Liquid–Liquid Equilibria for the Quaternary Systems of Water + *N*-Methyl-2-pyrrolidone + 1-Hexanol + NaCl, + KCl, or + KAc

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Liquid–liquid equilibrium data have been measured for one ternary system of water + *N*-methyl-2-pyrrolidone + 1-hexanol and three quaternary systems of water + *N*-methyl-2-pyrrolidone + 1-hexanol + sodium chloride, + potassium chloride, or + potassium acetate at temperatures (283.15 and 323.15) K under atmospheric pressure. The liquid-phase splitting for the ternary system of water + *N*-methyl-2-pyrrolidone + 1-hexanol can be enhanced by adding the same percentage of salts (sodium chloride, potassium chloride, or potassium acetate), and the influence follows the order of sodium chloride > potassium chloride > potassium acetate. The experimental data were also compared with the values calculated by the electrolyte-NRTL model. In general, the model reproduces reasonably for the LLE phase diagrams.

Introduction

The stripper agent is an important material for photolithography technology in the manufacture of electronic industries. It is imperative for electronic industries to investigate the recovery of the 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 stripper agent. The reliable liquid–liquid equilibrium (LLE) 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. The focus of this paper is placed on the phase behavior of LLE for the ternary system of water + *N*-methyl-2-pyrrolidone (NMP, the main component of the stripper agent) + 1-hexanol (extractant) and three quaternary systems of water + NMP + 1-hexanol + sodium chloride (NaCl), + potassium chloride (KCl), or + potassium acetate (KAc) at temperatures of (283.15 and 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 model.[1–3] The electrolyte-NRTL model can be reduced to the original NRTL model[4] for salt-free systems. Good quantitative agreement was obtained with these models.

Experimental Section

Chemicals. *N*-Methyl-2-pyrrolidone was obtained from Mallinckrodt. 1-Hexanol 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 chloride and potassium acetate were purchased from Riedel-deHaën. Potassium chloride was obtained from J. T. Baker. The salt compounds were dried in an oven until the weight remained as a constant before being used. All the liquid chemicals were checked with chromatographic analysis and 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,[5] basically including a jacketed glass cell, a thermostatically controlled bath, a magnetic agitator, and a gas chromatograp. 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. The prepared mixtures were introduced into the equilibrium cell and were agitated vigorously at least 3 h to sufficiently mix the compounds and then settled at least 8 h for complete phase separation. The sample of the organic-rich phase was carefully taken from the top sampling port of the cell with a syringe, and that of the water-rich phase was taken from a bottom sampling port of the cell. This operating method can avoid cross contamination by the other phase during the sampling procedure.

The composition of salt in each phase was determined gravimetrically by transferring a liquid sample (about 2 cm^3) on watch glasses and drying in a vacuum oven until the weight of salt remained constant. The uncertainty of the weight determination using an Ohaus AR2140 balance is ± 0.1 mg. The composition of salt-free constituents in each phase was analyzed by a gas chromatograph (GC) (model: 9800, China Chromatography Co., Taiwan) with a thermal conductivity detector (TCD) and using high-purity helium (99.99 %) as a carrier gas. A stainless steel column packed with 10 % Porapak Qs 60/80 (2 m × 1/8 in.) can clearly separate the constituent compounds of the salt-free samples. To prevent salt from entering into the gas chromatography column, a stainless steel tube packed with glass wools was used as a filter and was connected at the entry of the column. The filter was replaced when a significant amount of salt was trapped. Five samples were replicated for each phase at a fixed experimental condition. For the salt-free constituents, the area fraction 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

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Table 1. Average Deviations of GC Calibration Curves

mixture	phase	average deviations[a]
water + 1-hexanol	organic	0.001418
	aqueous	0.000012
NMP + 1-hexanol	organic	0.000204
	aqueous	0.000204

