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Liquid−Liquid Equilibria for the Quaternary Systems of Water + Dimethyl Sulfoxide + 1-Pentanol + NaBr or + KBr

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The effect of sodium bromide and potassium bromide on the liquid−liquid equilibrium (LLE) of the water + dimethyl sulfoxide + 1-pentanol system has been investigated at temperatures from (283.15 to 323.15) K under atmospheric pressure. The experimental results of the two quaternary systems (salt-containing) and the original ternary system (salt-free) show that the salt effect could be evaluated. The influence of sodium bromide is slightly more significant than that of potassium bromide. The compositions of the conjugated phases were correlated with the three-contribution electrolyte-NRTL model. In general, the model reproduces reasonably the LLE phase diagrams.

Introduction

The stripper agent is an important material for photolithography technology in the manufacture of electronic components. A favorable stripper agent must have good stripping abilities, must not corrode metals, and must be able to prevent a defective profile of signal lines such as undercut and overhang. In general, for the above purposes the stripper agents are composed of *N*-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), diethylene glycol monobutyl ether (DGBE), and monoethanolamine (MEA) solvents. It is imperative for electronic industries to investigate the recovery of stripper agent and reduce the pollution impact of the stripper agent on the environment. In our laboratory, we are interested in investigating the fundamental salting effect on the solubility properties of extractants and stripper agents in water for the extractive recovery application of the stripper agent. Reliable liquid−liquid equilibrium data of multicomponent mixture systems are very useful in many extractive process designs because those phase equilibrium properties of such mixture systems cannot be predicted from pure component values. In our previous research,[1,2] we have reported the salting effect (sodium chloride, NaCl; potassium chloride, KCl; and potassium acetate, KAc) on two ternary LLE systems of water + NMP + extractant (1-pentanol or 1-hexanol) at temperatures from (283.15 to 323.15) K. The experimental results show that the NMP can be effectively removed from the aqueous phase while the different salts are added, especially in the case of NaCl, and the extractive capability of 1-hexanol is slightly more significant than that of 1-pentanol. As a part of this continuing work, we research different kinds of stripper agent components and salts. The focus of this paper is placed on the phase behavior of LLE for the ternary system of water + dimethyl sulfoxide (DMSO) + 1-pentanol (extractant) and two quaternary systems of water + DMSO + 1-pentanol + sodium bromide (NaBr) or + potassium bromide (KBr) at temperatures from (283.15 to 323.15) K under atmospheric pressure. No literature data were found at comparable conditions. These new LLE data are correlated with the solution model of the electrolyte-NRTL.[3−6] The electrolyte-NRTL model can be reduced to the original NRTL model[7] for salt-free systems. Good quantitative agreement was obtained with these models.

Experimental Section

Chemicals. Dimethyl sulfoxide was obtained from Riedel-deHaën. 1-Pentanol was supplied by Fluka Chemicals (Germany). Deionized distilled water was prepared in our laboratory. The purities of these liquid compounds were greater than 99 %. Sodium bromide and potassium bromide were obtained from J. T. Baker. The salt compounds were dried in a vacuum oven at a temperature of 393.15 K until the weight remained constant before being used. All the liquid chemicals were checked with chromatographic analysis (model: 9800, China Chromatography Co., Taiwan; Stainless steel column: 10 % Porapak Qs 60/80 and 2 m × 1/8”) with a thermal conductivity detector (TCD) and using high purity helium (99.99 %) as a carrier gas. No impurity peaks were detected, and all reagents were used without further purification.

Apparatus and Procedure. Liquid−liquid equilibrium data for the ternary and quaternary systems were measured by an apparatus similar to that of Peschke and Sandler,[8] basically including a jacketed glass cell, a thermostatically controlled bath, a magnetic agitator, and a gas chromatograph. In the jacketed equilibrium glass cell (internal volume about 30 cm^3), the thermostatic water is circulated to control the temperature of the cell within ± 0.1 K. The cell temperature was measured by a precision thermometer (model-1506, Hart Scientific, USA) with a platinum RTD probe to an uncertainty of ± 0.03 K. In this paper, the detailed procedure of LLE data measurements and analyses or the validity test of our experimental procedure has been described elsewhere.[1,2]

Five samples were replicated for each phase at a fixed experimental condition. The composition of salt in each phase was determined gravimetrically by transferring a liquid sample (about 1∼2 cm^3) onto watch glasses and drying in a vacuum oven at a temperature of 393.15 K for about 12 h until the weight of salt remained constant. The uncertainty of the weight determination using an Ohaus AR2140 balance is ± 0.1 mg. For the salt-free constituents, the area fraction

