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Phase equilibrium and activity coefficients in ternary systems at 298.15 K: RbCl/CsCl + ethylene carbonate + water

Xiuhua Hao, Shuni Li *, Quanguo Zhai, Yucheng Jiang, Mancheng Hu *

Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, Shaanxi 710062, PR China

ABSTRACT

The (solid + liquid) equilibrium (SLE) and (liquid + liquid) equilibrium (LLE) of RbCl/CsCl + ethylene carbonate (EC) + H_2O ternary systems were carefully investigated at 298.15 K. The SLE and LLE data were correlated by the corresponding equations respectively. Furthermore, the thermodynamic properties of RbCl/CsCl in the EC–water systems were determined by potentiometric method at $T = 298.15$ K. The experiment data were correlated by the Pitzer, modified Pitzer and the extended Debye–Hückel equations. The mean activity coefficients, osmotic coefficients and excess Gibbs free energies, standard Gibbs free energy of transfer and the standard solubility product of systems were calculated. The mean activity coefficient $\gamma_\pm$ decreases with the increase of the molality of electrolyte at the fixed mass fraction of EC. But $\gamma_\pm$ vary abnormally with the increase of the EC content. The result of ΔG_t^0 reflects the spontaneously transfer of the electrolytes from water to the mixed solvents.

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1. Introduction

Electrolytes exist in nature widely and are regarded highly by people for its wider applications. The measurement or prediction of the activity coefficients and osmotic coefficients of electrolyte aqueous solutions is important for both experimental and theoretical solution chemistry studies. Ethylene carbonate (1,3-dioxolan-2-one, EC), a typical dipolar aprotic solvent, is of interest for industrial use. It is solid at room temperature with melting point 36.2 °C. The advantage of this compound over traditional solvents is also due to its low volatility (boiling point of 270.4 °C), excellent compatibility (almost iso-dielectric with water), and solubility properties. The properties of the binary mixtures of EC–H_2O were also investigated. For example, experimental viscosities, densities, refractive indices, freezing points and ionic conductivity of ethylene carbonate–water mixtures at 25 °C were determined [1,2]. Vapor–liquid equilibrium of water–ethylene carbonate was measured at different temperatures [3]. Moreover, Hernández-Luis et al. investigated the thermodynamic properties of NaF/NaCl/NaBr in EC–H_2O ternary mixtures [4–6]. The different solubility and ionic radius of electrolyte, and the special character of EC affect the thermodynamic properties of the solution markedly.

In our previous articles, the activity coefficients of heavy alkaline metal salts, Rb^+ and Cs^+, in alcohol/amino acid/amide–water

mixture solutions [7–9] were reported. As an extension of our series work, we present herein the thermodynamics properties of the ternary systems RbCl/CsCl + EC + H_2O at 298.15 K. Moreover, the binodal curves of the (RbCl/CsCl + EC + H_2O) systems at 298.15 K were also determined and correlated by the three parameter equation. The LLE are also correlated by the Othmer–Tobias equation and Bancroft equation. The modeling of these two ternary systems was based on the Pitzer, modified Pitzer and the extended Debye–Hückel equations.

2. Experimental

The purity and resources of the chemicals used in this research are listed in Table 1. Purity of the samples are greater than 99% (by mass fraction) as stated by the supplier. RbCl and CsCl were dried in an oven to constant weight for 12 h at 453.15 K and 423.15 K respectively and then stored in desiccators prior to be used. Doubly distilled water was used throughout the experiment. Prior to the experiment, the water was boiled to remove dissolved air and to reduce the CO_2 content in order to eliminate the tendency for bubbles to form between the electrodes.

The density ($\rho/g \cdot cm^{-3}$) of the mixture was measured with a density meter (Anton Paar DMA 4500) with double distilled water and air as the calibration substance under atmospheric pressure. The operation sequence was repeated in triplicate under the same conditions to ensure the reliability of experimental results. The values were in agreement with the literature [4,1], as plotted in

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Table 1
Description of chemicals used in this study.