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

Table 2. LLE Data for Water (1) + NMP (2) + 1-Hexanol (3) at Atmospheric Pressure

	organic phase			aqueous phase		
T/K	x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{I}
283.15	0.2809	0.0000	0.7191	0.9990	0.0000	0.0010
	0.3358	0.0399	0.6244	0.9868	0.0121	0.0012
	0.3560	0.0588	0.5852	0.9739	0.0246	0.0015
	0.3904	0.0806	0.5290	0.9590	0.0389	0.0021
	0.4113	0.0936	0.4951	0.9502	0.0472	0.0025
	0.4408	0.1076	0.4516	0.9356	0.0609	0.0035
	0.4676	0.1219	0.4105	0.9260	0.0696	0.0044
	0.4966	0.1359	0.3675	0.9091	0.0850	0.0059
323.15	0.3268	0.0000	0.6732	0.9993	0.0000	0.0007
	0.3639	0.0378	0.5983	0.9947	0.0044	0.0009
	0.3878	0.0543	0.5579	0.9905	0.0086	0.0010
	0.4256	0.0738	0.5006	0.9837	0.0150	0.0013
	0.4636	0.0943	0.4421	0.9677	0.0298	0.0025
	0.5216	0.1080	0.3704	0.9597	0.0369	0.0034
	0.5519	0.1150	0.3331	0.9471	0.0479	0.0050
	0.5722	0.1180	0.3098	0.9385	0.0550	0.0065

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. Because no literature LLE data are available at comparable conditions for those ternary and quaternary systems above, the LLE measurements of the ternary system water + ethanol + 1-pentanol and a quaternary system water + ethanol + 1-pentanol + KCl at 298.15 K were conducted to test the validity of our experimental procedure. Figure 1 compares the experimental results with the literature values.[6] It shows that our measurements agree with literature values within the experimental uncertainties.

Experimental Results

The experimental apparatus was first employed to measure the LLE data of water + *N*-methyl-2-pyrrolidone + 1-hexanol at (283.15 and 323.15) K under atmospheric pressure. Table 2 reports the experimental results. The superscript I represents the organic-rich phase, and II represents the aqueous phase. Figure 2 is the phase diagram for the ternary system of water + *N*-methyl-2-pyrrolidone + 1-hexanol. Because water/1-hexanol 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, especially near the plait point. The experimental results show that the solubilities of water in the 1-hexanol increase with an increase of temperature. Because the system of water + *N*-methyl-2-pyrrolidone + 1-hexanol behaves as a type 1 LLE, the effects of adding an electrolyte (a salt) on the mutual solubilities of water + 1-hexanol can provide useful indications for the liquid-phase splitting enhancement. The electrolytes used in this research are NaCl, KCl, and KAc. The experimental results show that the immiscibility gaps are substantially enlarged as NaCl, KCl, or KAc was introduced in the aqueous solutions. Figure 3 illustrates that the solubilities of water in the organic-rich phase decrease with increasing concentration of the electrolytes (NaCl, KCl, or KAc) at (283.15 and 323.15) K. The influential magnitudes follow the order of NaCl > KCl > KAc. As seen from Figure 3, the concentrations higher than 5 wt % of NaCl and KCl will be saturated at the isotherm of (283.15 or 323.15) K. Mutual solubilities of water and 1-hexanol at 5 wt % salt are given in Table 3.

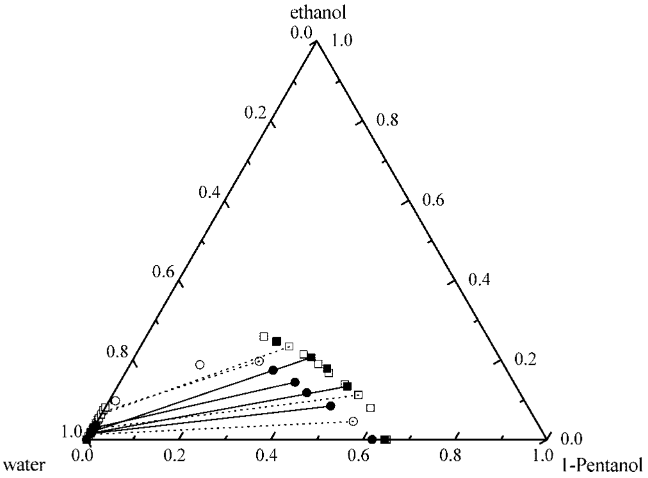

Figure 1. LLE phase diagram for water (1) + ethanol (2) + 1-pentanol (3) + KCl (4) at 298.15 K: •, this work (KCl-free); ■, this work (5 wt % KCl); ○, ref 6 data (KCl-free); □, ref 6 data (5 wt % KCl); —, this work tie line; . . ., ref 6 tie line, each coordinate variable is the mole fraction on a KCl-free basis.

