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Equilibrium Phase Behavior for Water + 1-Propanol + Potassium Chloride + Cesium Chloride Quaternary Systems at Different Temperatures and Data Correlation

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The methodology for the study of the liquid−liquid equilibrium of quaternary systems including two inorganic salts, water, and an organic solvent has been reviewed and applied to the water + 1-propanol + potassium chloride (KCl) + cesium chloride (CsCl) system. Mutual solubility, tie-line, and binodal curve data for the quaternary system at (35 and 45) °C were measured, and it was found that the effect of temperature on the phase equilibrium was insignificant within the investigated temperature range. Furthermore, the binodal curve data were satisfactorily correlated using a five-parameter equation, and the experimental tie-line data were compared with values predicated by a modification of the Eisen−Joffe equation.

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1. Introduction

Aqueous solutions containing salts are of increasing importance and influence on separation processes in chemical engineering, and the salts can significantly change the equilibrium composition.[1] When adding a salt to such systems made by water and organic solvent, some of the water may become unavailable for the solution, and the organic solvent could be "salted out" from the aqueous phase. In recent years, liquid extraction with an inorganic salt has become a useful separation and purification technology in chemical and biological processes.[2,3] Furthermore, some research groups have recently focused on the phase equilibrium data of quaternary systems, and these systems consisted of two inorganic salts, water and organic solvent.[4,5]

In our series of work, we have systematically investigated the phase equilibria for about 50 ternary systems consisting of inorganic salts, water, and organic solvent. The salts we selected were rare alkali metallic salts, such as RbCl, Rb_2SO_4, $RbNO_3$, CsCl, Cs_2SO_4, $CsNO_3$, and so on. The organic solvents were some aliphatic alcohols that are completely miscible or partly miscible with water, such as methanol, ethanol, 1-propanol, 2-propanol, as well as PEG (poly-(ethylene glycol)) 400 to 10000. Recently, to expand this work, we have focused on the research of quaternary systems with two salts, water, and organic solvent. Our methodology has been successfully used to study the liquid−liquid equilibria for water + 1-propanol + Cs_2SO_4 + CsCl and water + 1-propanol/2-propanol + KCl + CsCl quaternary systems at 25 °C.[6,7] This work continues our efforts to extend the systematic methodology suggested previously and investigate the effect of temperature on the liquid−liquid equilibrium of the water + 1-propanol + KCl + CsCl quaternary system at (35 and 45) °C. Moreover, the equilibrium data were correlated with a five-parameter equation and a modification of the Eisen−Joffe equation, respectively.

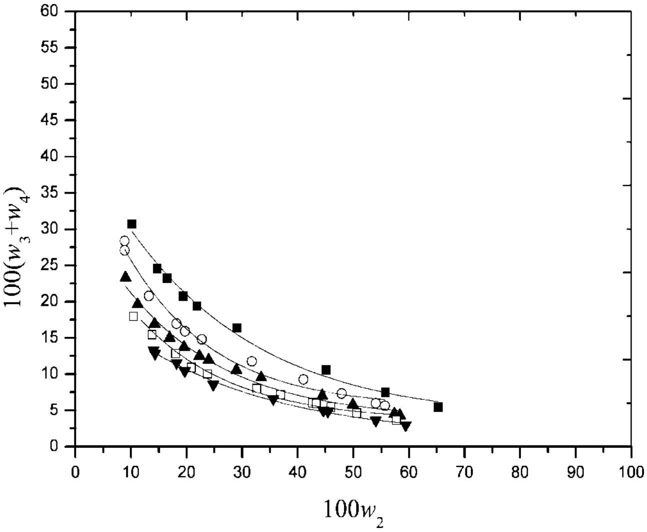

Figure 1. Binodal curves for water (1) + 1-propanol (2) + KCl (3) + CsCl (4) system at 35 °C of different KCl/CsCl rations: ■, $w_3/(w_3 + w_4) = 0/1$; ○, $w_3/(w_3 + w_4) = 0.25/0.75$; ▲, $w_3/(w_3 + w_4) = 0.5/0.5$; □, $w_3/(w_3 + w_4) = 0.75/0.25$; ▼, $w_3/(w_3 + w_4) = 1/0$.