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Table 1. Average Deviations of GC Calibration Curves

mixture	phase	average deviations[a]
water + 1-pentanol	organic	0.0007
	aqueous	0.0001
water + DMSO	organic	0.0002
	aqueous	0.0002

[a] Average deviations $= (1/n_p) \sum_{j=1}^{n_p} |x_{\text{act}} - x_{\text{calb}}|_j$, where n_p is the number of calibration points and x the minor constituent compound. The subscripts "act" and "calb" represent the actual values and calibrated values, respectively.

Table 2. LLE Data for Water (1) + DMSO (2) + 1-Pentanol (3) at Different Temperatures

	organic phase			aqueous phase		
T/K	x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
283.15	0.3442	0.0000	0.6558	0.9969	0.0000	0.0031
	0.3427	0.0196	0.6378	0.9651	0.0309	0.0040
	0.3356	0.0676	0.5968	0.9032	0.0923	0.0046
	0.3252	0.1332	0.5415	0.8261	0.1682	0.0057
	0.3279	0.2109	0.4613	0.7308	0.2607	0.0086
	0.3505	0.2914	0.3582	0.6783	0.3094	0.0123
	0.3507	0.3076	0.3417	0.6611	0.3254	0.0135
	0.3514	0.3135	0.3351	0.6563	0.3298	0.0138
	0.3598	0.3353	0.3050	0.6305	0.3532	0.0164
	0.3806	0.3648	0.2546	0.5883	0.3881	0.0236
303.15	0.3604	0.0000	0.6396	0.9978	0.0000	0.0022
	0.3574	0.0260	0.6166	0.9659	0.0306	0.0035
	0.3515	0.0751	0.5734	0.9069	0.0883	0.0048
	0.3493	0.1011	0.5497	0.8755	0.1193	0.0053
	0.3481	0.1331	0.5188	0.8253	0.1679	0.0068
	0.3482	0.1815	0.4703	0.7985	0.1936	0.0079
	0.3560	0.2389	0.4051	0.7431	0.2457	0.0112
	0.3720	0.2819	0.3461	0.7114	0.2742	0.0144
	0.3942	0.3240	0.2819	0.6764	0.3061	0.0176
	0.4494	0.3718	0.1788	0.6072	0.3615	0.0313
323.15	0.3850	0.0000	0.6150	0.9979	0.0000	0.0021
	0.3813	0.0302	0.5885	0.9696	0.0274	0.0030
	0.3783	0.0867	0.5350	0.9126	0.0824	0.0050
	0.3799	0.1661	0.4540	0.8284	0.1628	0.0088
	0.3837	0.1819	0.4344	0.7918	0.1973	0.0108
	0.3886	0.2212	0.3902	0.7620	0.2241	0.0140
	0.3960	0.2490	0.3550	0.7346	0.2496	0.0158
	0.4093	0.2756	0.3151	0.7068	0.2743	0.0190
	0.4158	0.2881	0.2962	0.6840	0.2916	0.0244
	0.4246	0.3064	0.2690	0.6446	0.3237	0.0317

was converted into mole fraction by the calibration equations. Two calibration lines were previously constructed according to the organic-rich or the water-rich phases for each binary system. The deviations of the calibration curves from the actual values are tabulated in Table 1. The experimental mole fractions for each phase were obtained by averaging the results from these five replications.

Experimental Results

The experimental apparatus was first employed to measure the LLE data of water + dimethyl sulfoxide + 1-pentanol at 283.15 K, 303.15 K, and 323.15 K under atmospheric pressure. Table 2 reports the experimental results, the superscript I represents the organic-rich phase and II the aqueous phase. Figure 1 is the phase diagram for the ternary system of water + dimethyl sulfoxide + 1-pentanol. Because water/1-pentanol is the only pair that is partially miscible, the ternary system behaves as a type 1 LLE. Very small amounts of the organic compounds were found in the aqueous phase, while water dissolved appreciably in the organic-rich phase. The experimental results show that the solubilities of water in the 1-pentanol increase with an increase of temperature. Since the system of water + dimethyl sulfoxide + 1-pentanol behaves as a type 1 LLE, the effects of adding an electrolyte (a salt) on the mutual solubilities of water + 1-pentanol can provide useful indications for the liquid phase-splitting enhancement. The electrolytes used in this research are NaBr and KBr. The experimental results show that the immiscibility gaps are substantially enlarged as NaBr or KBr was introduced in the aqueous solutions. Figure 2 illustrates that the solubilities of water in the organic-rich phase decrease with increasing concentration of the electrolytes (NaBr or KBr) at 283.15 K, 303.15 K, and 323.15 K. The influence of NaBr is slightly more significant than that of KBr. As seen from Figure 2, it shows that the concentrations over 5 wt % of NaBr and KBr will be saturated at the isotherm of 283.15 K, 303.15 K, or 323.15 K. Mutual solubilities of water and 1-pentanol at 5 wt % salt are given in Table 3.