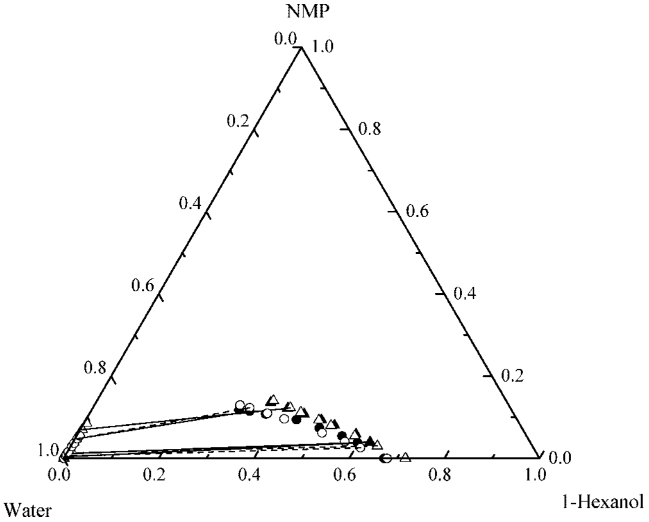

Figure 2. LLE phase diagram for water (1) + NMP (2) + 1-hexanol (3): ▲, exptl data at 283.15 K; •, exptl data at 323.15 K; —, exptl tie line; Δ, NRTL correlation at 283.15 K; ○, NRTL correlation at 323.15 K; —, NRTL tie line.

In this paper, the LLE measurements of three quaternary systems, water + *N*-methyl-2-pyrrolidone + 1-hexanol with NaCl, KCl, or KAc, were further made at temperatures (283.15 and 323.15) K under atmospheric pressure. The composition of the salt compounds in the initial feed was 5 wt % in each run. Tables 4 to 6 list the experimental results for water + *N*-methyl-2-pyrrolidone + 1-hexanol with NaCl, KCl, or KAc, respectively. The 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

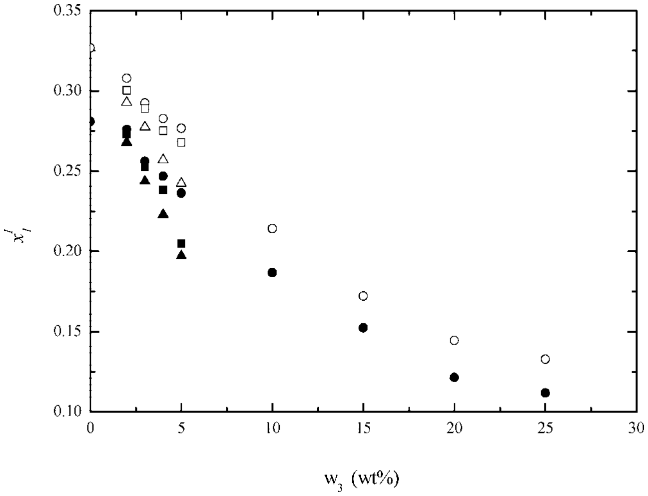

Figure 3. Solubilities of water in the organic-rich phase for water (1) + 1-hexanol (2) + salt (3): (•, KAc; ■, KCl; ▲, NaCl) at 283.15 K; (○, KAc; □, KCl; Δ, NaCl) at 323.15 K.

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

	organic phase			aqueous phase		
salt used	1-hexanol	water	salt	1-hexanol	water	salt
			T = 283.15 K			
no salt used	0.7191	0.2809	. . .	0.0010	0.9990	. . .
potassium acetate	0.7636	0.2364	. . .	0.0001	0.9753	0.0246
potassium chloride	0.7952	0.2048	. . .	0.0002	0.9715	0.0283
sodium chloride	0.8029	0.1971	. . .	0.0000	0.9602	0.0398
			T = 323.15 K			
no salt used	0.6732	0.3268	. . .	0.0007	0.9993	. . .
potassium acetate	0.7162	0.2838	. . .	0.0004	0.9747	0.0249
potassium chloride	0.7232	0.2768	. . .	0.0001	0.9663	0.0336
sodium chloride	0.7450	0.2550	. . .	0.0000	0.9578	0.0422

