Liquid−Liquid Equilibria for Systems of 1-Butanol + Water + 2,6-Diaminopyridine and 1-Butanol + Water + 2-Aminopyridine

Wei-Lan Xue,* Chuan-Shun Zhang, Zuo-Xiang Zeng, and Xu-Hui Chen

Institute of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

Liquid−liquid equilibrium (LLE) data were measured under atmospheric pressure for (1-butanol + water + 2,6-diaminopyridine) at (289.55, 300.65, and 317.05) K and for (1-butanol + water + 2-aminopyridine) at (295.85, 307.15, and 319.65) K. The experimental data were correlated by the Hand equation. The correlated tie line results were compared with the experimental ones, and good agreements were obtained with an average deviation of 3 %. Both the selectivities (*S*) and distribution ratios (*K*) of the aminopyridines were calculated from the LLE data, and the results showed that 1-butanol was a suitable solvent used for the extraction of the aminopyridines from water.

Introduction

Solvent extraction is a common separation process in various chemical, petrochemical, and fine chemical industries. Many processes use single or mixed solvents to separate organic compounds from water.[1−3] The importance of the availability of LLE data in the design of liquid−liquid extraction has been the subject of much interest in recent years.

2,6-Diaminopyridine (CAS Registry No. 141-86-6) is a white to gray crystal, which is useful in the chemical industry. For example, it is an intermediate in the manufacturing of the analgesic phenazopyridine hydrochloride[4,5] and a novel antibacterial dihydropyridone carboxylic acid derivative.[6] It can also be used in the production of polyamides.[7] Additionally, a hair dye that is synthesized using 2,6-diaminopyridine as a coupler agent shows a good dyeing capacity.[8,9]

2-Aminopyridine (CAS Registry No. 504-29-0) is also a useful intermediate of dyestuffs and pharmaceuticals.[10,11] Both 2,6-diaminopyridine and 2-aminopyridine are mainly prepared by the Chichibabin reaction and hydrolysis reaction.[12] After the reaction is completed, the products exist in an aqueous solution. Organic solvents can be used for the extraction of the aminopyridines to obtain pure products. Hence the solubility and LLE data related to the aminopyridines are important. The solubilities of the aminopyridines in some solvents have been reported,[13,14] but the LLE data are not available in the literature. In this paper, LLE for systems of 1-butanol + water + 2,6-diaminopyridine and 1-butanol + water + 2-aminopyridine were reported at three temperatures. The experimental data were correlated by the Hand equation. The usefulness of 1-butanol as a solvent used for extracting the aminopyridines from water solution was discussed based on the LLE data.

Experimental Section

Materials. 2,6-Diaminopyridine and 2-aminopyridine prepared in the laboratory were recrystallized prior to use. Their mass fraction purities determined by HPLC were better than 99.8 %. The melting temperature range of 2,6-diaminopyridine and 2-aminopyridine was determined to be (394.25 to 395.15) K and (330.45 to 330.95) K, respectively, and the values reported in the literature were (394.65 and 330.65) K, respectively.[15] 1-Butanol with analytical reagent grade was purchased from Shanghai Chemistry Reagent Co., China. It was stored over molecular sieves to remove trace water shortly before use. The mass fraction purity of 1-butanol was higher than 99.9 % (GC). Karl Fischer titration gave a water mass fraction of less than 0.02 %. Water was purified by a Millipore Milli-RO PLUS 10 and Milli-Q system with a resistivity of more than 18.2 MΩ·cm.

Apparatus and Procedure. The apparatus and the procedure were similar to that described in the literature.[16,17] The equilibrium runs were performed in 150 cm^3 extraction cells surrounded by water jackets. A mercury-in-glass thermometer was used to determine the temperature of the cell. The thermometer had a measurement range from (273.15 to 323.15) K with an uncertainty of 0.05 K. First, 1-butanol [(40 ± 2) g] and water [(70 ± 2) g] were added into the cell. When the required temperature of the cell was reached, 2,6-diaminopyridine or 2-aminopyridine weighted was added in batches. The mixture was vigorously shaken for 2 h with a mangnetic stirrer and allowed to settle for 2 h to make the liquid−liquid system reach equilibrium. Longer mixing and setting periods did not result in any sensible change in the phase compositions. A Mettler H542 balance used here had a range of measurement up to 160 g with an uncertainty of 0.00001 g, and the estimated uncertainties in the mole fraction were less than 0.3 %.