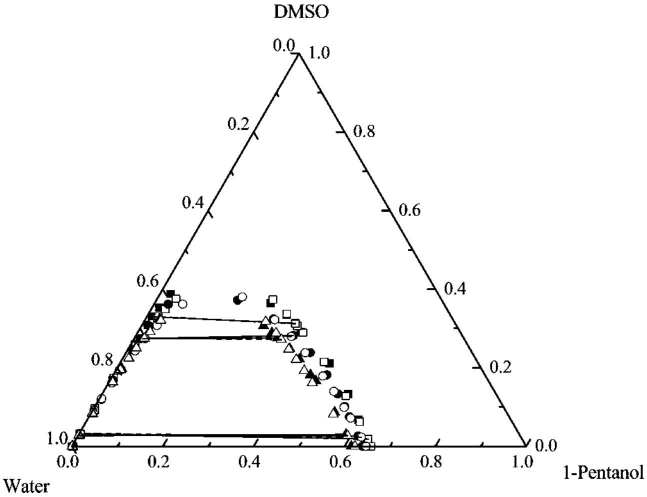

Figure 1. LLE phase diagram for water (1) + DMSO (2) + 1-pentanol (3): ■, exptl data at 283.15 K; ●, exptl data at 303.15 K; ▲, exptl data at 323.15 K; —, exptl tie line; □, NRTL correlation at 283.15 K; ○, NRTL correlation at 303.15 K; △, NRTL correlation at 323.15 K; ----, NRTL tie line.

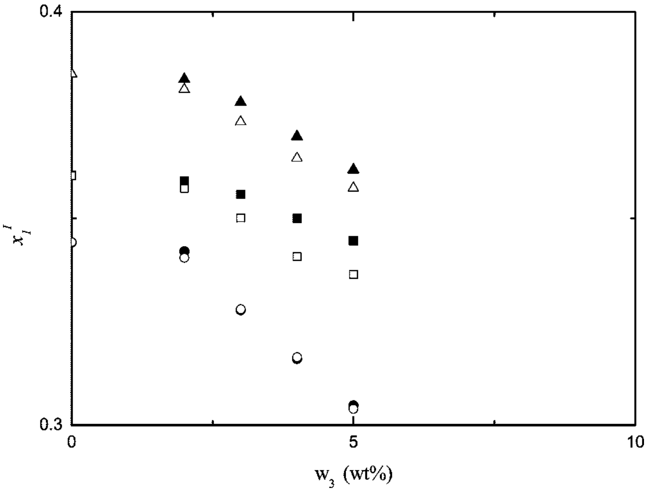

Figure 2. Solubilities of water in the organic-rich phase for water (1) + 1-pentanol (2) + salt (3): (●, KBr; ○, NaBr at 283.15 K); (■, KBr; □, NaBr at 303.15 K); (▲, KBr; △, NaBr at 323.15 K).

In this paper, the LLE measurements of two quaternary systems, water + dimethyl sulfoxide + 1-pentanol with NaBr or KBr, were made at temperatures from (283.15 to 323.15) K under atmospheric pressure. The composition of the salt compounds in the initial feed was 5 wt % in each run. Tables 4 and 5 list the experimental results for water + dimethyl sulfoxide + 1-pentanol with NaBr or KBr, respectively. The