Table 4. LLE Data for Water (1) + NMP (2) + 1-Hexanol (3) + NaCl (4) at Atmospheric Pressure

	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	0.1971	0.0000	0.8029	0.0000	0.9602	0.0000	0.0000	0.0398
	0.2392	0.0575	0.7033	0.0000	0.9467	0.0110	0.0003	0.0420
	0.2577	0.0829	0.6594	0.0001	0.9365	0.0185	0.0004	0.0446
	0.2728	0.1040	0.6215	0.0017	0.9283	0.0262	0.0005	0.0450
	0.2880	0.1253	0.5850	0.0018	0.9204	0.0338	0.0008	0.0451
	0.3035	0.1438	0.5502	0.0025	0.9098	0.0426	0.0011	0.0464
	0.3166	0.1645	0.5157	0.0031	0.9009	0.0500	0.0014	0.0477
	0.3410	0.1852	0.4682	0.0056	0.8875	0.0603	0.0020	0.0503
323.15	0.2550	0.0000	0.7450	0.0000	0.9578	0.0000	0.0000	0.0422
	0.3122	0.0776	0.6097	0.0005	0.9494	0.0066	0.0002	0.0438
	0.3365	0.1004	0.5617	0.0013	0.9429	0.0105	0.0003	0.0463
	0.3756	0.1381	0.4846	0.0016	0.9315	0.0197	0.0005	0.0483
	0.3907	0.1541	0.4516	0.0037	0.9242	0.0246	0.0009	0.0504
	0.4030	0.1637	0.4294	0.0039	0.9198	0.0278	0.0010	0.0514
	0.4121	0.1707	0.4123	0.0049	0.9161	0.0298	0.0012	0.0529
	0.4241	0.1782	0.3912	0.0065	0.9103	0.0352	0.0015	0.0530

temperature for the three investigated quaternary systems. Figure 4 compares the LLE phase diagrams for the systems of water + N-methyl-2-pyrrolidone + 1-hexanol with NaCl, KCl, or KAc at 283.15 K. By adding the same percentage of salts, the magnitudes of phase-splitting enhancement also follow the order of NaCl > KCl > KAc.

Table 5. LLE Data for Water (1) + NMP (2) + 1-Hexanol (3) + KCl (4) at Atmospheric Pressure

	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	0.2048	0.0000	0.7952	0.0000	0.9715	0.0000	0.0002	0.0283
	0.2388	0.0389	0.7223	0.0000	0.9608	0.0066	0.0003	0.0324
	0.2579	0.0547	0.6873	0.0001	0.9561	0.0105	0.0005	0.0329
	0.2880	0.0772	0.6346	0.0002	0.9476	0.0179	0.0006	0.0339
	0.3019	0.0842	0.6132	0.0007	0.9427	0.0225	0.0007	0.0341
	0.3135	0.0949	0.5908	0.0008	0.9374	0.0267	0.0008	0.0352
	0.3353	0.1125	0.5511	0.0010	0.9283	0.0347	0.0012	0.0359
	0.3471	0.1217	0.5299	0.0013	0.9234	0.0377	0.0012	0.0377
323.15	0.2768	0.0000	0.7232	0.0000	0.9663	0.0000	0.0001	0.0336
	0.3282	0.0687	0.6027	0.0004	0.9564	0.0068	0.0003	0.0365
	0.3624	0.0966	0.5401	0.0009	0.9510	0.0117	0.0005	0.0368
	0.3999	0.1326	0.4662	0.0013	0.9366	0.0238	0.0011	0.0386
	0.4173	0.1467	0.4334	0.0026	0.9298	0.0277	0.0014	0.0411
	0.4349	0.1568	0.4054	0.0028	0.9254	0.0298	0.0015	0.0433
	0.4461	0.1634	0.3869	0.0036	0.9228	0.0319	0.0017	0.0436
	0.4587	0.1723	0.3651	0.0040	0.9164	0.0374	0.0023	0.0439

Table 6. LLE Data for Water (1) + NMP (2) + 1-Hexanol (3) + KAc (4) at Atmospheric Pressure

