 293.15 K.

the solvent layer and the octane layer, respectively, and w_{21} and w_{22} are the octane mass fraction in the solvent layer and the octane layer, respectively. The maximum selectivity for pure sulfolane + 2-methoxyethanol is given in Table 3. The two-phase region for the system containing only sulfolane as a solvent (Figure 1) is large, indicating a large range of separation compositions. The systems containing sulfolane (1) + 2-methoxyethanol (2) (0, 5, 25, 50, 75) mass% (Figures 1–5) showed a decrease in the two-phase region compared to the pure sulfolane system.

Table 4. NRTL Parameters (g_{ij} (J·mol^{-1})) and (α_{ij}) for the Mixtures w_1(Sulfolane + 2-Methoxyethanol) + w_2(Octane) + w_3(Toluene) at 293.15 K

g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	rmsd
Pure Sulfolane									
1076	811	1878	5607	8824	9699	0.292	0.412	0.401	0.085
Sulfolane + 5 mass % 2-Methoxyethanol									
1063	702	160	5038	2094	1468	0.346	0.331	0.460	0.031
Sulfolane + 25 mass % 2-Methoxyethanol									
2086	453	411	5582	7954	1125	0.123	0.386	0.342	0.012
Sulfolane + 50 mass % 2-Methoxyethanol									
1702	283	7195	5358	8518	9342	0.275	0.305	0.313	0.020
Sulfolane + 75 mass % 2-Methoxyethanol									
2765	541	6871	5280	9885	9660	0.295	0.367	0.259	0.019

Table 5. Comparison of Experimental and Predicted Tie Lines for the Mixtures w_1(Sulfolane + 2-Methoxyethanol) + w_2(Octane) + w_3(Toluene) at 293.15 K

Sulfolane

solvent-rich phase				octane-rich phase			
w_{11}		w_{21}		w_{12}		w_{22}	
exptl	pred	exptl	pred	exptl	pred	exptl	pred
0.918	0.959	0.012	0.013	0.014	0.013	0.851	0.767
0.861	0.915	0.014	0.014	0.016	0.015	0.714	0.693
0.810	0.816	0.015	0.015	0.018	0.018	0.587	0.583
0.774	0.676	0.016	0.015	0.020	0.023	0.460	0.478
0.748	0.686	0.017	0.016	0.030	0.033	0.345	0.371
0.730	0.684	0.018	0.017	0.070	0.060	0.240	0.249

Sulfolane + 5 mass % 2-Methoxyethanol

solvent-rich phase				octane-rich phase			
w_{11}		w_{21}		w_{12}		w_{22}	
exptl	pred	exptl	pred	exptl	pred	exptl	pred
0.915	0.731	0.015	0.015	0.010	0.012	0.820	0.810
0.860	0.749	0.020	0.019	0.014	0.016	0.706	0.732
0.810	0.744	0.025	0.023	0.015	0.018	0.600	0.647
0.765	0.773	0.030	0.026	0.025	0.025	0.490	0.559
0.705	0.809	0.035	0.030	0.050	0.038	0.380	0.432
0.670	0.846	0.040	0.031	0.085	0.065	0.275	0.356

Sulfolane + 25 mass % 2-Methoxyethanol

solvent-rich phase				octane-rich phase			
w_{11}		w_{21}		w_{12}		w_{22}	
exptl	pred	exptl	pred	exptl	pred	exptl	pred
0.950	0.872	0.020	0.021	0.018	0.015	0.932	0.844
0.886	0.819	0.024	0.025	0.020	0.019	0.810	0.778
0.815	0.685	0.030	0.029	0.020	0.024	0.695	0.705
0.735	0.673	0.040	0.036	0.030	0.032	0.575	0.626
0.675	0.639	0.045	0.043	0.045	0.047	0.455	0.472
0.570	0.619	0.070	0.065	0.090	0.083	0.330	0.356

Sulfolane + 50 mass % 2-Methoxyethanol

solvent-rich phase				octane-rich phase			
w_{11}		w_{21}		w_{12}		w_{22}	
exptl	pred	exptl	pred	exptl	pred	exptl	pred
0.910	0.888	0.050	0.052	0.020	0.021	0.930	0.893
0.830	0.879	0.060	0.059	0.030	0.028	0.810	0.818
0.755	0.747	0.070	0.068	0.040	0.040	0.675	0.691
0.670	0.640	0.090	0.086	0.055	0.058	0.550	0.579
0.575	0.570	0.110	0.112	0.090	0.091	0.415	0.407

Sulfolane + 75 mass % 2-Methoxyethanol

solvent-rich phase				octane-rich phase			
w_{11}		w_{21}		w_{12}		w_{22}	
exptl	pred	exptl	pred	exptl	pred	exptl	pred
0.875	0.879	0.090	0.087	0.030	0.028	0.930	0.956
0.820	0.784	0.095	0.096	0.030	0.031	0.870	0.865
0.775	0.716	0.100	0.102	0.035	0.037	0.805	0.785
0.720	0.721	0.115	0.116	0.050	0.049	0.730	0.726
0.640	0.647	0.140	0.138	0.065	0.046	0.660	0.667
0.540	0.545	0.180	0.175	0.090	0.089	0.575	0.591

Data Correlation. The NRTL thermodynamic model was used to correlate the experimental data for these systems. The objective function F was used to minimize the difference between the experimental and calculated mole fractions

$$F = \sum_{i=1}^{n} \min \sum_{j=1}^{3}\sum_{L=1}^{2}(x_{jL}^{\text{exptl}}(i) - x_{jL}^{\text{calcd}}(i))^2 \tag{3}$$

where $x_{jL}^{\text{exptl}}(i)$ is the experimental mole fraction of component j in phase L, $x_{jL}^{\text{calcd}}(i)$ is the calculated mole fraction, and n is the number of experimental tie lines.

The values of the parameters that minimized this objective function were sought, using the NRTL model. Applying the direct search method of Hooke and Jeeve,[15] the values of g_{11}, α_{12}, α_{13}, and α_{23} were set, and the values of the five parameters of the NRTL model g_{22}, g_{33}, g_{12}, g_{13}, and g_{23} (J/mol) were calculated. The parameters calculated in this way are given in Table 4. Also included in the Table is the root-mean-square deviation (rmsd):

$$\text{rmsd} = 100\left(\sum_{i=1}^{n} \min \sum_{j=1}^{3}\sum_{L=1}^{2}\frac{(x_{jL}^{\text{exptl}}(i) - x_{jL}^{\text{calcd}}(i))^2}{6n}\right)^{1/2} \tag{4}$$

The rmsd is a measure of the agreement between the experimental and calculated data.

The calculations based on the NRTL model gave a good representation of the tie-line data for the systems octane + toluene + (sulfolane + 2-methoxyethanol). The experimental and calculated data using the NRTL model for the systems are presented in Table 5.

Conclusions

Liquid−liquid equilibrium data for the systems sulfolane + 2-methoxyethanol + octane + toluene were determined at 293.15 K.

The Othmer−Tobias correlation was used to ascertain the reliability of the experimental data. The good fit confirms the reliability of the data.

The calculations based on the NRTL model gave a good representation of the tie-line data for all systems studied.

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