2. Experimental

2.1. Materials. The 1-propanol and potassium chloride used in this work were analytical reagent grade with purity > 99.5 % (Xi'an Chemical Reagent Factory), and cesium chloride was supplied by the Shanghai China Lithium Industrial Co., Ltd. (purity > 99.5 %). Specpure potassium dichromate (Tianjin Chemical Factory) was used without further purification. Water was distilled twice before utilization.

2.2. Apparatus and Procedure. For phase equilibrium experiments, a detailed description of the experimental apparatus has been given previously.[8] The saturated solutions were prepared by mixing appropriate amounts of known masses of 1-propanol and water with excess amounts of salt mixtures (KCl, CsCl). The samples were stirred on the carrier plate for at least

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Table 1. Binodal Curve Data As a Function of the Mass Fractions for the Water (1) + 1-Propanol (2) + KCl (3) + CsCl (4) at 35 °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
$w_3/(w_3 + w_4) = 0$							
13.30	84.59	0.00	2.11	58.78	21.87	0.00	19.35
29.28	65.27	0.00	5.45	59.87	19.41	0.00	20.72
36.74	55.76	0.00	7.50	60.28	16.48	0.00	23.24
42.65	47.58	0.00	9.78	60.72	14.71	0.00	24.57
43.61	46.19	0.00	10.20	59.13	10.17	0.00	30.70
44.33	45.07	0.00	10.60	55.79	9.28	0.00	34.93
54.63	29.01	0.00	16.36	53.07	7.88	0.00	39.05
$w_3/(w_3 + w_4) = 0.25$							
12.48	86.08	0.36	1.08	64.42	19.68	3.98	11.93
28.58	68.00	0.86	2.57	64.88	18.18	4.24	12.71
38.67	55.68	1.41	4.24	66.02	13.21	5.19	15.58
39.98	54.04	1.50	4.49	66.42	11.42	5.54	16.62
44.79	47.88	1.83	5.50	64.06	8.87	6.77	20.30
49.71	41.03	2.32	6.95	62.78	8.85	7.09	21.28
56.49	31.74	2.94	8.83	61.99	8.41	7.40	22.20
62.46	22.74	3.70	11.10	60.70	7.92	7.85	23.54
$w_3/(w_3 + w_4) = 0.5$							
14.18	84.51	0.66	0.66	65.17	22.30	6.27	6.27
29.59	67.30	1.56	1.56	66.75	19.51	6.87	6.87
37.32	58.36	2.16	2.16	68.05	16.94	7.51	7.51
38.11	57.38	2.25	2.25	68.31	16.60	7.55	7.55
44.30	49.91	2.90	2.90	68.86	14.22	8.46	8.46
48.57	44.40	3.52	3.52	69.17	11.18	9.83	9.83
57.08	33.42	4.75	4.75	67.14	10.80	11.03	11.03
60.47	28.96	5.29	5.29	67.70	9.01	11.65	11.65
64.06	23.97	5.99	5.99				
$w_3/(w_3 + w_4) = 0.75$							
17.65	80.98	1.03	0.34	59.37	32.61	6.02	2.01
30.70	66.70	1.95	0.65	66.20	23.75	7.54	2.51
38.64	57.74	2.72	0.91	68.21	20.89	8.18	2.73
44.74	50.61	3.49	1.16	69.09	18.05	9.65	3.22
48.60	45.96	4.08	1.36	70.77	13.81	11.57	3.86
50.73	43.34	4.45	1.48	71.59	10.46	13.46	4.49
51.34	42.61	4.54	1.51	70.23	10.73	14.28	4.76
55.89	36.94	5.38	1.79				
$w_3/(w_3 + w_4) = 1$							
13.39	85.89	0.72	0.00	50.40	44.59	5.01	0.00
16.20	82.85	0.95	0.00	57.83	35.57	6.60	0.00
18.17	80.65	1.18	0.00	66.60	24.80	8.60	0.00
26.93	71.16	1.91	0.00	69.86	19.67	10.47	0.00
37.60	59.41	2.99	0.00	71.50	16.91	11.59	0.00
42.35	54.01	3.64	0.00	72.85	14.32	12.83	0.00
49.74	45.40	4.86	0.00	72.62	14.06	13.32	0.00