	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	0.2364	0.0000	0.7636	0.0000	0.9753	0.0000	0.0001	0.0246
	0.2715	0.0577	0.6708	0.0000	0.9634	0.0105	0.0004	0.0256
	0.2938	0.0811	0.6242	0.0009	0.9556	0.0170	0.0006	0.0269
	0.3217	0.1011	0.5757	0.0016	0.9441	0.0260	0.0010	0.0289
	0.3446	0.1182	0.5353	0.0019	0.9358	0.0331	0.0012	0.0299
	0.3726	0.1372	0.4883	0.0020	0.9252	0.0419	0.0022	0.0307
	0.4010	0.1570	0.4399	0.0022	0.9156	0.0509	0.0026	0.0309
	0.4182	0.1658	0.4127	0.0033	0.9086	0.0548	0.0032	0.0334
323.15	0.2838	0.0000	0.7162	0.0000	0.9747	0.0000	0.0004	0.0249
	0.3442	0.0697	0.5858	0.0003	0.9651	0.0077	0.0007	0.0265
	0.3788	0.1001	0.5205	0.0005	0.9583	0.0131	0.0010	0.0276
	0.4046	0.1293	0.4642	0.0020	0.9480	0.0222	0.0014	0.0285
	0.4199	0.1457	0.4320	0.0024	0.9403	0.0290	0.0019	0.0287
	0.4382	0.1614	0.3966	0.0038	0.9377	0.0306	0.0020	0.0297
	0.4499	0.1652	0.3805	0.0043	0.9314	0.0337	0.0021	0.0328
	0.4849	0.1703	0.3401	0.0047	0.9251	0.0384	0.0025	0.0341

To estimate the capability of 1-hexanol for separating the water + N-methyl-2-pyrrolidone mixture by adding different salts at LLE, the distribution ratio, K, and the selectivity, S, for component N-methyl-2-pyrrolidone were calculated. The distribution ratio and the selectivity are

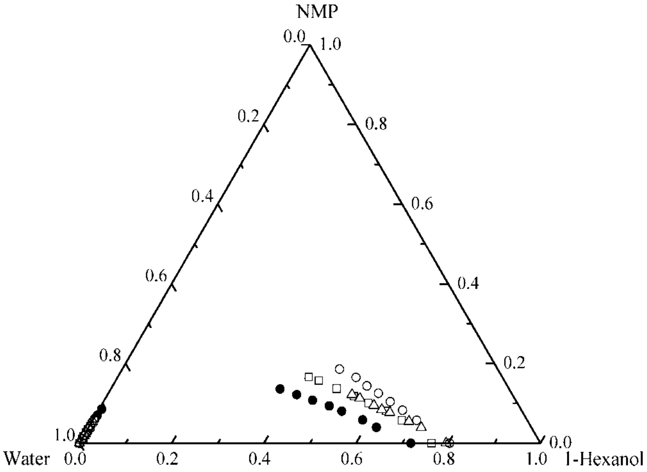

Figure 4. Comparison of LLE phase diagrams for water (1) + NMP (2) + 1-hexanol (3) with different salts at 283.15 K. Each coordinate variable is in mole fraction on a salt-free basis: •, ternary (salt-free); □, 5 wt % KAc; Δ, 5 wt % KCl; ○, 5 wt % NaCl.

$$K_{\mathrm{NMP}} = \frac{x_{\mathrm{NMP}}^{\mathrm{II}}}{x_{\mathrm{NMP}}^{\mathrm{I}}} \tag{1}$$

$$S_{\mathrm{NMP}} = \frac{x_{\mathrm{NMP}}^{\mathrm{I}} \cdot x_{\mathrm{w}}^{\mathrm{II}}}{x_{\mathrm{NMP}}^{\mathrm{II}} \cdot x_{\mathrm{w}}^{\mathrm{I}}} \tag{2}$$

where x is the molar fraction; the superscript I represents the organic-rich phase and II the aqueous phase; and the subscripts NMP and w represent the components *N*-methyl-2-pyrrolidone and water, respectively. Figures 5 and 6 show the distribution ratio, K, and the selectivity, S, as a function of *N*-methyl-2-pyrrolidone composition on the aqueous phase for the investigated systems at 323.15 K, respectively. As seen from Figures 5 and 6, the *N*-methyl-2-pyrrolidone is effectively removed from the aqueous phase while the different salts are added, especially in the case of NaCl.