Analysis. The relative concentrations of 1-butanol and water were determined by GC equipped with a thermal conductivity detector (TCD), a column (2 m × 2 mm) packed with 10 % porapak QS 80/100,[18] and a Shimadzu C-R2AX integrator. Samples of (0.5 to 1.0) μL were taken from both phases by a microsyringe and introduced very quickly into the GC. The injection temperature was 440 K, and the detector temperature was 380 K. The carrier gas (hydrogen) flow rate was maintained at 40 $mL \cdot min^{-1}$. A series of standard samples were confected by 1-butanol and water of known masses of different components, and they were analyzed using the same GC conditions as those for the equilibrium samples. After obtaining the corresponding assay value, the functional relation of the assay value, and the real value of the sample, the standard studying curves were established. According to

---

* Corresponding author. E-mail: wlxue@ecust.edu.cn.

10.1021/je8007843 CCC: $40.75

Table 1. Experimental LLE Data for Water (1) + 2,6-Diaminopyridine (2) + 1-Butanol (3) at 289.55 K, 300.65 K, and 317.05 K

100 x_1^w	100 x_2^w	100 x_3^w	100 x_1^o	100 x_2^o	100 x_3^o	100 x_{2cal}^o	$(x_2^o - x_{2cal}^o)/(x_2^o)$	S	K
Water (1) + 2,6-Diaminopyridine (2) + 1-Butanol (3) at 289.55 K									
97.90	0.000	2.098	50.47	0.000	49.53	0.000	0.000		
97.76	0.084	2.152	50.96	0.400	48.64	0.438	−0.095	9.14	4.76
97.60	0.237	2.167	52.09	1.120	46.79	1.176	−0.050	8.85	4.73
97.54	0.279	2.185	53.33	1.290	45.38	1.341	−0.040	8.46	4.62
97.40	0.377	2.221	54.09	1.727	44.18	1.760	−0.019	8.25	4.58
97.28	0.463	2.257	55.57	2.088	42.35	2.070	0.009	7.90	4.51
97.11	0.595	2.294	57.25	2.550	40.20	2.521	0.011	7.27	4.29
97.03	0.660	2.315	58.22	2.795	38.99	2.712	0.030	7.06	4.23
96.96	0.709	2.336	58.48	2.915	38.61	2.884	0.011	6.82	4.11
96.76	0.848	2.390	60.03	3.166	36.80	3.287	−0.038	6.02	3.73
96.43	1.051	2.516	62.51	3.790	33.70	3.733	0.015	5.56	3.61
96.20	1.217	2.582	64.47	4.174	31.36	4.025	0.036	5.12	3.43
95.96	1.369	2.670	67.29	4.250	28.46	4.113	0.032	4.43	3.10
95.52	1.681	2.800	70.89	4.279	24.84	4.417	−0.032	3.43	2.55
Water (1) + 2,6-Diaminopyridine (2) + 1-Butanol (3) at 300.65 K									
98.18	0.000	1.820	50.56	0.000	49.44	0.000	0.000		
97.99	0.050	1.960	50.97	0.300	48.73	0.270	0.100	11.53	6.00
97.72	0.194	2.087	52.97	0.926	46.10	0.946	−0.022	8.80	4.77
97.48	0.336	2.180	54.91	1.501	43.59	1.532	−0.021	7.93	4.47
97.38	0.408	2.215	55.55	1.730	42.72	1.816	−0.050	7.43	4.24
97.30	0.463	2.235	56.67	1.954	41.37	1.990	−0.018	7.25	4.22
97.15	0.595	2.260	57.22	2.439	40.34	2.482	−0.018	6.96	4.10
96.99	0.723	2.288	57.99	2.803	39.21	2.921	−0.042	6.48	3.88
96.78	0.826	2.390	59.50	3.042	37.46	3.183	−0.046	5.99	3.68
96.45	0.994	2.557	62.62	3.569	33.82	3.454	0.032	5.53	3.59
96.13	1.139	2.732	63.68	3.666	32.65	3.820	−0.042	4.86	3.22
95.97	1.214	2.821	65.36	3.874	30.77	3.837	0.009	4.69	3.19
95.58	1.358	3.064	63.38	4.174	27.45	3.833	0.082	4.30	3.07
95.36	1.567	3.072	70.58	4.273	25.14	4.045	0.053	3.68	2.73
Water (1) + 2,6-Diaminopyridine (2) + 1-Butanol (3) at 317.05 K									
98.35	0.000	1.652	52.88	0.000	47.13	0.000	0.000		
98.27	0.070	1.660	53.76	0.330	45.91	0.300	0.091	8.62	4.71
98.17	0.134	1.692	54.78	0.559	44.66	0.561	−0.004	7.48	4.17
97.89	0.330	1.779	56.69	1.208	42.10	1.311	−0.085	6.32	3.66
97.37	0.501	2.133	59.04	1.828	39.14	1.863	−0.019	6.02	3.65
97.22	0.582	2.203	59.79	2.077	38.13	2.114	−0.018	5.80	3.57
96.94	0.760	2.303	60.36	2.771	36.87	2.680	0.033	5.86	3.65
96.64	0.941	2.418	62.58	3.123	34.29	3.099	0.008	5.12	3.32
96.46	1.051	2.491	64.04	3.354	32.60	3.298	0.017	4.81	3.19
96.24	1.205	2.557	66.37	3.485	30.14	3.507	−0.006	4.19	2.89
96.03	1.345	2.625	69.35	3.610	27.04	3.520	0.025	3.72	2.68
95.72	1.445	2.833	69.93	3.842	26.23	3.681	0.042	3.64	2.66
95.51	1.544	2.949	70.00	4.047	25.96	3.903	0.036	3.58	2.62
95.32	1.696	2.988	70.67	4.095	25.23	4.178	−0.020	3.26	2.41

