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Liquid–liquid equilibria for water + 1-propanol/2-propanol + potassium chloride + cesium chloride quaternary systems at 298.1 ± 0.1 K

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Abstract

In this paper, we present the results of our study of the phase equilibria for two quaternary systems: water + 1-propanol/2-propanol + potassium chloride (KCl) + cesium chloride (CsCl) at 298.1 ± 0.1 K. We also produced the binodal curves and tie-lines at different KCl/CsCl mass-fraction ratios, and produced integrated phase diagrams for the quaternary systems. We also discuss the solvation abilities of KCl and CsCl, and the effect of the polarity of the organic solvent on the liquid–liquid equilibrium. We compared the experimental tie-lines derived for the quaternary systems with values predicated by modifying the Eisen–Joffe equation. The model produced satisfactory results.

Keywords: Liquid–liquid equilibria; Quaternary systems; Cesium chloride; Potassium chloride; 1-Propanol; 2-Propanol

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1. Introduction

In recent years, liquid extraction with inorganic salts has become a useful separation and purification technology in a range of chemical and biological processes [1,2]. Many liquid–liquid equilibria for ternary systems have been systematically studied to investigate salting-out effects. Some liquid–liquid–solid equilibria for quaternary systems containing two inorganic salts, water, and an organic solvent that is (partly) miscible with water have also been investigated, such as the $H_2O + NaCl + KCl + 1\text{-}C_4H_9OH$, $H_2O + NaCl + KCl + 1\text{-}C_3H_7OH$, and the $H_2O + CsCl + Cs_2SO_4 + 1\text{-}C_3H_7OH$ quaternary systems [3–5] at 25 °C.

The work described in the present paper continues our efforts to extend the systematic methodology suggested in previous papers [3–7]. The quaternary system in the present study comprises water, 1-propanol or 2-propanol, KCl and CsCl at 298.1 ± 0.1 K. We acquired solubility, tie-line, and binodal curve data for the two quaternary systems, and used these results to discuss the solvation abilities of the inorganic salts (KCl and CsCl) and the effect of the polarity of the two organic solvents (1-propanol and 2-propanol) on the liquid–liquid equilibrium. We also obtained an integrated phase diagram for each quaternary system. These results may provide a possible method to apply the salting-out technique to increase the yield of CsCl or to enrich the organic phase content at a considerable reduction of the energy cost [7]. The equilibrium data were correlated with the tie-line data using a modification of the Eisen–Joffe equation [8–10].

2. Experimental

2.1. Materials

The 1-propanol, 2-propanol, and KCl used in this work were analytical grade (purity >99.5%). CsCl (Shang-hai, purity >99.5%) and primary standard potassium dichromate were used without further purification. The water used in all experiments was doubly distilled.

2.2. Apparatus and procedure

The experimental apparatus we employed is similar to the one we used previously [11]. In order to study the saturated

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solubility of KCl and CsCl in these quaternary systems, the saturated solution was made by mixing appropriate amounts of a known mass of the aliphatic alcohol (1-propanol or 2-propanol) and water with known amount of the salt mixtures (KCl and CsCl). The samples were fixed on the carrier plate and stirred for 48 h, and the solution was allowed to settle for a further 24 h. After equilibrium was achieved, solutions were withdrawn using syringes maintained at a slightly elevated temperature to avoid salt precipitation.

The mixtures of KCl and CsCl were set at different ratios (0.75/0.25, 0.5/0.5 and 0.25/0.75, respectively) to obtain the tie-lines of the unsaturated solutions. The binodal curve measurement was carried out in a 25 cm^3 glass vessel containing solution made from salt mixtures (KCl and CsCl) at different ratios (1/0, 0.75/0.25, 0.5/0.5, 0.25/0.75 and 0/1, respectively). The vessel was placed in an apparatus containing water held at a constant temperature of 298.1 K, and the temperature was controlled in this manner to within ±0.1 K. The binodal curves were determined by titration with the aliphatic alcohol.

The total quantities of salts in the organic and aqueous phases were determined by evaporation to dryness at 110 °C. The uncertainty in the measurement of the total mass fraction of the salt mixture was estimated to be within ±0.2%. The amounts of KCl in both phases were determined using atomic absorption spectrometry (AAS). The AAS measurements were performed using a TAS-986 (Bei-jing) atomic absorption spectrometry at a wavelength of 766.5 nm, and the uncertainty in the measurement was within ±0.2%. The amounts of CsCl were determined using the same apparatus at a wavelength of 852.1 nm, and the relative accuracy in the measurement was within ±1.0%. The concentration of the aliphatic alcohol was determined by means of oxidation with potassium dichromate [12,13]. The relative accuracy in the measurement was within ±0.5%. The quantities of water in the aqueous phase and of the alcohol in the organic phase were obtained using mass-balance equations [5,6].