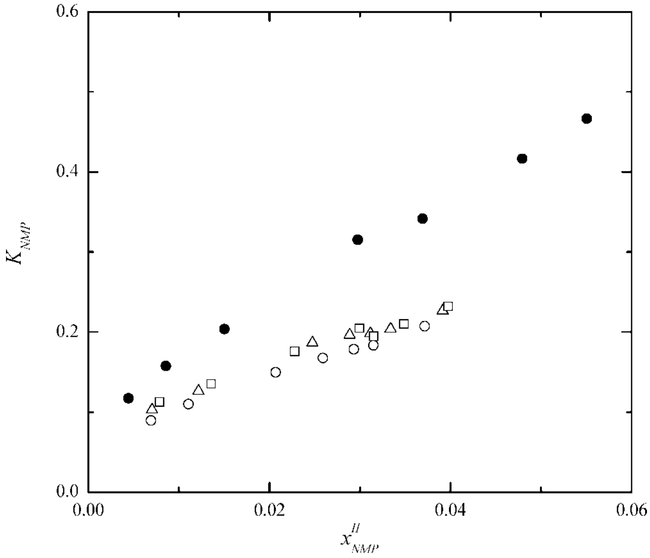

Figure 5. Distribution ratio of *N*-methyl-2-pyrrolidone in two liquid phases at 323.15 K: •, ternary (salt-free); □, 5 wt % KAc; Δ, 5 wt % KCl; ○, 5 wt % NaCl.

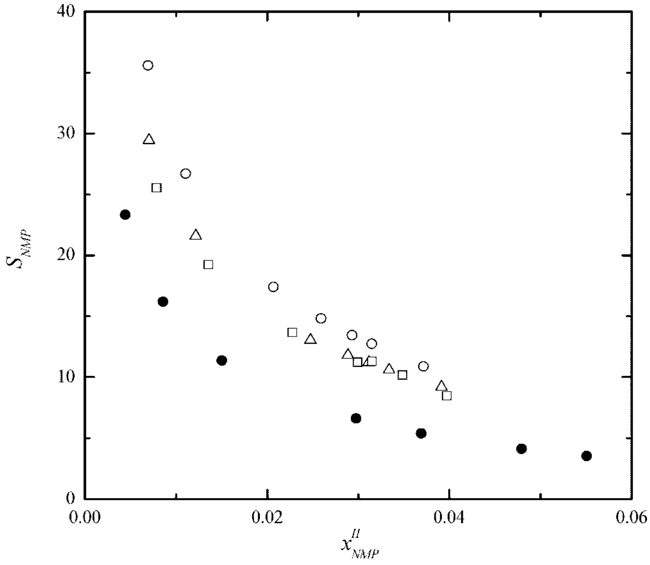

Figure 6. Selectivity of *N*-methyl-2-pyrrolidone in two liquid phases at 323.15 K: •, ternary (salt-free); □, 5 wt % KAc; Δ, 5 wt % KCl; ○, 5 wt % NaCl.

Table 7. Properties of Solvents

solvent	d/kg·m^{-3}	ϵ_r^{a,11} a	b	c
water	0.9980 (298.15 K)[8]	249.2100	−0.79069	0.00073
1-hexanol	0.81841 (293.15 K)[9]	62.7440	−0.24214	0.00024
NMP	1.0157 (313.15 K)[10]	32.55	0.0	0.0

[a] $\epsilon_r = a + bT + cT^2$.

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 3, together with the material balance equation.

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

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 by Walas.[7] On the basis of 1 mol of feed with total composition z_i, the compositions of the coexistent liquid phases were solved simultaneously from the following equations:

$$1 - \sum_{i=1}^{n_c} \frac{z_i}{\beta + K_i(1-\beta)} = 0 \tag{4}$$

with

$$K_i = x_i^{\mathrm{II}}/x_i^{\mathrm{I}} = \gamma_i^{\mathrm{I}}/\gamma_i^{\mathrm{II}} \tag{5}$$

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[1–3]

$$\ln r_i^* = \ln r_i^{*\mathrm{pdh}} + \ln r_i^{*\mathrm{Born}} + \ln r_i^{*\mathrm{lc}} \tag{6}$$

where $\gamma^{*\mathrm{pdh}}$ is the long-range interaction contribution term (the Pitzer–Debye–Hückel equation); $\gamma^{*\mathrm{Born}}$ 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 $\gamma^{*\mathrm{lc}}$ 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.[1–3] In the LLE calculation for salt-containing systems, the density (d) and the specific dielectric constant (ϵ_r) of each solvent in this research are given in Table 7.