Table 2. Binodal Curve Data As a Function of the Mass Fractions for the Water (1) + 1-Propanol (2) + KCl (3) + CsCl (4) at 45 °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
$w_3/(w_3 + w_4) = 0$							
21.29	75.30	0.00	3.41	54.39	29.96	0.00	15.65
28.53	65.97	0.00	5.49	60.33	19.22	0.00	20.45
36.65	56.05	0.00	7.31	58.86	14.09	0.00	27.05
37.66	54.63	0.00	7.71	58.91	12.73	0.00	28.36
39.07	52.98	0.00	7.95	56.81	10.65	0.00	32.54
44.44	45.27	0.00	10.29	52.87	7.59	0.00	39.54
49.47	37.65	0.00	12.88	53.09	7.30	0.00	39.61
53.77	30.97	0.00	15.26				
$w_3/(w_3 + w_4) = 0.25$							
13.97	84.35	0.42	1.26	64.76	18.95	4.07	12.22
23.74	73.34	0.73	2.19	64.96	16.60	4.61	13.83
29.67	66.48	0.96	2.89	65.12	13.04	5.46	16.38
37.57	57.14	1.32	3.97	63.15	12.16	6.17	18.52
44.19	48.82	1.75	5.24	62.48	10.13	6.85	20.54
48.24	43.46	2.08	6.23	61.49	10.03	7.12	21.36
55.11	33.84	2.76	8.29	59.97	9.70	7.58	22.75
62.52	23.18	3.58	10.73	59.73	9.28	7.75	23.24
$w_3/(w_3 + w_4) = 0.5$							
14.85	83.72	0.72	0.72	63.89	24.60	5.76	5.76
29.76	67.18	1.53	1.53	67.35	18.23	7.21	7.21
37.80	57.97	2.12	2.12	68.65	14.45	8.45	8.45
43.56	51.01	2.72	2.72	69.28	12.49	9.12	9.12
47.72	45.87	3.21	3.21	67.71	11.39	10.45	10.45
55.92	35.33	4.37	4.37	67.19	10.67	11.07	11.07
$w_3/(w_3 + w_4) = 0.75$							
15.11	83.68	0.91	0.30	67.72	21.80	7.86	2.62
22.98	75.06	1.47	0.49	69.57	18.89	8.66	2.89
34.99	61.90	2.33	0.78	69.80	17.90	9.23	3.08
40.31	55.85	2.88	0.96	71.19	13.52	11.47	3.82
48.18	46.56	3.95	1.32	70.35	13.40	12.19	4.06
53.35	40.18	4.85	1.62	70.93	12.21	12.65	4.22
54.63	38.69	5.01	1.67	71.45	11.21	13.01	4.34
64.36	26.44	6.90	2.30	71.39	11.04	13.18	4.39
$w_3/(w_3 + w_4) = 1$							
15.73	83.35	0.92	0.00	66.86	24.72	8.42	0.00
18.07	80.73	1.20	0.00	69.73	20.18	10.09	0.00
24.00	74.32	1.68	0.00	70.88	18.66	10.46	0.00
31.57	66.17	2.26	0.00	71.88	16.19	11.93	0.00
40.70	56.03	3.27	0.00	72.46	15.44	12.10	0.00
48.55	47.04	4.41	0.00	73.00	14.40	12.60	0.00
57.19	36.69	6.12	0.00	72.41	14.38	13.21	0.00
66.37	25.32	8.31	0.00				

24 h at a constant temperature with an uncertainty of ± 0.1 °C. An intimate contact between the phases was allowed, and the equilibrium was achieved by letting the phases rest and separate for a further 24 h. After that, samples were taken from the liquid phases (using syringes) and analyzed. The unsaturated tie-line measurements of the quaternary systems at (35 and 45) °C were carried out, and the system was made from water, 1-propanol, and mixtures of KCl and CsCl in different ratios (from 0.75/0.25, 0.5/0.5, to 0.25/0.75) in mass fraction determined with an analytical balance of precision $\pm\ 1 \cdot 10^{-7}$ kg (Shanghai Precision & Scientific Instrument Co., Ltd., FA-1104). Data for the binodal curves were determined by using the cloud point method, and the experimental device employed was that used previously;[9,10] moreover, the salt ratio of KCl/CsCl was 1/0, 0.75/0.25, 0.5/0.5, 0.25/0.75, and 0/1.