the standard curve, the real relative concentration of 1-butanol and water can be obtained. The uncertainties of mole fraction measurements for each component were estimated to be less than 0.3 %.

The quantitative concentrations of the aminopyridines were determined by HPLC with an internal standard method. Analyses were performed using a Shimadzu LC-4A HPLC system equipped with a M481 UV-detector and a Shimadzu C-R2A data system. Samples [about (1 ± 0.00001) g] were taken from both phases by a syringe and mixed with a quantified internal standard. After uniform mixing, the mixtures were analyzed by HPLC. The HPLC working conditions were as follows: C_{18} column; mobile phase, methanol−water containing 0.1 % triethylamine and 0.02 $\text{mol} \cdot \text{L}^{-1}$ NH_4Ac (pH = 5.20) (10:90, vol./vol.); column temperature, 298.15 K; flow rate, 1.5 $\text{mL} \cdot \text{min}^{-1}$; injection volume, 5 μL; detector wavelength, 254 nm.[19] The HPLC was calibrated with pure aminopyridines and 2-amino-3-methylpyridine as an internal standard of known masses of different components covering a wide range of compositions. The standard samples were analyzed by HPLC at the same conditions. The uncertainties of mole fraction measurements for the aminopyridines were estimated to be less than 0.3 % for two phases.

If the sample taken from the organic or aqueous phase at high temperature was not clear at room temperature, more 1-butanol or water weighted was added to it, and then the diluted samples were analyzed by HPLC, which will tend to a 2-fold increase in the uncertainties of mole fraction of components.

All of the analyses were repeated four times, and the real concentrations of compositions can be obtained on the basis of the standard curves.

Results and Discussion

The LLE data for systems of (water + 2,6-diaminopyridine + 1-butanol) at (289.55, 300.65, and 317.05) K and (water + 2-aminopyridine + 1-butanol) at (295.85, 307.15, and 319.65) K were listed in Tables 1 and 2 and shown in Figures 1 to 6. For the systems studied, the selectivity (S) and distribution ratio (K) were important parameters in assessing the feasibility of utilizing 1-butanol to extract aminopyridines from water solution. They were given in terms of mole fraction[20]

$$S = \frac{x_2^o / x_1^o}{x_2^w / x_1^w} \tag{1}$$

$$K = \frac{x_2^o}{x_2^w} \tag{2}$$

where x_1^o and x_2^o are the mole fractions of water and aminopyridines in the organic phase and x_1^w and x_2^w are the mole fractions of water and aminopyridines in the aqueous phase. The values of S and K for the two systems were obtained according to eqs 1 and 2 and also listed in Tables 1 and 2. It is clear that the selectivities and distribution ratios

Table 2. Experimental LLE Data for Water (1) + 2-Aminopyridine (2) + 1-Butanol (3) at 295.85 K, 307.15 K, and 319.65 K