Table 3. Mutual Solubilities of Water and 1-Pentanol at 5 wt % Salt

	T = 283.15 K					
	organic phase			aqueous phase		
salt used	1-pentanol	water	salt	1-pentanol	water	salt
no salt used	0.6558	0.3442	...	0.0031	0.9969	...
potassium bromide	0.6952	0.3048	...	0.0019	0.9788	0.0193
sodium bromide	0.6959	0.3038	0.0003	0.0017	0.9760	0.0223
	T = 303.15 K					
	organic phase			aqueous phase		
salt used	1-pentanol	water	salt	1-pentanol	water	salt
no salt used	0.6396	0.3604	...	0.0022	0.9978	...
potassium bromide	0.6553	0.3445	0.0001	0.0019	0.9784	0.0198
sodium bromide	0.6631	0.3361	0.0008	0.0017	0.9753	0.0230
	T = 323.15 K					
	organic phase			aqueous phase		
salt used	1-pentanol	water	salt	1-pentanol	water	salt
no salt used	0.6150	0.3850	...	0.0021	0.9979	...
potassium bromide	0.6258	0.3740	0.0001	0.0021	0.9772	0.0208
sodium bromide	0.6422	0.3572	0.0006	0.0014	0.9757	0.0229

Table 4. LLE Data for Water (1) + DMSO (2) + 1-Pentanol (3) + NaBr (4) at Different Temperatures

	organic phase				aqueous phase			
T/K	x_1^{I}	x_2^{I}	x_3^{I}	x_4^{I}	x_1^{II}	x_2^{II}	x_3^{II}	x_4^{II}
283.15	0.3038	0.0000	0.6959	0.0003	0.9760	0.0000	0.0017	0.0223
	0.2962	0.0221	0.6812	0.0005	0.9382	0.0358	0.0022	0.0238
	0.2895	0.0467	0.6632	0.0006	0.9003	0.0732	0.0026	0.0239
	0.2829	0.0742	0.6421	0.0008	0.8618	0.1096	0.0030	0.0256
	0.2774	0.1048	0.6165	0.0013	0.8268	0.1429	0.0036	0.0267
	0.2737	0.1384	0.5861	0.0017	0.7881	0.1790	0.0042	0.0287
	0.2710	0.1717	0.5545	0.0028	0.7504	0.2136	0.0059	0.0300
	0.2696	0.2060	0.5214	0.0031	0.7149	0.2470	0.0069	0.0312
303.15	0.3361	0.0000	0.6631	0.0008	0.9753	0.0000	0.0017	0.0230
	0.3302	0.0316	0.6372	0.0010	0.9409	0.0334	0.0021	0.0235
	0.3234	0.0632	0.6123	0.0011	0.9010	0.0713	0.0027	0.0251
	0.3195	0.1006	0.5785	0.0014	0.8596	0.1101	0.0039	0.0265
	0.3195	0.1360	0.5426	0.0018	0.8230	0.1451	0.0048	0.0272
	0.3192	0.1787	0.5000	0.0021	0.7781	0.1883	0.0056	0.0281
	0.3206	0.2423	0.4335	0.0037	0.7189	0.2430	0.0078	0.0302
	0.3317	0.2767	0.3855	0.0061	0.6840	0.2747	0.0093	0.0320
323.15	0.3572	0.0000	0.6422	0.0006	0.9757	0.0000	0.0014	0.0229
	0.3508	0.0403	0.6082	0.0006	0.9396	0.0340	0.0022	0.0242
	0.3467	0.0726	0.5799	0.0007	0.9073	0.0652	0.0030	0.0245
	0.3407	0.1211	0.5369	0.0013	0.8601	0.1092	0.0041	0.0266
	0.3370	0.1567	0.5036	0.0027	0.8253	0.1411	0.0060	0.0276
	0.3364	0.1900	0.4690	0.0047	0.7872	0.1765	0.0062	0.0302
	0.3355	0.2262	0.4319	0.0064	0.7511	0.2099	0.0078	0.0311
	0.3400	0.2572	0.3936	0.0092	0.7127	0.2445	0.0098	0.0331

salts were found to be hardly soluble in the organic phase; that is, most of the salts dissolve in the aqueous phase. The areas of immiscibility increase with decreasing temperature for the two investigated quaternary systems. Figure 3 compares the LLE phase diagrams for the systems of water + dimethyl sulfoxide + 1-pentanol with NaBr or KBr at 283.15 K. By adding the same percentage of salts, the magnitude of phase-splitting enhancement of NaBr is also slightly more significant than that of KBr. For comparing and contrasting the results obtained in our earlier paper[1] for NMP with those given in the present paper for DMSO, Figure 3 also compares the LLE phase diagrams for the systems of water + NMP or DMSO + 1-pentanol when adding the same percentage (5 wt %) of different salts (NaCl, KCl, and KAc for the NMP system; NaBr and KBr for the DMSO system) at 283.15 K. As also seen from Figure 3, NMP shows higher solubility in water and 1-pentanol in comparison with DMSO. The salting-out effects on the systems of water + NMP or DMSO + 1-pentanol can be evaluated, and the effective magnitude of NaCl or NaBr is slightly more significant than that of others.