The total salt concentration was determined by gravimetrical analysis, evaporating the solution at 150 °C, until constant mass. In this way, the mass of salt was determined, and the uncertainty in the measurement of the mass fraction was estimated to be ± 0.2 %. For saturated solutions, the concentration of KCl or CsCl was determined utilizing an atomic absorption spectrometer (AAS). The AAS measurements were performed on a TAS-986 (Beijing Purkinje General Instrument Co., Ltd.) atomic absorption spectrometer at a wavelength of 766.5 nm (K) and 852.1 nm (Cs), and the uncertainty was within ± 0.5 %. Furthermore, the amount of 1-propanol was determined using an oxidation process, and $K_2Cr_2O_7$ was used as oxidant.[11,12] The reproducibility of the determination of the 1-propanol mass fraction was less than ± 0.5 %. Finally, the water concentration was computed using mass-balance equations.

3. Results and Discussion

In this work, to discuss the solvation ability of KCl and CsCl, we created three different ratios of KCl to CsCl (0.25/0.75, 0.5/0.5, 0.75/0.25) for the quaternary systems made by water + 1-propanol + KCl + CsCl at (35 and 45) °C. The experimental results show that with an increasing addition of KCl the size of the liquid−liquid region for the water + 1-propanol + KCl + CsCl system at 35 °C gradually decreases. In addition, we determined a similar phenomenon for the water + 1-propanol + KCl + CsCl system at 45 °C, and the binodal curve data as well as the tie-line data are based on those in Tables 1 to 3. To further explain this result, the binodal curves for the water + 1-propanol + KCl + CsCl system at 35 °C with five different ratios of KCl/CsCl (from 0/1 to 0.25/0.75, 0.5/0.5, 0.75/0.25,