To represent the phase equilibrium of mixed electrolyte systems by using the electrolyte-NRTL model, it is necessary to determine the binary adjustable 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 + *N*-methyl-2-pyrrolidone + 1-hexanol. 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 original NRTL model to correlate the LLE data of water + *N*-methyl-

Table 8. Correlated Results from the NRTL Model for Water (1) + NMP (2) + 1-Hexanol (3)

T/K	α_{ij}	$i-j$	$\Delta g_{ij}{}^{\mathrm{a}}$ / kJ·mol^{-1}	$\Delta g_{ji}{}^{a}$ / kJ·mol^{-1}
283.15	0.276	1–2	8.575	−4.967
	0.275	1–3	15.535	1.617
	0.313	2–3	2.389	−1.063
323.15	0.276	1–2	13.405	−6.142
	0.275	1–3	16.607	1.129
	0.313	2–3	2.063	−0.014

T/K	phase	$\Delta x_1{}^c$ AAD	Δx_2 AAD	Δx_3 AAD	grand AAD^b
283.15	organic	0.0059	0.0032	0.0063	0.0027
	aqueous	0.0003	0.0002	0.0002	
323.15	organic	0.0062	0.0074	0.0098	0.0042
	aqueous	0.0007	0.0005	0.0004	

[a] Δg_{ij} is a parameter of the NRTL model, where g_{ij} is the interaction energy between the $i-j$ pair. [b] Grand ADD = $(\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}|(x_{ijk}^{\mathrm{calcd}} - x_{ijk}^{\mathrm{obsd}})|)/6n$, where n is the number of tie-lines. [c] Δx_i is the deviation between calculated x_i and observed x_i for component i.

2-pyrrolidone + 1-hexanol by adjusting nine model parameters simultaneously. The objective function of the parameter determination is defined as

$$\triangle = \left(\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}|(x_{ijk}^{\mathrm{calcd}} - x_{ijk}^{\mathrm{obsd}})|\right)/6n \tag{7}$$

where n is the number of tie-lines and x_{ijk}^{calcd} and x_{ijk}^{obsd} are the calculated and the observed mole fractions of component i in phase j on tie-line k, respectively. Table 8 presents the correlated results from the NRTL model. Figure 2 also compares the calculated binodal locus and tie-lines from the NRTL model with the experimental results. As seen from Figure 2, good agreements between the calculated results from the NRTL model and experimental values have been obtained for the water + *N*-methyl-2-pyrrolidone + 1-hexanol system.

For the three quaternary systems of water + *N*-methyl-2-pyrrolidone + 1-hexanol + NaCl, KCl, or KAc, the isothermal LLE data were correlated with the electrolyte-NRTL model by adjusting the other nine salt-related parameters simultaneously. The objective function of the parameter determination is defined as

$$\triangle = \left(\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}|(x_{ijk}^{\mathrm{calcd}} - x_{ijk}^{\mathrm{obsd}})|\right)/8n \tag{8}$$

where n is the number of tie-lines and x_{ijk}^{calcd} and x_{ijk}^{obsd} are the calculated and observed mole fractions of component i in phase j on tie-line k, respectively. Tables 9 to 11 present the correlated results from the electrolyte-NRTL model for three quaternary systems of water + *N*-methyl-2-pyrrolidone + 1-hexanol + NaCl, KCl, or KAc, respectively. As seen from Tables 9 to 11, good agreements between the calculated results from the electrolyte-NRTL model and experimental values have been obtained for the three investigated quaternary systems.