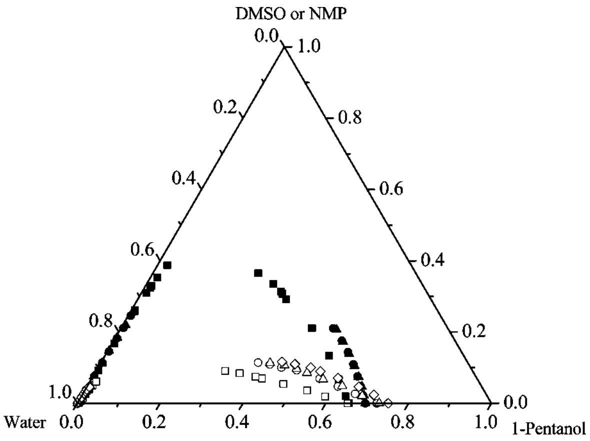

Figure 3. Comparison of LLE phase diagrams for water (1) + NMP (2) or DMSO (2) + 1-pentanol (3) with different salts at 283.15 K. Each coordinate variable is mole fraction on a salt-free basis: [DMSO systems: ■, ternary (salt-free); ●, 5 wt % KBr; ▲, 5 wt % NaBr] and [NMP systems: □, ternary (salt-free); ○, 5 wt % KAc; Δ, 5 wt % KCl; ◊, 5 wt % NaCl].

Table 5. LLE Data for Water (1) + DMSO (2) + 1-Pentanol (3) + KBr (4) at Different Temperatures

	organic phase				aqueous phase			
T/K	x_1^{I}	x_2^{I}	x_3^{I}	x_4^{I}	x_1^{II}	x_2^{II}	x_3^{II}	x_4^{II}
283.15	0.3048	0.0000	0.6952	0.0000	0.9788	0.0000	0.0019	0.0193
	0.2993	0.0211	0.6793	0.0003	0.9411	0.0363	0.0024	0.0202
	0.2919	0.0475	0.6603	0.0003	0.9018	0.0743	0.0027	0.0211
	0.2848	0.0757	0.6389	0.0005	0.8629	0.1117	0.0033	0.0221
	0.2784	0.1096	0.6113	0.0007	0.8307	0.1425	0.0041	0.0228
	0.2738	0.1436	0.5816	0.0011	0.7929	0.1784	0.0046	0.0241
	0.2727	0.1756	0.5505	0.0012	0.7636	0.2059	0.0055	0.0250
	0.2759	0.2104	0.5119	0.0018	0.7283	0.2391	0.0064	0.0262
303.15	0.3445	0.0000	0.6553	0.0001	0.9784	0.0000	0.0019	0.0198
	0.3376	0.0323	0.6300	0.0002	0.9425	0.0346	0.0023	0.0207
	0.3323	0.0650	0.6019	0.0008	0.9068	0.0687	0.0032	0.0214
	0.3276	0.0989	0.5725	0.0010	0.8665	0.1071	0.0038	0.0226
	0.3258	0.1355	0.5375	0.0012	0.8289	0.1425	0.0046	0.0239
	0.3252	0.1842	0.4886	0.0020	0.7782	0.1907	0.0060	0.0251
	0.3289	0.2317	0.4365	0.0029	0.7305	0.2356	0.0076	0.0263
	0.3378	0.2808	0.3770	0.0044	0.6818	0.2801	0.0102	0.0279
323.15	0.3740	0.0000	0.6258	0.0001	0.9772	0.0000	0.0021	0.0208
	0.3657	0.0401	0.5938	0.0004	0.9426	0.0338	0.0027	0.0209
	0.3575	0.0821	0.5597	0.0006	0.9033	0.0714	0.0036	0.0218
	0.3503	0.1174	0.5311	0.0012	0.8656	0.1066	0.0042	0.0236
	0.3439	0.1592	0.4952	0.0017	0.8259	0.1444	0.0056	0.0242
	0.3419	0.1933	0.4622	0.0026	0.7892	0.1787	0.0068	0.0253
	0.3413	0.2328	0.4216	0.0043	0.7541	0.2117	0.0080	0.0262
	0.3427	0.2653	0.3862	0.0058	0.7166	0.2464	0.0098	0.0272

Table 6. Properties of Solvents

		ε_{r}[a] [13]		
solvent	ρ (g·cm^{-3})	a	b	c
water	0.9980 (298.15 K)[10]	249.2100	−0.79069	0.00073
1-pentanol	0.81412 (293.15 K)[11]	73.397	−0.28165	0.00028
DMSO	1.09537 (298.15 K)[12]	38.478	0.16939	−0.00047

[a] $\varepsilon_{\mathrm{r}} = a + bT + cT^2$.