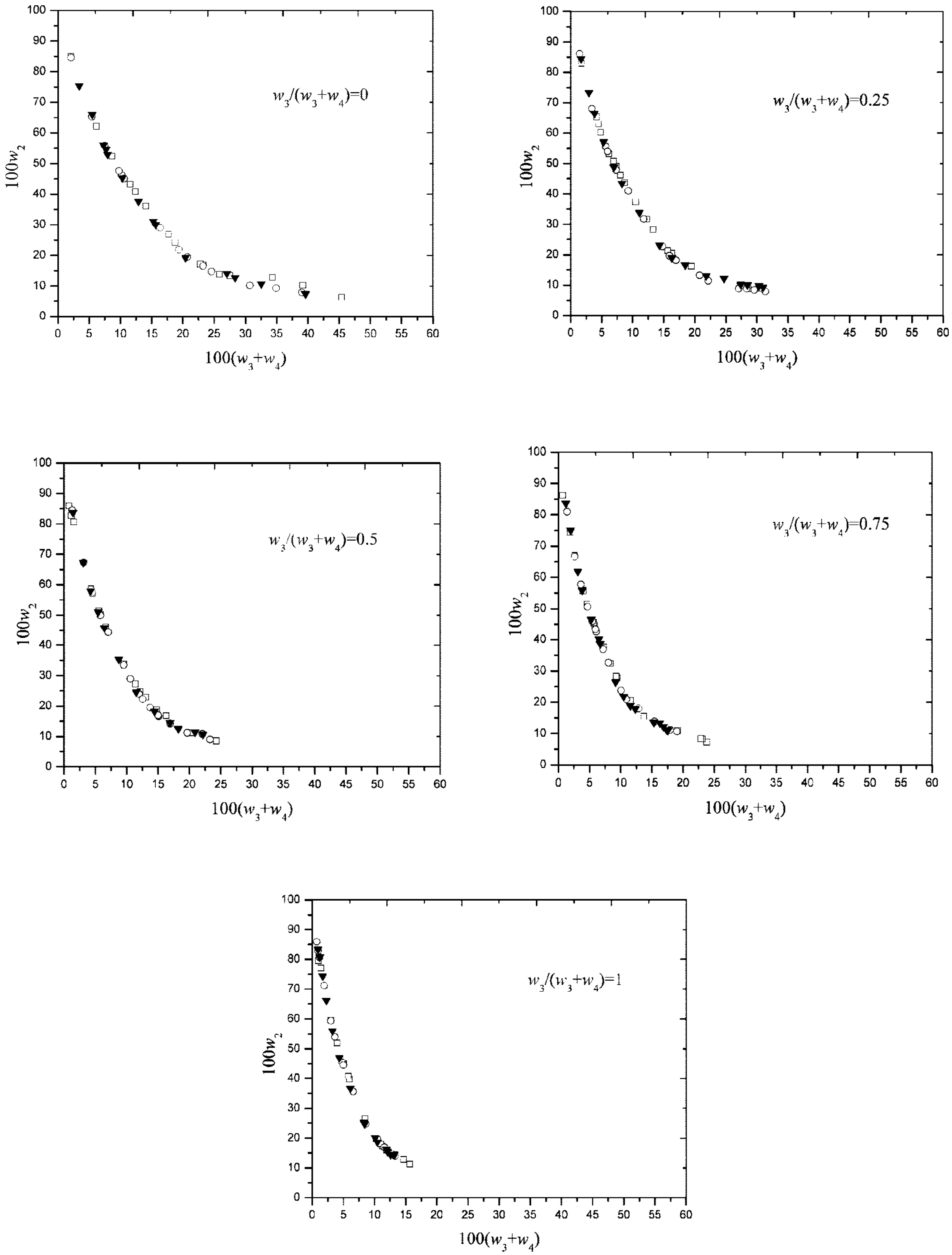

Figure 2. Binodal curves for water (1) + 1-propanol (2) + KCl (3) + CsCl (4) at (25, 35, and 45) °C of different salt ratios. □, 25 °C; ○, 35 °C; ▼, 45 °C. (*The data for the system at 25 °C are based on those in ref 7.

and 1/0) are presented together in Figure 1. It is obvious that with an increasing KCl/CsCl ratio the binodal curves shift to lower 1-propanol and salt concentrations. Via experiment, we discovered the phenomena for these two systems were similar to the quaternary system made by water + 1-propanol + KCl + CsCl at 25 °C.[7] Although KCl has greater solvation ability than CsCl, its solubility in water is much less than that of CsCl (less than 20 %). Consequently, the effect of the CsCl addition was shown by the area of the two-phase region enlarging. Moreover, we provide the binodal curves for water + 1-propanol + KCl + CsCl systems at different temperatures with the same salt ratio in Figure 2. Obviously, the effects of the temperature on the two-phase area were insignificant, and the data at 25 °C are based on those in ref 7. Finally, the integrated phase diagram for the quaternary system water + 1-propanol + KCl + CsCl at (25, 35, and 45) °C is provided in Figure 3. From this diagram, we can see clearly the insignificant effects of temperature on the liquid−liquid equilibrium. However, for the water

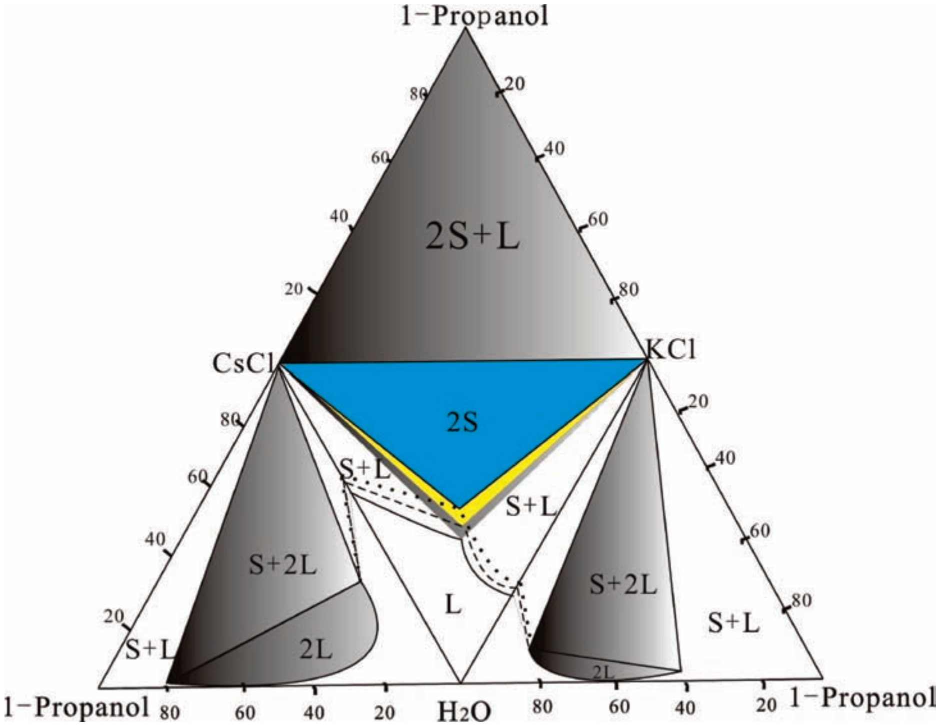

Figure 3. Complete phase diagram for the water + 1-propanol + KCl + CsCl quaternary system at (25, 35, and 45) °C. (Black, 25 °C; Yellow, 35 °C; Blue, 45 °C and S, solid; L, liquid. The data for the system at 25 °C are based on those in ref 7).