$100\,x_1^w$	$100\,x_2^w$	$100\,x_3^w$	$100\,x_1^o$	$100\,x_2^o$	$100\,x_3^o$	$100\,x_{2\mathrm{cal}}^o$	$(x_2^o - x_{2\mathrm{cal}}^o)/(x_2^o)$	S	K
Water (1) + 2-Aminopyridine (2) + 1-Butanol (3) at 295.85 K									
98.04	0.000	1.962	50.98	0.000	49.02	0.000	0.000		
97.74	0.120	2.144	51.91	1.608	46.48	1.484	0.077	25.23	13.40
97.61	0.216	2.177	54.24	2.535	43.23	2.508	0.011	21.12	11.74
97.46	0.334	2.211	55.61	3.605	40.78	3.687	−0.023	18.91	10.79
97.29	0.490	2.221	56.64	5.128	38.24	5.107	0.004	17.98	10.47
96.98	0.720	2.301	58.35	6.785	34.87	6.901	−0.017	15.66	9.42
96.74	0.933	2.329	61.08	7.892	31.03	8.006	−0.014	13.40	8.46
96.57	1.081	2.347	63.62	8.329	28.06	8.419	−0.011	11.70	7.70
96.35	1.262	2.392	66.39	8.553	25.06	8.818	−0.031	9.84	6.78
95.84	1.469	2.694	67.74	9.238	23.02	9.500	−0.028	8.90	6.29
95.55	1.712	2.742	69.86	9.719	20.42	9.873	−0.016	7.76	5.68
95.06	2.073	2.865	73.57	9.704	16.73	9.868	−0.017	6.05	4.68
94.66	2.433	2.906	76.46	9.616	13.92	9.704	−0.009	4.89	3.95
94.30	2.781	2.924	78.73	9.552	11.72	9.387	0.017	4.11	3.43
Water (1) + 2-Aminopyridine (2) + 1-Butanol (3) at 307.15 K									
98.26	0.000	1.742	52.24	0.000	47.76	0.000	0.000		
97.50	0.335	2.167	53.70	2.131	44.17	2.291	−0.075	11.55	6.36
97.25	0.551	2.198	56.11	3.488	40.40	3.639	−0.043	10.97	6.33
97.07	0.709	2.217	56.60	4.226	39.17	4.669	−0.105	10.22	5.96
96.77	0.905	2.321	59.81	5.321	34.87	5.459	−0.026	9.51	5.88
96.43	1.083	2.483	62.26	6.117	31.62	6.060	0.009	8.75	5.65
95.98	1.484	2.534	68.43	6.933	24.64	6.719	0.031	6.55	4.67
95.56	1.711	2.729	70.51	7.274	22.22	7.124	0.021	5.76	4.25
95.15	1.940	2.912	74.61	7.102	18.29	6.769	0.047	4.67	3.66
94.77	2.229	3.002	77.71	6.762	15.53	6.728	0.005	3.70	3.03
93.54	2.702	3.761	81.05	6.612	12.34	6.708	−0.015	2.82	2.45
93.17	3.048	3.780	83.60	6.451	9.949	6.203	0.038	2.36	2.12
92.97	3.166	3.860	85.51	5.736	8.755	5.705	0.005	1.97	1.81
92.60	3.457	3.942	87.48	5.110	7.412	5.346	−0.046	1.56	1.48
Water (1) + 2-Aminopyridine (2) + 1-Butanol (3) at 319.65 K									
98.34	0.000	1.661	54.01	0.000	45.99	0.000	0.000		
97.54	0.291	2.172	54.41	2.410	43.18	2.239	0.071	14.85	8.28
97.35	0.469	2.180	57.79	3.357	38.86	3.510	−0.046	12.06	7.16
97.17	0.641	2.191	59.46	4.469	36.07	4.689	−0.049	11.39	6.97
96.95	0.841	2.211	61.77	5.616	32.62	5.822	−0.037	10.48	6.68
96.70	1.003	2.301	65.74	6.277	27.99	6.145	0.021	9.21	6.26
96.23	1.349	2.419	68.37	7.526	24.10	7.502	0.003	7.85	5.58
95.82	1.550	2.629	71.08	7.707	21.21	7.793	−0.011	6.70	4.97
95.42	1.741	2.839	73.50	8.071	18.43	7.782	0.036	6.02	4.64
94.99	1.957	3.051	76.19	7.734	16.08	7.816	−0.011	4.93	3.95
93.90	2.260	3.841	79.14	7.613	13.25	7.711	−0.013	4.00	3.37
93.60	2.480	3.921	81.24	7.417	11.35	7.382	0.005	3.45	2.99
93.40	2.583	4.019	83.09	7.006	9.904	6.772	0.033	3.05	2.71
93.13	2.684	4.191	85.20	6.360	8.442	6.055	0.048	2.59	2.37

for the systems decreased along with the increase in total mole fraction of aminopyridines.