LLE Calculations

At liquid−liquid equilibrium, the mole fractions x_i^{I} and x_i^{II} of two coexistent liquid phases can be calculated using the following criteria, eq 1, together with the material balance equation

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} \tag{1}$$

Table 7. Correlated Results from the NRTL Model for Water (1) + DMSO (2) + 1-Pentanol (3)

T/K	α_{ij}	$i-j$	$a_{ij}{}^{a}$/K	$a_{ji}{}^{a}$/K
283.15	0.3	1−2	−4731.741	−222.453
	0.3	1−3	2095.957	291.309
	0.3	2−3	602.538	−4931.603
303.15	0.3	1−2	−6508.875	−184.939
	0.3	1−3	1990.471	212.598
	0.3	2−3	562.382	−6758.399
323.15	0.3	1−2	176.076	−289.603
	0.3	1−3	2110.055	184.209
	0.3	2−3	684.664	−376.563

T/K	phase	$\Delta x_1{}^{c}$ AAD	Δx_2 AAD	Δx_3 AAD	grand AAD[b]
283.15	organic	0.0001	0.0002	0.0003	0.0020
	aqueous	0.0051	0.0006	0.0056	
303.15	organic	0.0005	0.0001	0.0003	0.0022
	aqueous	0.0062	0.0003	0.0060	
323.15	organic	0.0001	0.0003	0.0002	0.0001
	aqueous	0.0000	0.0001	0.0001	

[a] $a_{ij} = (g_{ij} - g_{jj})/R$, where g_{ij} is the interaction energy between the $i-j$ pair and R is the gas constant. [b] See eq 5. [c] Δx_i is the deviation between calculated x_i and observed x_i for component i.

Table 8. Correlated Results from the Electrolyte-NRTL Model for Water (1) + DMSO (2) + 1-Pentanol (3) + NaBr (4)

T/K	α_{ij}	$i-j$	$a_{ij}{}^{a}$/K	$a_{ji}{}^{a}$/K
283.15	0.3	1−4	899.609	−789.687
	0.01	2−4	−115.842	199.019
	0.01	3−4	1379.238	1185.928
303.15	0.3	1−4	381.353	−247.903
	0.01	2−4	−37.476	−140.852
	0.01	3−4	7000.630	5205.475
323.15	0.3	1−4	193.079	−463.655
	0.01	2−4	−7.784	5.9405
	0.01	3−4	10821.938	3031.931

T/K	phase	$\Delta x_1{}^{c}$ AAD	Δx_2 AAD	Δx_3 AAD	Δx_4 AAD	grand AAD[b]
283.15	organic	0.0036	0.0014	0.0031	0.0014	0.0019
	aqueous	0.0013	0.0015	0.0011	0.0014	
303.15	organic	0.0047	0.0045	0.0113	0.0022	0.0046
	aqueous	0.0035	0.0043	0.0045	0.0019	
323.15	organic	0.0052	0.0020	0.0076	0.0033	0.0036
	aqueous	0.0014	0.0017	0.0047	0.0030	

[a] $a_{ij} = (g_{ij} - g_{jj})/R$, where g_{ij} is the interaction energy between the $i-j$ pair and R is the gas constant. The values of nonrandomness parameters (α_{ij}) and binary interaction parameters (a_{ij} and a_{ji}) for (1−2), (1−3), and (2−3) pairs are the same as in Table 7. [b] See footnote b in Table 7. [c] See footnote c in Table 7.