Table 3. Tie-Line Data As a Function of the Mass Fractions for the Quaternary System Comprising Water (1) + 2-Propanol (2) + KCl (3) + CsCl (4) at (35 and 45)°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
35 °C							
$w_3/(w_3 + w_4) = 0.25$							
29.35	66.36	1.04	3.26	64.10	12.58	5.82	17.50
22.51	74.46	0.76	2.27	61.78	7.87	7.58	22.76
25.39	71.04	0.89	2.68	64.28	9.33	9.33	6.59
$w_3/(w_3 + w_4) = 0.5$							
32.30	63.79	1.85	2.06	69.03	12.93	8.99	9.05
23.27	74.00	1.35	1.38	66.53	10.44	10.63	12.39
17.28	80.69	0.98	1.05	60.81	8.61	15.18	15.40
$w_3/(w_3 + w_4) = 0.75$							
31.95	64.99	2.28	0.79	70.29	15.18	10.64	3.88
24.27	73.47	1.56	0.70	69.90	10.64	14.33	5.13
14.70	83.84	1.08	0.38	63.30	6.96	20.31	7.42
20.97	77.33	1.24	0.46	66.83	8.03	18.66	6.49
45 °C							
$w_3/(w_3 + w_4) = 0.25$							
27.48	68.68	0.92	2.92	62.87	10.52	6.68	19.93
20.28	76.72	0.71	2.28	57.30	9.72	8.11	24.87
23.38	73.47	0.75	2.40	60.01	9.05	7.64	23.30
$w_3/(w_3 + w_4) = 0.5$							
29.55	66.27	2.09	2.09	68.04	10.63	10.66	10.66
26.78	70.02	1.60	1.60	67.35	9.28	11.68	11.68
21.57	75.98	1.22	1.22	64.63	7.37	14.00	14.00
24.51	72.61	1.44	1.44	66.49	9.29	12.11	12.11
$w_3/(w_3 + w_4) = 0.75$							
26.40	70.68	2.19	0.73	70.27	10.01	14.79	4.93
23.92	73.63	1.84	0.61	68.92	8.66	16.82	5.61
22.13	75.82	1.54	0.51	65.98	8.62	19.05	6.35
31.58	64.61	2.86	0.95	70.15	12.85	12.74	4.25

Table 4. Equilibrium Solubility as a Function of the Mass Fractions for Water (1) + KCl (2) + CsCl (3) at (35 and 45) °C

aqueous phase		solid phase	
100 w_1	100 w_2	100 w_3	
35 °C			
32.87	0	67.13	CsCl
33.40	3.11	63.49	CsCl
33.03	3.52	63.45	CsCl
33.28	3.87	62.85	CsCl
53.84	13.39	32.77	CsCl + KCl
71.53	28.47	0	KCl
45 °C			
31.85	0	68.15	CsCl
32.12	3.51	64.36	CsCl
57.85	3.22	38.93	CsCl + KCl
60.22	15.91	23.87	CsCl + KCl
31.99	27.36	40.65	CsCl + KCl
70.68	29.32	0	KCl

+ KCl + CsCl system, since the mutual solubility for inorganic salts in water was gradually increased with increasing temperature, the two solids region (2S) was slightly reduced. In addition, the equilibrium solubilities for the water + KCl + CsCl system at (35 and 45) °C are listed in Table 4.