In general, the LLE data can be correlated using NRTL and UNIQUAC activity coefficient models[21,22] and the Hand equation,[23] but for the systems of (1-butanol + water + 2,6-diaminopyridine) and (1-butanol + water + 2-aminopyridine), the pure component structural parameters of UNIQUAC cor-

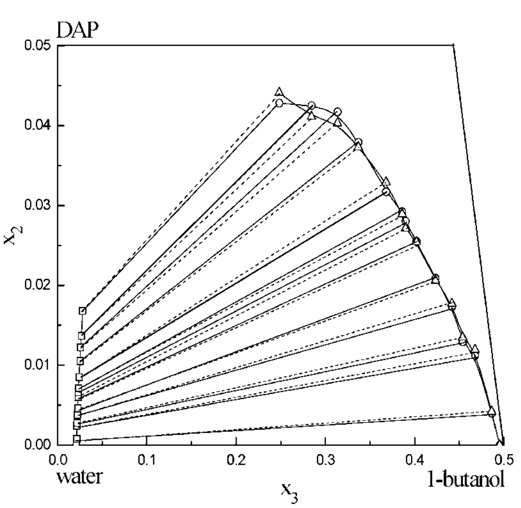

Figure 1. Water (1) + DAP (2) + 1-butanol (3) LLE data at 289.55 K: □, aqueous phase; ○, organic phase; △, calculated organic phase; —, tie line obtained by experiment; • • •, tie line obtained by the Hand model; DAP, 2,6-diaminopyridine.

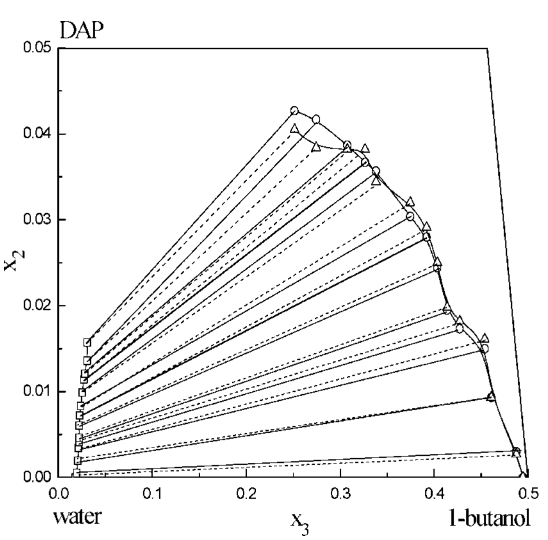

Figure 2. Water (1) + DAP (2) + 1-butanol (3) LLE data at 300.65 K: □, aqueous phase; ○, organic phase; △, calculated organic phase; —, tie line obtained by experiment; • • •, tie line obtained by the Hand model; DAP, 2,6-diaminopyridine.

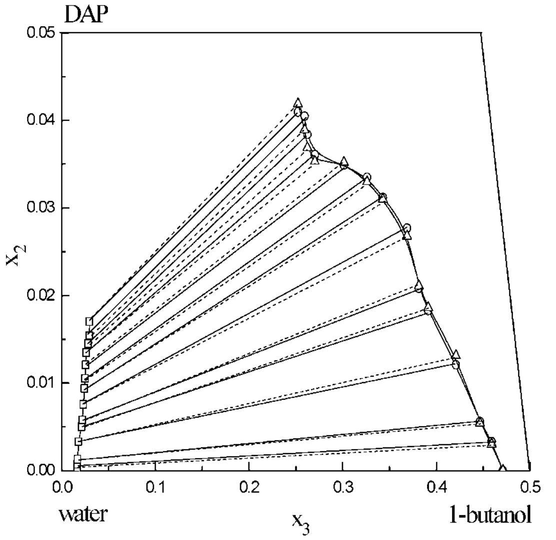

Figure 3. Water (1) + DAP (2) + 1-butanol (3) LLE data at 317.05 K: □, aqueous phase; ○, organic phase; △, calculated organic phase; —, tie line obtained by experiment; • • •, tie line obtained by the Hand model; DAP, 2,6-diaminopyridine.