where γ_i^{I} and γ_i^{II} are the activity coefficients of component i in phases I and II, respectively. The calculation procedure was detailed in Walas.[9] On the basis of one mole of feed with total composition z_i, the compositions of the coexistent liquid phases are solved simultaneously from the following equations

$$1 - \sum_{i=1}^{n_{\mathrm{c}}} \frac{z_i}{\beta + K_i(1-\beta)} = 0 \tag{2}$$

with

$$K_i = x_i^{\mathrm{II}}/x_i^{\mathrm{I}} = \gamma_i^{\mathrm{I}}/\gamma_i^{\mathrm{II}} \tag{3}$$

where n_{c} is the number of components; K_i is the distribution ratio for component i; β is the fraction of the total material that is present in the first liquid phase (the organic-rich phase); and the activity coefficient γ_i can be calculated from a solution model. In this paper, the isothermal LLE data were correlated with the electrolyte-NRTL model[3−6]

Table 9. Correlated Results from the Electrolyte-NRTL Model for Water (1) + DMSO (2) + 1-Pentanol (3) + KBr (4)

T/K	α_{ij}	$i-j$	$a_{ij}{}^{a}$/K	$a_{ji}{}^{a}$/K
283.15	0.3	1−4	1143.213	−944.556
	0.01	2−4	−1.046	836.478
	0.01	3−4	2737.110	284.916
303.15	0.3	1−4	712.456	−172.538
	0.01	2−4	4.427	14340.957
	0.01	3−4	14507.177	−635.180
323.15	0.3	1−4	1585.471	−773.653
	0.01	2−4	5.492	1258.581
	0.01	3−4	1748.775	1040.048

T/K	phase	$\Delta x_1{}^{c}$ AAD	Δx_2 AAD	Δx_3 AAD	Δx_4 AAD	grand AAD[b]
283.15	organic	0.0032	0.0013	0.0026	0.0007	0.0014
	aqueous	0.0011	0.0013	0.0008	0.0008	
303.15	organic	0.0063	0.0075	0.0169	0.0016	0.0062
	aqueous	0.0065	0.0071	0.0028	0.0010	
323.15	organic	0.0055	0.0039	0.0052	0.0020	0.0039
	aqueous	0.0042	0.0038	0.0006	0.0019	

[a] See footnote a in Table 8. [b] See footnote b in Table 8. [c] See footnote c in Table 8.

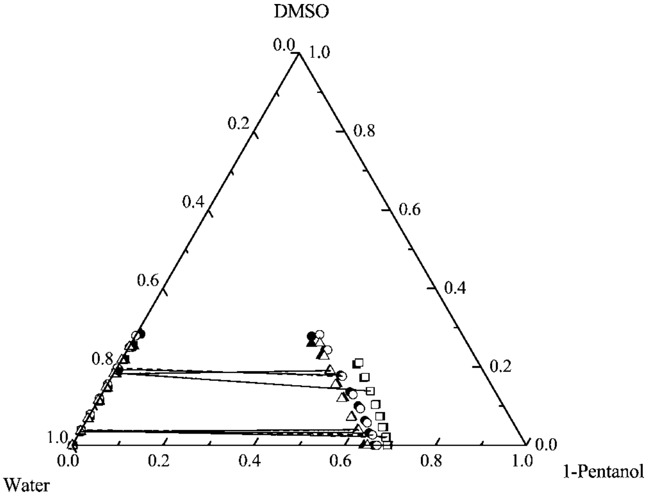

Figure 4. Comparison of calculated results with experimental values for water (1) + DMSO (2) + 1-pentanol (3) + NaBr (4). Each coordinate variable is mole fraction on a NaBr-free basis: ■, exptl data at 283.15 K; ●, exptl data at 303.15 K; ▲, exptl data at 323.15 K; −, exptl tie line; □, electrolyte-NRTL correlation at 283.15 K; ○, electrolyte-NRTL correlation at 303.15 K; △, electrolyte-NRTL correlation at 323.15 K; ----, electrolyte-NRTL tie line.

$$\ln \gamma_i^{*} = \ln \gamma_i^{*\mathrm{pdh}} + \ln \gamma_i^{*\mathrm{Born}} + \ln \gamma_i^{*\mathrm{lc}} \tag{4}$$

where $\gamma_i^{*\mathrm{pdh}}$ is the long-range interaction contribution term (the Pitzer−Debye−Hückel equation); $\gamma_i^{*\mathrm{Born}}$ is the Born term that transfers the reference state of ions from the infinitely dilute state in a mixed solvent into an aqueous infinitely dilute state; and $\gamma_i^{*\mathrm{lc}}$ is the short-range interaction contribution term (based on the local composition concept of the original NRTL model), respectively. The superscript * represents the unsymmetrical convention (reference state at infinite dilution). The electrolyte-NRTL model can be reduced to the original NRTL model for salt-free systems. The detailed expression for each term has been given elsewhere.[3−6] In the LLE calculation for salt-containing systems, the density (ρ) and the specific dielectric constant (ε_{r}) of each solvent in this research are given in Table 6.