In the former work, the binodal curve data were fitted to a five-parameter equation described as follows[8]

$$\ln w_2 = A + Bw_3^{0.5} + Cw_3 + Dw_3^2 + Ew_3^3 \qquad (1)$$

where w_2 and w_3 represented the mass fraction of aliphatic alcohol and inorganic salt, respectively. *A*, *B*, *C*, *D*, and *E* are coefficients. Our system has two salts, so the five-parameter equation must be expressed as

$$\ln w_2 = A + Bw_{(3+4)} + Cw_{(3+4)} + Dw_{(3+4)} + Ew_{(3+4)}^3 \qquad (2)$$

where *w* is the mass fraction of component (w_2: 1-propanol; $w_{(3+4)}$: KCl and CsCl), and *A*, *B*, *C*, *D*, and *E* are coefficients along with the corresponding standard deviations (100δ) for the investigated systems, which are listed in Table 5. Furthermore, the standard deviations between experimental and calculated

Table 5. Values of Parameters of Equation 2

temperature (°C)	A	B	C	D	E	100δ
			$w_3/(w_3 + w_4) = 0$			
25[a]	−0.1701	1.6687	−11.5631	4.4976	8.3614	1.3428
35	−0.1534	1.5294	−11.4985	4.0931	7.4095	0.7383
45	−0.1934	1.5987	−11.3991	4.2105	7.4142	0.6830
			$w_3/(w_3 + w_4) = 0.25$			
25[a]	−0.0548	0.4041	−11.0494	5.1937	6.4236	0.8977
35	−0.0615	0.6634	−12.4093	6.9548	7.8916	1.0460
45	−0.0905	1.1737	−14.4690	12.5120	10.9181	0.7734
			$w_3/(w_3 + w_4) = 0.5$			
25[a]	−0.1132	0.8525	−14.1115	9.2489	5.7608	0.4272
35	−0.0790	0.9092	−15.2287	11.3797	8.7188	0.8476
45	−0.0197	0.3510	−14.3820	12.7589	8.7988	0.7126
			$w_3/(w_3 + w_4) = 0.75$			
25[a]	−0.1310	1.2162	−18.0395	19.4161	10.2765	0.6948
35	−0.0761	0.8458	−17.8405	20.0924	11.0469	0.7880
45	−0.0621	1.0238	−19.4328	25.2922	12.0595	0.8032
			$w_3/(w_3 + w_4) = 1$			
25[a]	−0.2719	2.9856	−25.6878	33.9584	14.2398	0.6748
35	−0.0377	0.0725	−16.5236	11.4421	4.5755	0.5278
45	−0.0668	0.8699	−21.2926	31.7475	10.4164	0.5344

[a] The correlated data for the systems at 25 °C are based on those in ref 7.

Table 6. Saturated Solubilities for Water (1) + 1-Propanol (2) + KCl (3) + CsCl (4) at (35 and 45) °C

organic phase				aqueous phase			
$100\ w_1$	$100\ w_2$	$100\ w_3$	$100\ w_4$	$100\ w_1$	$100\ w_2$	$100\ w_3$	$100\ w_4$
			35 °C				
5.12	93.00	0.07	1.81	31.99	2.32	4.02	61.67
5.37	92.82	0.06	1.75	31.33	3.00	3.33	62.34
5.66	92.48	0.07	1.78	32.42	2.24	3.82	61.52
5.74	92.26	0.08	1.92	33.53	2.29	4.06	60.13
7.00	90.92	0.12	1.97	39.22	3.06	6.48	51.23
7.05	91.32	0.04	1.59	32.11	2.17	4.04	61.68
7.46	90.79	0.05	1.70	31.78	2.36	3.73	62.13
			45 °C				
6.79	91.19	0.02	2.00	33.28	0.06	4.20	62.47
8.09	88.08	0.07	3.76	31.52	2.84	5.04	60.60
8.28	89.83	0.09	1.82	30.53	2.31	3.51	63.65
8.49	89.31	0.12	2.08	33.32	2.95	5.82	57.90
9.67	88.26	0.11	1.95	36.49	2.98	6.60	53.93

Table 7. Values of Parameters of Equations 3 and 4

	α	β	γ	δ	λ	η	O.F.
				25 °C[a]			
eq 3	−2.3618	0.0397	−5.2913	0.1707	−2.0843	0.1179	0.1235
eq 4	0.6479	−0.0950	1.1364	−0.1825	0.9252	−0.0786	0.0990
				35 °C			
eq 3	−5.4785	0.5382	−11.3038	1.1590	−4.8300	0.6109	0.1000
eq 4	0.4539	−0.1214	1.0325	−0.2595	1.2545	−0.1307	0.0759
				45 °C			
eq 3	−2.7419	0.2561	−5.9452	0.5985	−2.2525	0.3269	0.0708
eq 4	0.3412	−0.0042	1.0726	−0.0365	1.2916	−0.0255	0.0441

[a] The correlated data and the values of parameters for the systems at 25 °C are based on those in ref 7.