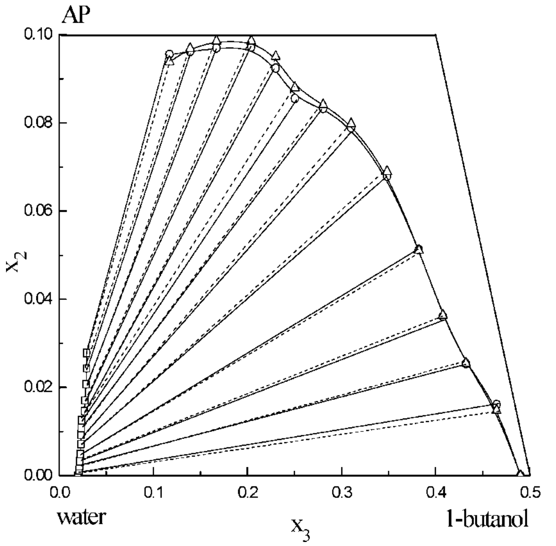

Figure 4. Water (1) + AP (2) + 1-butanol (3) LLE data at 295.85 K: □, aqueous phase; ○, organic phase; △, calculated organic phase; —, tie line obtained by experiment; • • •, tie line obtained by the Hand model; AP, 2-aminopyridine.

relation and the binary interaction parameters of the UNIQUAC and NRTL models cannot be estimated by the method proposed in the literature.[24,25] So in this work, the Hand equation was used to describe the LLE data of the above two ternary systems due to its simpleness

$$\frac{x_2^{\mathrm{w}}}{x_1^{\mathrm{w}}} = a\left[\frac{x_2^{\mathrm{o}}}{x_3^{\mathrm{o}}}\right]^b \tag{3}$$

where x_3^{o} is the mole fraction of 1-butanol in the organic phase and a and b are the fit parameters. As can be seen, linear regression [$\ln(x_2^{\mathrm{w}}/x_1^{\mathrm{w}})$ vs $\ln(x_2^{\mathrm{o}}/x_3^{\mathrm{o}})$] was made, and the values of parameters of eq 3 together with the standard deviation σ were given in Table 3. The linearity of the plot $\ln(x_2^{\mathrm{w}}/x_1^{\mathrm{w}})$ against $\ln(x_2^{\mathrm{o}}/x_3^{\mathrm{o}})$ indicated the degree of consistency of the data. The standard deviation σ was presented by eq 4

$$\sigma = \sqrt{\sum_{i=1}^{N}(x_2^{\mathrm{o}} - x_{2\mathrm{cal}}^{\mathrm{o}})^2/N} \tag{4}$$

where N is the number of experimental data, and $x_{2\mathrm{cal}}^{\mathrm{o}}$ is the mole fraction of aminopyridines in the organic phase calculated by eq 3. The values of $x_{2\mathrm{cal}}^{\mathrm{o}}$ were listed in Tables 1 and 2. The differences between the estimated values and the experimental ones were also listed in Tables 1 and 2, from which it can be seen that the maxium difference was 10 % and the average one was 3 %. The comparisons between the experimental tie lines and the theoritical values were shown in Figures 1 to 6, and good agreements were obtained. The figures were orthogonal triangular diagrams in which a solid line represented a two-phase equilibrium system obtained by experiment and a dashed line represented that obtained by the Hand model.

From Tables 1 and 2, it can be seen that the mole fractions of 1-butanol in the aqueous phase and water in the organic phase

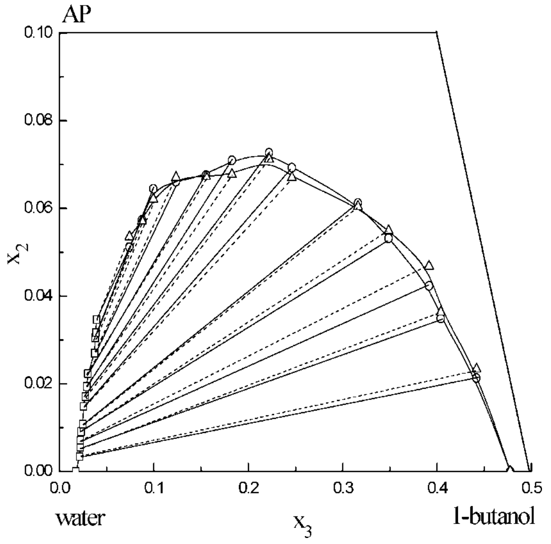

Figure 5. Water (1) + AP (2) + 1-butanol (3) LLE data at 307.15 K: □, aqueous phase; ○, organic phase; △, calculated organic phase; —, tie line obtained by experiment; • • •, tie line obtained by the Hand model; AP, 2-aminopyridine.