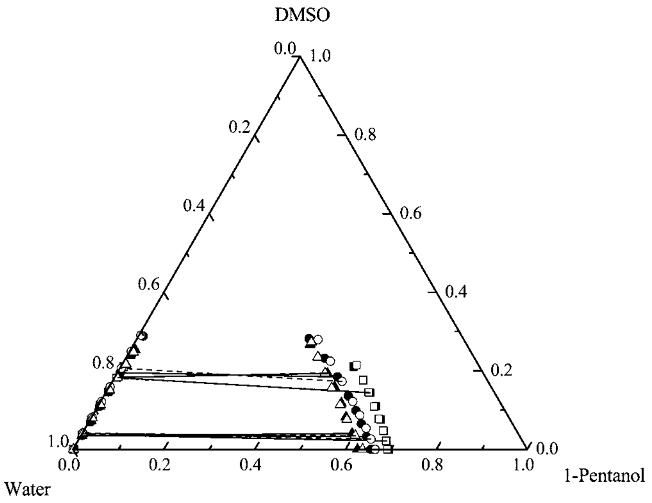

Figure 5. Comparison of calculated results with experimental values for water (1) + DMSO (2) + 1-pentanol (3) + KBr (4), each coordinate variable is mole fraction on KBr-free basis: ■, exptl data at 283.15 K; ●, exptl data at 303.15 K; ▲, exptl data at 323.15 K; −, exptl tie line; □, electrolyte-NRTL correlation at 283.15 K; ○, electrolyte-NRTL correlation at 303.15 K; Δ, electrolyte-NRTL correlation at 323.15 K; ----, electrolyte-NRTL tie line.

To represent the phase equilibrium of mixed electrolyte systems by using the electrolyte-NRTL model, it is necessary to determine the binary interaction parameters for each pair in the system. To make the parameter determination tractable for multicomponent systems, we first determine nine model parameters including nonrandomness parameters in the salt-free ternary system from liquid−liquid phase equilibrium data of water + dimethyl sulfoxide + 1-pentanol. After the pair parameters of the salt-free system have been determined, we will then determine the other nine salt-related model parameters for each salt-containing quaternary system from their liquid−liquid phase equilibrium data.

According to the procedure above, we employ the electrolyte-NRTL model to correlate ternary LLE data of water + dimethyl sulfoxide + 1-pentanol and two quaternary systems of water + dimethyl sulfoxide + 1-pentanol + NaBr or + KBr by adjusting binary interaction parameters. The objective function of the parameter determination is defined as

$$\Delta = \left(\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{n_c} |(x_{ijk}^{\mathrm{calc}} - x_{ijk}^{\mathrm{obs}})|\right)/2n_c n \tag{5}$$

where n is the number of tie-lines; n_c is the number of components; and x_{ijk}^{calc} and x_{ijk}^{obs} are the calculated and the observed mole fractions of component i in phase j on tie line k, respectively. Tables 7 to 9 present the correlated results from the electrolyte-NRTL for the ternary system of water + dimethyl sulfoxide + 1-pentanol and two quaternary systems of water + dimethyl sulfoxide + 1-pentanol + NaBr or + KBr, respectively. Figures 1, 4, and 5 also compare the calculated binodal locus and tie-lines from the electrolyte-NRTL model with the experimental results on a salt-free basis. As seen from Figures 1, 4, and 5, good agreement between the calculated results from the electrolyte-NRTL model and experimental values have been obtained for these investigated systems.

Conclusions

Liquid−liquid equilibrium (LLE) data for one ternary system of water + dimethyl sulfoxide + 1-pentanol and two quaternary systems of water + dimethyl sulfoxide + 1-pentanol + NaBr or + KBr were determined at atmospheric pressure over a temperature range of (283.15 to 323.15) K. All the investigated systems formed a type 1 phase diagram of LLE. The two-phase region decreased with increasing temperature for each ternary or quaternary system. The liquid phase splitting for the ternary system of water + dimethyl sulfoxide + 1-pentanol can be enhanced by adding the same percentage of salts, and the influence of NaBr is slightly more significant than that of KBr. In general, the binodal locus and tie lines of LLE could be correlated well with the electrolyte-NRTL model in this research.

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