Liquid–Liquid–Solid Equilibrium of the Quaternary Systems Sodium Chloride + Rubidium Chloride + Propanols + Water at 25 °C

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The liquid–liquid–solid equilibria of the two quaternary systems sodium chloride + rubidium chloride + (1-propanol or 2-propanol) + water were investigated at 25 °C. The binodal curves and tie lines together with the integrated phase diagrams for the two quaternary systems have been determined to investigate salting effects. The different equilibrium regions are discussed in detail. The results of the fitting for experimental tie line data by the Eisen−Joffe equation are reasonable.

Introduction

The salting-out effect in the system aliphatic alcohol + water is of industrial interest.[1] The addition of an organic solvent to the aqueous solution of a salt normally decreases the solubility of the salt. Gomis et al.[2] have reported five ternary systems at 25 °C of water + sodium chloride + 1-pentanol/2-pentanol/3-pentanol/2-methyl-1-butanol/2-methyl-2-butanol. They obtained the complete phase diagrams for the two examined systems, water + sodium chloride + 1-pentanol, water + sodium chloride + 2-methyl-2-butanol, and concluded that the salting-out effect of the five pentanols is similar except for 2-methyl-2-butanol which presents the most significant decrease in the solubility of water. Recently, the investigation of quaternary systems has attracted more interest. Marcilla et al.[3,4] studied the water + acetone or ethanol + 1-butanol + sodium chloride systems at 25 °C. They observed that the addition of sodium chloride improved acetone or ethanol extraction by 1-butanol. Gomis et al.[5,6] reported data for the water + sodium chloride + potassium chloride + 1-propanol or 1-butanol quaternary systems at 25 °C. Marcilla et al.[7] determined the water + ethanol + 1-pentanol + sodium chloride quaternary system at 25 °C, obtaining the complete phase diagrams for the examined systems.

In a previous paper,[8] we studied the quaternary system of cesium sulfate + cesium chloride + 1-propanol + water at 25 °C. As a part of the series of work, we report here the study of sodium chloride + rubidium chloride + 1-propanol or 2-propanol + water at 25 °C. This work continues our efforts to extend the systematic methodology suggested in the previous papers.[8] We acquired solubility, tie line, and binodal curve data at different NaCl/RbCl mass fraction ratios of the two quaternary systems. The solvation abilities of the two inorganic salts (NaCl, RbCl) and the effect of the polarity of the two organic solvents (1-propanol, 2-propanol) on the liquid−liquid equilibrium have been discussed on the basis of our experimental results. These data can be of value when applied to extractive processes and may provide a possible method to apply the salting-out technique to increase the yield of RbCl or to enrich the organic phase content at a considerable reduction of the energy cost.[9] The results of the fitting for experimental tie line data by the Eisen−Joffe equation are satisfactory.

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Experimental

Sodium chloride, 1-propanol, and 2-propanol used in the systems were analytical reagent grade and supplied by Xi'an. Rubidium chloride was supplied by Shanghai (purity > 99.5 %). Potassium dichromate supplied by Xi'an was specpure and used without further purification. Water was doubly distilled in all experiments.

Equilibrium samples were made by preparing mixtures of known overall composition by mass and stirring intensely at a constant temperature of 25 °C by fixing on a carrier plate, and the temperature was controlled in this manner to within ± 0.1 °C. The total duration of the processes of mixing and setting was longer than 60 h to ensure that equilibrium was reached, after which samples were taken from both phases and analyzed.

The total concentration of salts in the aqueous and organic phases was determined from the mass of the solid residue of a known mass of sample, obtained by evaporation at 120 °C. The uncertainty in the measurement of the total mass fraction of the salt mixture was estimated to be within ± 0.2 %. Rubidium chloride was measured by atomic absorption spectrometry (TAS-986 Beijing), and the uncertainty in the measurement was within ± 1.0 %. The amount of sodium chloride was determined by mass balance. The concentration of the 1-propanol and 2-propanol was determined using the oxidation process with potassium dichromate, and the relative accuracy in the measurement was within ± 0.5 %.[10,11] The concentration of water was obtained by mass balance. The solid phase in equilibrium with the liquids was analyzed by thermogravimetric analysis (TGA) (TA-SDT Q600). The TGA results show that the solid phases are anhydrous sodium chloride and anhydrous rubidium chloride. The binodal curves of the two systems were determined by the cloud-point method.[12,13] The methodology applied in selecting the points to be determined experimentally was as reported in a previous paper.[8]