3. Results and discussion

In order to obtain the integrated phase diagrams for these two quaternary systems, it is first necessary to study and understand similar ternary systems. Gomis' group studied the system of water + 1-propanol + KCl at 25 °C [4], and our group investigated the system comprising water + 1-propanol/2-propanol + CsCl at 25 °C [7]. In this work, we also investigated the water + 2-propanol + KCl, and water + KCl + CsCl ternary systems at 298.1 ± 0.1 K. Table 1 provides the mutual solubility data for KCl and CsCl in water. We did not examine the other ternary systems (1-propanol/2-propanol + KCl + CsCl) because the solubilities of the inorganic salts are very low in these systems. Thus, we completed the integrated quaternary phase diagram for the water + 1-propanol + KCl + CsCl system at 298.1 ± 0.1 K, and the results are present in Fig. 1. Fig. 2 shows the phase diagram for the water + 2-propanol + KCl + CsCl system at 298.1 ± 0.1K. These two diagrams are similar, and the only difference is that the two-phase region in Fig. 2 is slightly smaller than that in Fig. 1.

Table 1
Equilibrium solubility as a function of the mass fractions for water (1) + KCl (2) + CsCl (3) at 298.1 ± 0.1 K

Aqueous phase			Solid phase
$100w_1$	$100w_2$	$100w_3$	
34.1	0	65.9	CsCl
34.6	1.4	64.0	CsCl
42.4	7.0	50.6	CsCl + KCl
43.9	9.2	46.9	CsCl + KCl
40.4	17.5	42.1	KCl
73.2	26.8	0	KCl

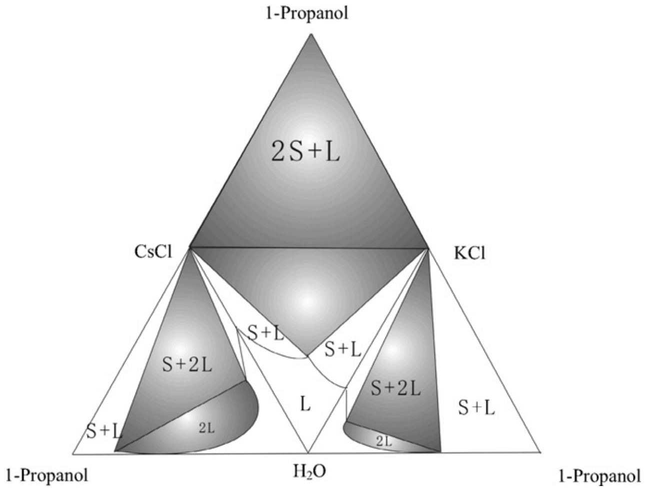

Fig. 1. The quaternary diagram for the water + 1-propanol + KCl + CsCl system at 298.1 ± 0.1 K (S, solid; L, liquid).

To investigate the solvation ability of KCl and CsCl, we created three different ratios of KCl to CsCl (0.25/0.75, 0.5/0.5 and 0.75/0.25). The effect of the mixture ratio on the binodal curves and the unsaturated tie-lines (data in Tables 2–5) is presented in Fig. 3. The experimental results show that

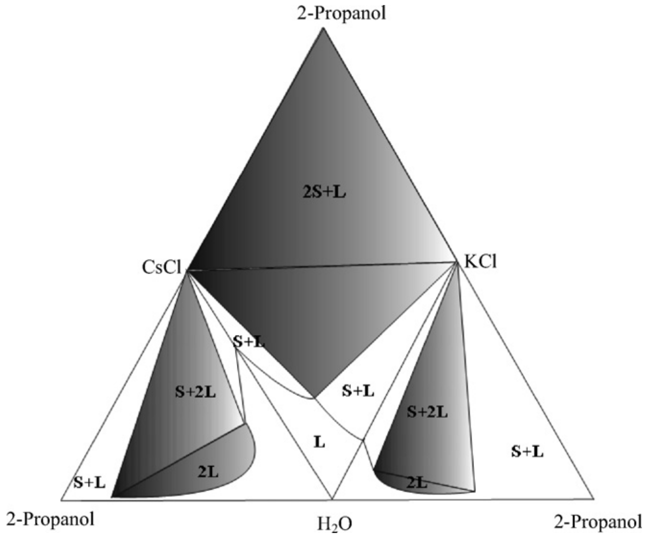

Fig. 2. The quaternary diagram for the water + 2-propanol + KCl + CsCl system at 298.1(±0.1) K (S, solid; L, liquid).