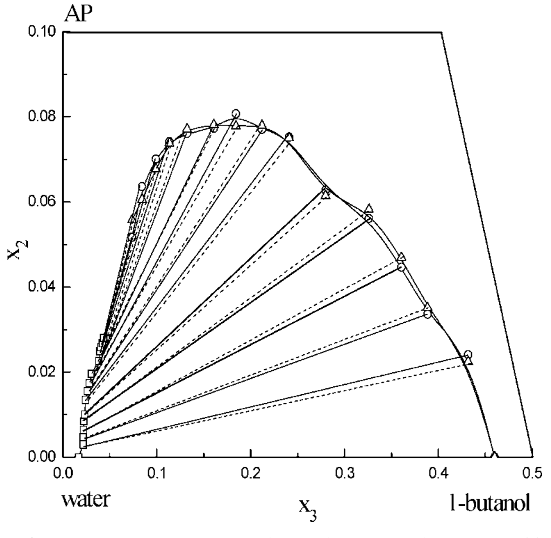

Figure 6. Water (1) + AP (2) + 1-butanol (3) LLE data at 319.65 K: □, aqueous phase; ○, organic phase; △, calculated organic phase; —, tie line obtained by experiment; • • •, tie line obtained by the Hand model; AP, 2-aminopyridine.

Table 3. Values of Parameters of Equation 3

T/K	a	b	$10^3\sigma$
Water (1) + 2,6-Diaminopyridine (2) + 1-Butanol (3)			
289.55	0.1011	1.0124	0.8
300.65	0.1072	1.0265	1.3
317.05	0.1066	0.9955	0.8
Water (1) + 2-Aminopyridine (2) + 1-Butanol (3)			
295.85	0.0367	0.9865	1.4
307.15	0.0502	0.9063	2.0
319.65	0.0384	0.8633	1.7

increased with the increase in total mole fraction of aminopyridines. For the system of (water + 2,6-diaminopyridine + 1-butanol), the mole fraction of 2,6-diaminopyridine in two phases increased all along, but for the other system, the mole fraction of 2-aminopyridine in the organic phase increased to a maximum and then decreased. For instance, at $T = 307.15$ K, the maximum mole fraction of 2-aminopyridine was 7.3 %, and at $T = 319.65$ K, it was 8.1 %.

It also can be seen from Tables 1 and 2 that the selectivities and distribution ratios of aminopyridines were more than 3 in most cases, which indicated that 1-butanol can be used for extracting aminopyridines from water. For example, we took a set of LLE data shown in Table 1 for the system of 1-butanol + water + 2,6-diaminopyridine at 289.55 K: $100x_1^{\mathrm{w}} = 97.03$, $100x_2^{\mathrm{w}} = 0.660$, $100x_3^{\mathrm{w}} = 2.315$, $100x_1^{\mathrm{o}} = 58.22$, $100x_2^{\mathrm{o}} = 2.795$, $100x_3^{\mathrm{o}} = 38.99$. When the masses of the extract phase and raffinate phase were both 50 kg, the extraction efficiency should be 67 % if 2,6-diaminopyridine was extracted using 1-butanol (38.35 kg) from water solution (61.65 kg) with the mass fraction 8.8 % of 2,6-diaminopyridine.

Conclusions

The LLE data for systems of (1-butanol + water + 2,6-diaminopyridine) and (1-butanol + water + 2-aminopyridine) were reported at three different temperatures. The estimated values of aminopyridines in the organic phase $x_{2\mathrm{cal}}^{\mathrm{o}}$ were calculated by the Hand equation. The deviations between the model data and the experimental ones were 10 % (maximum) and 3 % (average). The selectivities and distribution ratios of aminopyridines were obtained, and they were more than 3 in most cases. It is concluded that 1-butanol exhibited a probability as a solvent to extract aminopyridines from water.

Literature Cited

(1) Patel, B. H.; Paricaud, P.; Galindo, A.; Maitland, G. C. Prediction of the Salting-Out Effect of Strong Electrolytes on Water + Alkane Solutions. *Ind. Eng. Chem. Res.* **2003**, *42*, 3809–3823.

(2) Santos, F. S.; d'Avila, S. G.; Aznar, M. Salt Effect on Liquid-Liquid Equilibrium of Water + 1-Butanol + Acetone System: Experimental Determination and Thermodynamic Modeling. *Fluid Phase Equilib.* **2001**, *187−188*, 265–274.