Results and Discussion

The experimental data are given in Tables 1 to 6. First, three ternary systems, water + propanol + rubidium chloride, water + propanol + sodium chloride, and water + rubidium chloride

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Table 1. Equilibrium Solubility as Mass Fraction for Sodium Chloride (1) + Rubidium Chloride (2) + Water (4) at 25 °C

aqueous phase			
100 w_1	100 w_2	100 w_4	solid phase
26.61	0.00	73.39	NaCl
20.45	15.19	64.36	NaCl
16.68	30.34	52.98	NaCl
13.78	32.84	53.38	NaCl + RbCl
13.17	32.64	54.19	NaCl + RbCl
8.75	33.16	50.08	RbCl
8.16	33.23	58.61	RbCl
0	49.02	50.98	RbCl

Table 2. Binodal Curve Data as Mass Fraction for the Quaternary System Sodium Chloride (1) + Rubidium Chloride (2) + 1-Propanol (3) + Water (4) at 25 °C

100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4
$w_1/(w_1 + w_2) = 1$							
22.91	0	4.55	72.54	3.95	0	47.28	48.78
17.87	0	7.23	74.90	2.94	0	54.77	42.29
17.65	0	7.79	74.56	2.79	0	57.57	39.64
14.85	0	10.02	75.13	2.23	0	62.69	35.08
9.89	0	16.01	74.10	0.69	0	87.53	11.78
8.07	0	21.29	70.64	0.63	0	88.78	10.59
6.74	0	26.53	66.74	0.59	0	89.19	10.22
5.91	0	33.03	61.06				
$w_1/(w_1 + w_2) = 0.75$							
14.94	4.98	5.76	74.31	3.42	1.14	42.75	52.69
12.69	4.23	7.12	75.95	3.06	1.02	45.57	50.35
10.29	3.43	8.82	77.46	3.01	1.00	45.63	50.35
8.83	2.94	10.79	77.43	2.28	0.76	54.44	42.51
6.58	2.19	17.66	73.56	1.50	0.50	66.19	31.81
5.77	1.92	22.39	69.91	1.26	0.42	70.80	27.52
4.72	1.57	30.09	63.62				
$w_1/(w_1 + w_2) = 0.5$							
14.99	14.99	5.26	64.76	5.23	5.23	20.62	68.93
12.70	12.70	4.83	69.77	4.47	4.47	26.23	64.83
11.78	11.78	6.62	69.81	3.06	3.06	40.93	52.96
10.34	10.34	7.70	71.61	2.60	2.60	46.57	48.23
9.01	9.01	9.13	72.85	2.54	2.54	46.91	48.01
8.10	8.10	10.81	72.99	2.20	2.20	51.32	44.27
7.44	7.44	11.23	73.89	1.50	1.50	62.05	34.95
6.44	6.44	15.72	71.40	1.04	1.04	71.62	26.31
$w_1/(w_1 + w_2) = 0.25$							
0.22	0.66	86.93	12.19	3.05	9.16	21.42	66.37
8.66	25.98	7.48	57.88	2.13	6.38	34.67	56.82
6.94	20.83	6.74	65.49	1.94	5.83	38.73	53.50
5.80	17.40	8.99	67.81	1.70	5.09	43.15	50.07
4.96	14.87	11.14	69.03	1.37	4.11	49.60	44.91
4.03	12.10	14.70	69.17	1.14	3.43	55.14	40.29
3.31	9.93	19.28	67.48	0.94	2.81	62.04	34.22
$w_1/(w_1 + w_2) = 0$							
0	37.09	6.34	56.57	0	12.46	27.76	59.77
0	32.84	6.71	60.45	0	10.50	34.78	54.73
0	28.57	7.73	63.70	0	9.59	38.52	51.89
0	25.29	9.20	65.52	0	6.92	51.66	41.42
0	19.12	13.94	66.94	0	2.61	77.00	20.39
0	17.63	15.62	66.75	0	1.17	86.38	12.45
0	14.83	21.55	63.63	0	0.76	89.15	10.08