Table 9. Correlated Results from the Electrolyte-NRTL Model for Water (1) + NMP (2) + 1-Hexanol (3) + NaCl (4)

T/K	α_{ij}	$i-j$	$\Delta g_{ij}{}^{a}$ / kJ·mol^{-1}	$\Delta g_{ji}{}^{a}$ / kJ·mol^{-1}
283.15	0.20	1–4	14.279	−13.448
	0.05	2–4	20.899	−13.564
	0.05	3–4	64.977	>1.168
323.15	0.20	1–4	15.124	−13.660
	0.05	2–4	31.946	−10.952
	0.05	3–4	71.238	21.894

T/K	phase	$\Delta x_1{}^c$ AAD	Δx_2 AAD	Δx_3 AAD	Δx_4 AAD	grand AAD^b
283.15	organic	0.0052	0.0030	0.0035	0.0018	0.0026
	aqueous	0.0024	0.0024	0.0004	0.0017	
323.15	organic	0.0070	0.0042	0.0054	0.0028	0.0037
	aqueous	0.0041	0.0031	0.0006	0.0027	

[a] Δg_{ij} is a parameter of the electrolyte-NRTL model, where g_{ij} is the interaction energy between the $i-j$ pair. The values of nonrandomness parameters (α_{ij} and binary interaction parameters (Δg_{ij} and Δg_{ji}) for (1–2), (1–3), and (2–3) pairs are the same as in Table 8. [b] Grand ADD = $(\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}|(x_{ijk}^{\mathrm{calcd}} - x_{ijk}^{\mathrm{obsd}})|)/8n$, where n is the number of tie-lines. [c] Δx_i is the deviation between calculated x_i and observed x_i for component i.

Table 10. Correlated Results from the Electrolyte-NRTL Model for Water (1) + NMP (2) + 1-Hexanol (3) + KCl (4)

T/K	α_{ij}	$i-j$	$\Delta g_{ij}{}^{a}$ / kJ·mol^{-1}	$\Delta g_{ji}{}^{a}$ / kJ·mol^{-1}
283.15	0.20	1–4	10.665	−13.077
	0.05	2–4	51.178	−15.044
	0.05	3–4	27.391	−0.368
323.15	0.20	1–4	16.238	−13.770
	0.05	2–4	61.146	−15.174
	0.05	3–4	74.521	−0.019

T/K	phase	$\Delta x_1{}^c$ AAD	Δx_2 AAD	Δx_3 AAD	Δx_4 AAD	grand AAD^b
283.15	organic	0.0089	0.0037	0.0061	0.0005	0.0034
	aqueous	0.0030	0.0032	0.0013	0.0005	
323.15	organic	0.0077	0.0037	0.0056	0.0019	0.0035
	aqueous	0.0039	0.0027	0.0006	0.0019	

[a] See footnote *a* in Table 9. [b] See footnote *b* in Table 9. [c] See footnote *c* in Table 9.

Table 11. Correlated Results from the Electrolyte-NRTL Model for Water (1) + NMP (2) + 1-Hexanol (3) + KAc (4)

T/K	α_{ij}	$i-j$	$\Delta g_{ij}{}^{a}$ / kJ·mol^{-1}	$\Delta g_{ji}{}^{a}$ / kJ·mol^{-1}
283.15	0.20	1–4	15.623	−13.783
	0.05	2–4	25.626	−15.500
	0.05	3–4	35.500	224.915
323.15	0.20	1–4	18.252	−15.758
	0.05	2–4	25.167	−12.827
	0.05	3–4	54.677	6.508

T/K	phase	$\Delta x_1{}^c$ AAD	Δx_2 AAD	Δx_3 AAD	Δx_4 AAD	grand AAD^b
283.15	organic	0.0116	0.0041	0.0087	0.0015	0.0043
	aqueous	0.0031	0.0030	0.0012	0.0015	
323.15	organic	0.0121	0.0037	0.0084	0.0022	0.0044
	aqueous	0.0035	0.0024	0.0008	0.0023	

[a] See footnotes *a* in Table 9. [b] See footnotes *b* in Table 9. [c] See footnote *c* in Table 9.

Conclusions

Liquid–liquid equilibrium (LLE) data for one ternary system of water + *N*-methyl-2-pyrrolidone + 1-hexanol and three quaternary systems of water + *N*-methyl-2-pyrrolidone + 1-hexanol + NaCl, + KCl, or + KAc 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 + *N*-methyl-2-pyrrolidone + 1-hexanol can be enhanced by adding the same percentage of salts, and the influence follows the order of NaCl > KCl > KAc. 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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