(3) Izadifar, M.; Baik, O. D. An Optimum Ethanol-Water Solvent for Extraction of Podophyllotoxin: Experimental Study, Diffusivity Determination and Modeling. *Sep. Purif. Technol.* **2008**, *63*, 53–60.

(4) Shreve, R. Norris; Swaney, M. W.; Riechers, E. H. Azo Dyes. I. Preparation and Bacteriostatic Properties of Azo Derivatives of 2,6-Diaminopyridine. *J. Am. Chem. Soc.* **1943**, *65*, 2241–2243.

(5) Ostromislensky, I. Aryl-azo-diaminopyridines Useful as Bactericides and Process of Making the Same. U.S. Patent 1680108, 1928.

(6) Yoshiko, N.; Yuzo, H. 2,6-Diaminopyridine Compounds as Intermediates for Producing Antibacterial Dihydropyridone Carboxylic Acid Derivatives. CA 2290709, 1997.

(7) Yasushi, M.; Zenjiro, H. Selective Semipermeable Membrane of Polyimide. JP 63283704, 1988.

(8) Heribert, L. Hair Dye and Process for Dyeing Human Hair. EP 1293192, 2003.

(9) Rorentsu, H.; Tenihikaito, Y. Hair Dyeing Agent Composition. JP 7173039, 1995.

(10) Harnisch; Rasche, H. P. Acid Monomethine-metal Complex Dyestuffs. U.S. Patent 4268668, 1981.

(11) Cannizzaro; Chen, C.; Chen, J. Anti-inflammatory Phosphonate Compounds. U.S. Patent 7432261, 2008.

(12) Lawin; Sherman, P. B.; Grendze, A. R.; Martin P. Chichibabin Aminations of Pyridine Bases. U.S. Patent 5808081, 1998.

(13) Chen, X. H.; Zeng, Z. X.; Xue, W. L.; Pu, T. Solubility of 2,6-Diaminopyridine in Toluene, o-Xylene, Ethylbenzene, Methanol, Ethanol, 2-Propanol, and Sodium Hydroxide Solutions. *J. Chem. Eng. Data* **2007**, *52*, 1911–1915.

(14) Shreve, R. N.; Riechers, E. H.; Rubenkoenig, H.; Goodman, A. H. Amination in the Heterocyclic Series by Sodium Amide. *Ind. Eng. Chem.* **1940**, *32*, 173–178.

(15) Lide, D. R. *CRC Handbook of Chemistry and Physics*; New York, 2002.

(16) Peschke, N.; Sandler, S. I. Liquid-Liquid Equilibria of Fuel Oxygenate + Water + Hydrocarbon Mixtures. 1. *J. Chem. Eng. Data* **1995**, *40*, 315–320.

(17) Zijlema, T. G.; Witkamp, G.-J.; van Rosmalen, G. M. Liquid-Liquid and Solid-Liquid Equilibria of 2-Isopropoxyethanol-H_2O-NaCl Mixtures. *J. Chem. Eng. Data* **1999**, *44*, 1338–1340.

(18) Ghanadzadeh, H.; Ghanadzadeh, A. Liquid-Liquid Equilibria of Water + 1-Butanol + 2-Ethyl-1-hexanol System. *J. Chem. Eng. Data* **2004**, *49*, 783–786.

(19) Shao, B. H.; Yan, J. W.; Xu, X. Z.; Fu, X. Y. Determination of Constituents in Hair Dyes by Reversed-phase High-performance Liquid Chromatography. *Chin. Chem. Lett.* **2000**, *11*, 471–472.

(20) Mohammad Doulabi, F. S.; Mohsen-Nia, M. Ternary Liquid-Liquid Equilibria for Systems of (Sulfolane + Toluene or Chloronaphthalene + Octane). *J. Chem. Eng. Data* **2006**, *51*, 1431–1435.

(21) Mohsen-Nia, M.; Paikar, I. Ternary and Quaternary Liquid + Liquid Equilibria for Systems of (Water + Toluene + *m*-Xylene + Phenol). *J. Chem. Eng. Data* **2007**, *52*, 180–183.

(22) Zhang, W. L.; Hou, K. H.; Mi, G. J.; Chen, N. Liquid-Liquid Equilibria of Ternary Systems Sulfide + Octane + Solvents at Different Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 2275–2281.

(23) Hand, D. B. The Distribution of a Consolute Liquid between Two Immiscible Liquids. *J. Phys. Chem.* **1930**, *34*, 1961–2000.

(24) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116–128.

(25) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086–1099.

Received for review October 21, 2008. Accepted February 17, 2009.

JE8007843