+ sodium chloride, had been investigated in our experiment. It should be pointed out that Gomis et al. also determined the water + propanol + sodium chloride system.[14] Gomis' and our LLE data both are depicted Figure 1. The two results are basically consistent, and our data complete the two liquid regions since Gomis only gave four tie line data. The ternary system, propanol + rubidium chloride + sodium chloride, was not investigated since the solubility of rubidium chloride and sodium chloride in propanol is very low and a very small amount of water occurring as an impurity in propanol has an important influence on the values of the concentrations in equilibrium.

Table 3. Binodal Curve Data as Mass Fraction for the Quaternary System Sodium Chloride (1) + Rubidium Chloride (2) + 2-Propanol (3) + Water (4) at 25 °C

100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4
$w_1/(w_1 + w_2) = 1$							
21.68	0	9.68	68.64	6.30	0	47.95	45.75
17.79	0	12.89	69.33	5.31	0	52.18	42.51
14.29	0	20.08	65.64	4.20	0	58.87	36.92
13.41	0	20.80	65.79	3.13	0	65.56	31.31
10.79	0	29.24	59.98	2.44	0	71.26	26.30
10.00	0	32.65	57.34	1.68	0	77.01	21.32
8.85	0	36.78	54.37	1.41	0	78.95	19.64
7.69	0	42.05	50.26				
$w_1/(w_1 + w_2) = 0.75$							
19.37	6.46	3.83	70.34	4.96	1.65	46.32	47.06
17.05	5.68	6.89	70.38	4.95	1.65	46.29	47.11
16.27	5.42	7.29	71.01	4.92	1.64	46.21	47.23
15.37	5.12	9.62	69.89	3.58	1.19	54.78	40.45
10.70	3.57	19.05	66.69	3.22	1.07	57.53	38.18
8.64	2.88	25.95	62.53	1.80	0.60	71.93	25.66
7.39	2.46	32.63	57.52	1.05	0.35	78.61	19.98
$w_1/(w_1 + w_2) = 0.5$							
15.70	15.70	3.80	64.80	5.21	5.21	39.51	50.06
10.81	10.81	10.76	67.62	3.18	3.18	53.55	40.08
10.12	10.12	14.31	65.45	2.87	2.87	56.27	37.99
8.35	8.35	21.54	61.76	2.51	2.51	59.35	35.63
7.76	7.76	24.33	60.15	2.43	2.43	60.17	34.97
7.53	7.53	24.79	60.16	1.46	1.46	71.68	25.41
6.74	6.74	29.43	57.09	0.43	0.43	86.18	12.96
5.71	5.71	35.72	52.86				
$w_1/(w_1 + w_2) = 0.25$							
5.85	17.56	15.19	61.39	3.09	9.28	37.93	49.70
4.76	14.28	21.70	59.25	2.55	7.65	45.33	44.47
4.49	13.48	24.20	57.82	1.94	5.82	52.55	39.70
4.14	12.41	27.76	55.69	1.84	5.53	54.05	38.58
3.96	11.89	29.32	54.84	1.04	3.12	68.20	27.64
3.73	11.18	31.69	53.40	0.96	2.87	69.32	26.86
3.72	11.16	31.37	53.75	0.42	1.27	80.88	17.43
$w_1/(w_1 + w_2) = 0$							
0	41.47	4.07	54.46	0	9.06	53.73	37.21
0	35.89	7.05	57.05	0	7.24	61.22	31.54
0	30.91	10.85	58.24	0	6.06	64.58	29.36
0	22.77	22.10	55.13	0	4.92	68.23	26.85
0	18.68	30.13	51.19	0	4.61	68.63	26.76
0	16.41	36.10	47.49	0	2.22	79.44	18.34
0	10.48	49.86	39.66				