Table 8. Standard Deviations for Each Component at Different Temperatures

temperature (°C)	σ_2 (%)	σ_3 (%)	σ_4 (%)
25[a]	8.13	4.27	8.18
35	7.35	6.06	7.80
45	5.30	7.34	3.97

[a] The correlated data for the systems at 25 °C are based on those in ref 7.

values are below 1.3 %. As a result, eq 2 can be satisfactorily used to correlate the binodal curve data of the investigated systems. In addition, the saturated equilibrium data for water + 1-propanol + KCl + CsCl at (35 and 45) °C are listed in Table 6, and the solid phases are anhydrous KCl and anhydrous CsCl. Marcilla's group[13,14] has used a modified version of the Eisen−Joffe equation[15] for the correlation of LLE data of quaternary systems including one salt. Since our systems have two salts, the modified Eisen−Joffe equation is written as two equations[16]

$$\lg(w_2/w_1)_{\mathrm{or}} = (\alpha_1 + \beta_1 100(w_3)_{\mathrm{aq}}) + (\gamma_1 + \delta_1 100(w_3)_{\mathrm{aq}}) \cdot \lg(w_2/w_1)_{\mathrm{aq}} + (\lambda_1 + \eta_1 100(w_3)_{\mathrm{aq}}) \cdot (\lg(w_2/w_1)_{\mathrm{aq}})^2 \quad (3)$$

$$\lg(w_2/w_1)_{\mathrm{or}} = (\alpha_2 + \beta_2 100(w_3)_{\mathrm{aq}}) + (\gamma_2 + \delta_2 100(w_3)_{\mathrm{aq}}) \cdot \lg(w_2/w_1)_{\mathrm{aq}} + (\lambda_2 + \eta_2 100(w_3)_{\mathrm{aq}}) \cdot (\lg(w_2/w_1)_{\mathrm{aq}})^2 \quad (4)$$

where w is the mass fraction of the component (w_1: water, w_2: 1-propanol, w_3: KCl, w_4: CsCl). In the equations, or is the organic phase and aq is the aqueous phase. α, β, γ, δ, λ, and η are a set of parameters associated with each salt. The tie-line data as well as the saturated equilibrium data were correlated by eqs 3 and 4. The simplex flexible method [17]has been used as the optimization method to determine the parameters of the correlation. The objective function and the standard deviation used have been calculated using the following equations, respectively

$$\mathrm{OF} = \sum_{k=1}^{n} [(\log(w_2/w_1)_{k,\mathrm{or}})_{\mathrm{exptl}} - (\log(w_2/w_1)_{k,\mathrm{or}})_{\mathrm{calcd}}]^2 \quad (5)$$

$$\sigma_j = \left\{ \frac{1}{2n} \sum_{k=1}^{n} \left[\left(w_{k,j,\mathrm{calcd}}^{\mathrm{or}} - w_{k,j,\mathrm{exptl}}^{\mathrm{or}} \right)^2 + \left(w_{k,j,\mathrm{calcd}}^{\mathrm{aq}} - w_{k,j,\mathrm{exptl}}^{\mathrm{aq}} \right)^2 \right] \right\}^{0.5} \quad (6)$$

where n = number of tie-lines and saturated equilibrium data; exptl = experimental; and calcd = calculated. The index $j = 2 - 4$ and σ_2, σ_3, and σ_4 are the standard deviations for the mass of 1-propanol, KCl, and CsCl, respectively. Tables 7 and 8 show the results of the correlation, as well as the values of the objective function and the standard deviations of components obtained. A very good agreement can be observed for all the data.

4. Conclusions

In this work, we have produced the integrated phase diagrams for the quaternary system comprised by water + 1-propanol + KCl + CsCl at (35 and 45) °C. The saturated solubility, tie-line, and binodal curve data have been systematically determined. With the addition of CsCl, the two-phase quaternary region increases its size. The effect of temperature on the phase equilibrium was insignificant within the investigated range. Furthermore, the binodal curves were satisfactorily correlated using a five-parameter equation, and a modification of the Eisen−Joffe equation has been used to correlate the tie-line data and saturated equilibrium data, which yield good results.

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