Figure 2 shows the effect of the inorganic salt ratio on the binodal curves for two quaternary systems at 25 °C (data in Tables 2 and 3). The liquid–liquid region decreases with the ratios of NaCl/RbCl from 1/0, 0.75/0.25, 0.5/0.5, and 0.25/0.75 to 0/1. In our opinion, Figure 2 gives two results: one is that the salting-out effect of NaCl on the same water-miscible organic compound is greater than that of RbCl; the other is that the salting-out effect of 1-propanol on the same aqueous solution is greater than that of 2-propanol. These phenomena can be explained qualitatively according to hydration theory. Each salt ion binds a constant number of water molecules in the form of a shell of oriented water dipoles surrounding it, and this "bound" water is then unavailable as solvent to the nonelectrolyte. The Na^+ ion binds more molecules of water than Rb^+, so the salting-out is greater with NaCl than with RbCl. In addition, Figure 2 shows that the binodal curves and the two-phase liquid regions in the two quaternary systems are obviously different at the same NaCl/RbCl ratio when the organic component changes. This phenomenon can be explained by the different polarities of 1-propanol and 2-propanol. Since 2-propanol is more hydrophilic than 1-propanol, the liquid–liquid region formed by NaCl + RbCl + 1-propanol + water was larger than that in the NaCl + RbCl + 2-propanol + water at the same salt ratio.

Table 4. Tie Line Data as Mass Fraction for the Quaternary System Sodium Chloride (1) + Rubidium Chloride (2) + Propanol (3) + Water (4) at 25 °C

organic phase				aqueous phase			
100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4
1-Propanol							
$w_1/(w_1 + w_2) = 0.75$							
1.90	1.13	57.98	38.99	6.74	2.04	17.32	73.90
1.78	0.52	64.38	33.32	7.21	2.62	15.03	75.14
1.62	0.45	69.61	28.32	7.58	3.20	12.67	76.55
$w_1/(w_1 + w_2) = 0.5$							
0.97	1.28	70.10	27.65	5.39	12.00	10.84	71.77
0.90	1.24	74.63	23.23	5.03	15.30	8.02	71.65
0.88	1.33	76.46	21.33	5.50	15.88	7.80	70.82
$w_1/(w_1 + w_2) = 0.25$							
0.33	3.24	62.99	33.44	0.86	15.62	16.05	67.47
0.26	2.48	69.57	27.69	2.02	18.22	11.27	68.49
0.24	2.37	73.46	23.93	2.05	19.76	10.99	67.20
2-Propanol							
$w_1/(w_1 + w_2) = 0.75$							
3.69	0.86	58.12	37.33	15.95	4.35	9.03	70.67
2.76	0.69	63.93	32.62	17.83	5.03	5.66	71.48
2.13	0.52	69.02	28.33	18.93	5.12	5.86	70.09
$w_1/(w_1 + w_2) = 0.5$							
1.95	3.52	58.06	36.47	6.30	13.50	15.75	64.45
1.75	3.17	64.06	31.02	6.60	13.79	14.81	64.80
1.45	1.16	76.24	21.15	11.24	13.35	9.47	65.94
$w_1/(w_1 + w_2) = 0.25$							
1.39	3.72	64.37	30.52	6.64	17.95	14.11	61.30
0.90	2.00	72.70	24.40	9.22	21.11	8.81	60.86
0.49	1.36	78.41	19.74	10.40	26.75	5.62	57.23

Table 5. Equilibrium Solubility as Mass Fraction for the Quaternary System Sodium Chloride (1) + Rubidium Chloride (2) + Propanol (3) + Water (4) at 25 °C

organic phase				aqueous phase			
100 w_1	100 w_2	100 w_3	100 w_4	100 w_1	100 w_2	100 w_3	100 w_4
1-Propanol							
0.37	0.43	85.06	14.14	11.55	27.95	1.33	59.17
0.35	0.44	89.57	9.64	11.91	29.00	1.30	57.79
2-Propanol							
0.34	1.42	87.88	10.35	12.32	26.91	3.62	57.15
0.30	0.56	88.40	10.73	12.36	26.71	3.34	57.59

Table 6. Values of Parameters of Equations 1 and 2 for the Quaternary System Sodium Chloride (1) + Rubidium Chloride (2) + Propanol (3) + Water (4) at 25 °C

	α	β	λ	γ	δ	η	OF
1-Propanol							
eq 1	0.4333	−0.0410	0.7058	−0.0236	0.8821	0.0200	0.0425
eq 2	−0.2671	−0.0131	−0.0611	−0.0935	0.9688	−0.0935	0.0426
2-Propanol							
eq 1	−0.0598	0.0456	0.3354	0.0738	1.5606	−0.0211	0.0752
eq 2	−2.2730	0.1322	−5.2080	0.2709	−2.6705	0.1534	0.0708

Figure 3 shows the binodal curve (data in Tables 2 and 3) and unsaturated tie lines (data in Table 4) for the two systems in different salt ratios. The quaternary equilibrium diagrams are represented in Figures 4 and 5. In these two figures, the influence of both the inorganic salt and the organic solvent on the size of the different heterogeneous regions can be observed. Figure 6, in which a pseudoternary phase equilibrium is represented, shows that the two-phase liquid regions have similar shapes but different areas on planes with different salt ratios. The shape of the two liquid phases for quaternary systems containing partly miscible solvents is different from the trend reported by Ruiz et al.[15] The solubility surface of the quaternary system, sodium chloride + rubidium chloride + 1-propanol + water, is given in Figure 7 as the tetrahedral representation. It can be observed that this system shows a funnel-shaped solubility surface.

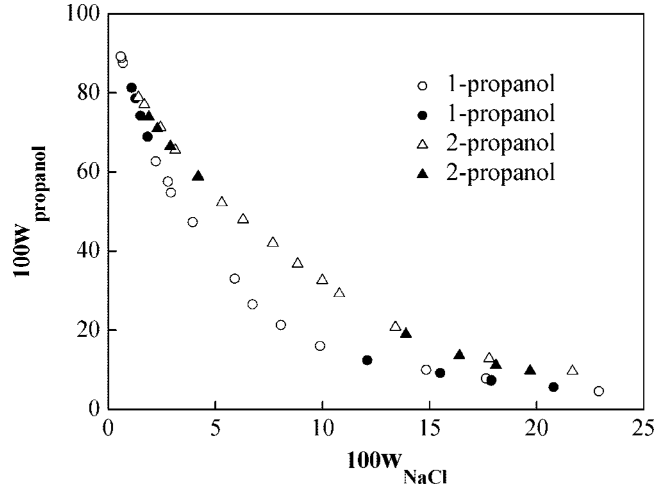

Figure 1. Binodal curves of the sodium chloride + water + 1-propanol and sodium chloride + water + 2-propanol system at 25 °C: •, ▲, Gomis' data;[14] ○, □, this work.

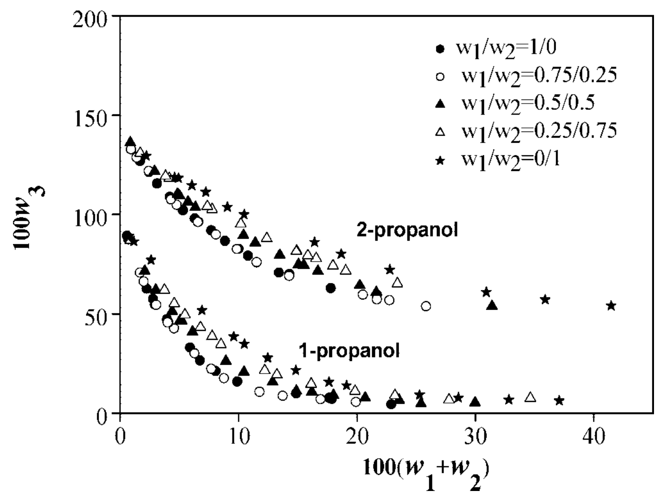

Figure 2. Binodal curves of the sodium chloride + rubidium chloride + 1-propanol/2-propanol + water systems at 25 °C with different NaCl/RbCl ratios.

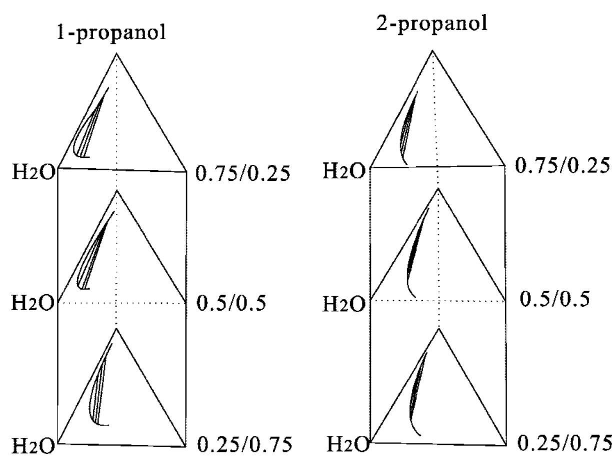

Figure 3. Binodal curves and tie lines for the sodium chloride + rubidium chloride + 1-propanol/2-propanol + water systems at 25 °C with different NaCl/RbCl ratios.

In the previous paper,[8] we used a modified version of the Eisen−Joffe[16] equation for the correlation of LLE data of the

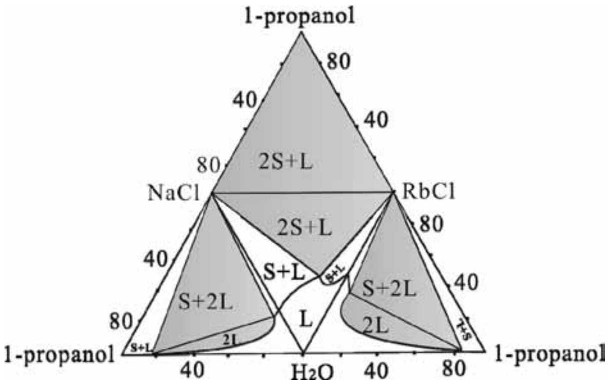

Figure 4. Representation of the phase equilibrium of four ternary mixtures making up the quaternary system sodium chloride + rubidium chloride + 1-propanol + water at 25 °C.

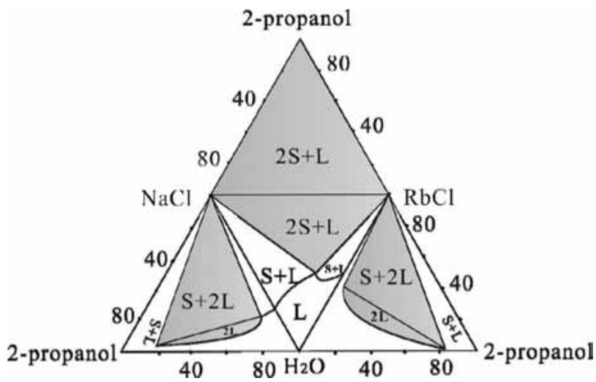

Figure 5. Representation of the phase equilibrium of four ternary mixtures making up the quaternary system sodium chloride + rubidium chloride + 2-propanol + water at 25 °C.

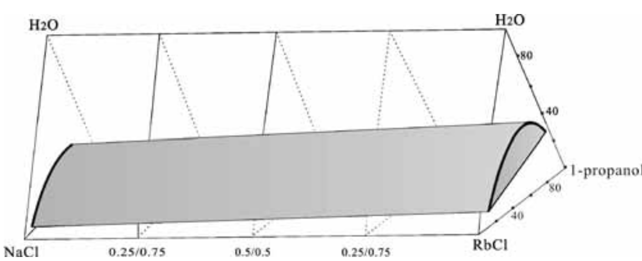

Figure 6. Pseudoternary representation of the phase equilibrium for each plane in different NaCl/RbCl ratios: 0.25/0.75, 0.5/0.5, and 0.75/0.25.

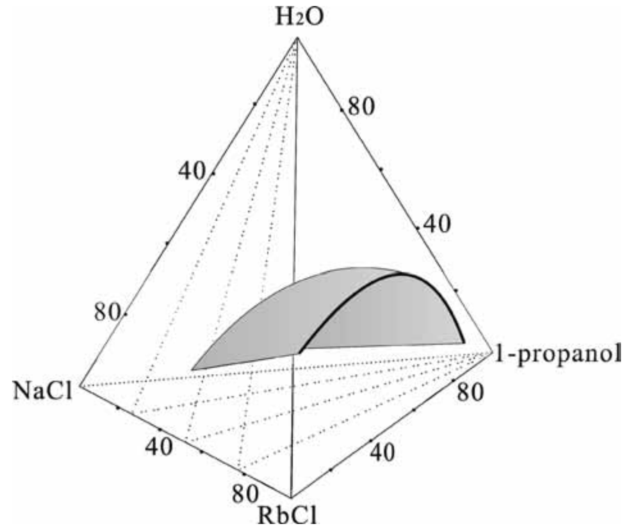

Figure 7. Tetrahedral representation of the phase equilibria of sodium chloride + rubidium chloride + 1-propanol + water with different sectional planes.

cesium sulfate + cesium chloride + 1-propanol + water quaternary system and found good agreement between experiment and calculations. Here, we also use the same modified Eisen−Joffe equation as follows for the two-salt case to correlate the LLE data[3]

$$\lg(w_3/w_4)_{\rm or} = (\alpha_1 + \beta_1 100(w_1)_{\rm aq} + (\gamma_1 + \delta_1 100(w_1)_{\rm aq})\cdot\lg(w_3/w_4)_{\rm aq} + (\lambda_1 + \eta_1 100(w_1)_{\rm aq})\cdot(\lg(w_3/w_4)_{\rm aq})^2 \quad (1)$$

$$\lg(w_3/w_4)_{\rm or} = (\alpha_2 + \beta_2 100(w_2)_{\rm aq}) + (\gamma_2 + \delta_2 100(w_2)_{\rm aq})\cdot\lg(w_3/w_4)_{\rm aq} + (\lambda_2 + \eta_2 100(w_2)_{\rm aq})\cdot(\lg(w_3/w_4)_{\rm aq})^2 \quad (2)$$

where w is the mass fraction of component (w_1 = sodium chloride, w_2 = rubidium chloride, w_3 = 1-propanol or 2-propanol, and w_4 = water) in two phases (or = organic phase and aq = aqueous phase). There is a set of parameters (α, β, γ, δ, λ, and η) associated with each salt. The unsaturated tie line data and saturated equilibrium data (Table 4 and Table 5) are modeled using eqs 1 and 2, and the resulting values of the parameters are given in Table 6. The estimation is performed using the maximum likelihood principle[17] to minimize the objective function

$$\mathrm{OF} = \sum_{k=1}^{n} [(\log(w_3/w_4)_{k,\rm or})_{\rm exptl} - (\log(w_3/w_4)_{k,\rm or})_{\rm calcd}]^2 \quad (3)$$

$$\sigma_j = \left\{ \frac{1}{2n} \sum_{k=1}^{n} [(w^{\rm or}_{k,j,\rm calcd} - w^{\rm or}_{k,j,\rm exptl})^2 + (w^{\rm aq}_{k,j,\rm calcd} - w^{\rm aq}_{k,j,\rm exptl})^2] \right\}^{0.5} \quad (4)$$

where n is the number of data and exptl and calcd represent experimental and calculated values, respectively. The indexes j = 1, 2, 3 and σ_1, σ_2, and σ_3 are the standard deviations for the mass of sodium chloride, rubidium chloride, and propanol, respectively. In the sodium chloride + rubidium chloride +1-propanol + water system, the standard deviations of the components were σ_1 = 3.12 %, σ_2 = 3.38 %, and σ_3 = 3.02 %, and in the sodium chloride + rubidium chloride + 2-propanol + water system, the standard deviations of the components were σ_1 = 4.06 %, σ_2 = 4.17 %, and σ_3 = 4.31 %. These standard deviations allow us to conclude that the modified Eisen−Joffe equation can be successfully used to correlate the LLS equilibrium data for these two quaternary systems.

Conclusions

The phase equilibrium for sodium chloride + rubidium chloride + 1-propanol/2-propanol + water quaternary systems at 25 °C has been investigated in this paper. The bimodal curves and tie lines at different NaCl/RbCl mass fraction ratios together with the integrated phase diagrams for the two quaternary systems are produced. The tie line data are successfully correlated by a modification of the Eisen−Joffe equation. Moreover, we also discuss the influences of the inorganic salts and the polarity of the organic solvents on the phase equilibrium.

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