Chemical name (the CAS code)	Source	Specification	Mass purity	Purification method
RbCl (7791-11-9)	Shanghai China Lithium Industrial Co., Ltd.	A.R.	>0.995	None
CsCl (7647-17-8)	Shanghai China Lithium Industrial Co., Ltd.	A.R.	>0.995	None
EC (96-49-1)	Aladdin regent, Shanghai	GC	>0.990	None

Table 2
Experimental SLE and LLE data (mass fraction) of EC (w_1) + RbCl (w_2) + H$_2$O (w_3) and EC (w_1) + CsCl (w_2) + H$_2$O (w_3) ternary systems at T = 298.15 K and p = 0.1 MPa.

w_1	w_2	Solid phase	w_1	w_2
SLE			LLE	
RbCl + EC + H$_2$O				
0.0000	0.4869	RbCl	0.2888	0.3338
0.0000	0.4842 [11]	RbCl	0.2979	0.3186
0.0374	0.4711	RbCl	0.2986	0.3197
0.0668	0.4577	RbCl	0.3075	0.3060
0.1015	0.4409	RbCl	0.3304	0.2736
0.1354	0.4247	RbCl	0.3559	0.2429
0.1637	0.4114	RbCl	0.3824	0.2195
0.1877	0.3984	RbCl	0.4084	0.1977
0.2083	0.3870	RbCl	0.4370	0.1770
0.2373	0.3724	RbCl	0.4566	0.1642
0.2412	0.3715	RbCl	0.4802	0.1527
0.2668	0.3596	RbCl	0.5191	0.1341
0.9190	0.0000	EC	0.5577	0.1201
			0.6009	0.1040
			0.6783	0.0795
			0.6981	0.0730
			0.7252	0.0653
			0.7694	0.0526
			0.7841	0.0498
			0.8600	0.0240
CsCl + EC + H$_2$O				
0.0000	0.6568	CsCl	0.2638	0.4664
0.0000	0.6564 [11]	CsCl	0.2786	0.4437
0.0355	0.6321	CsCl	0.2938	0.4220
0.0544	0.6205	CsCl	0.3047	0.3966
0.0758	0.6067	CsCl	0.3206	0.3739
0.1101	0.5855	CsCl	0.3383	0.3519
0.1286	0.5712	CsCl	0.3562	0.3302
0.1481	0.5591	CsCl	0.3788	0.3075
0.1719	0.5444	CsCl	0.4053	0.2833
0.1954	0.5268	CsCl	0.4335	0.2607
0.2166	0.5099	CsCl	0.4641	0.2380
0.2343	0.4994	CsCl	0.4653	0.2380
0.9190	0.0000	EC	0.4871	0.2245
			0.5120	0.2099
			0.5365	0.1966
			0.5658	0.1815
			0.6009	0.1648
			0.6256	0.1492
			0.6451	0.1406
			0.6731	0.1202
			0.7079	0.1050
			0.7350	0.0896
			0.7870	0.0549
			0.8043	0.0503

The expanded uncertainties are $U(w_1)$ = 0.0064, $U(w_2)$ = 0.0064, $U(T)$ = 0.1 K, and $U(p)$ = 3 kPa (0.95 level of confidence).

Fig. S1. The relative permittivity (ε) of the mixtures was obtained from the literature [4]. The values of relative permittivity and density for the mixed solvents are listed in Table S1.

The working electrode Rb ion-selective electrode (Rb-ISE) and Cs-ISE were the PVC membrane type and were filled with 0.1 mol · L^{-1} RbCl/CsCl as the internal liquid. The Ag/AgCl reference electrode was prepared in our laboratory as described by Wu [10] and was conditioned overnight in 0.1 mol · L^{-1} HCl solution to activate the electrode and rebalance the chloride ions before use. Both the electrodes were calibrated and showed a reasonably Nernst response. The electrodes and the solution were held in a double-walled glass cell with temperature maintained within 298.15 ± 0.1 K by circulating water. All primary stock solutions were prepared by direct weighing using doubly distilled water or the ethylene carbonate + water mixed solvent. For RbCl + EC + H$_2$O and CsCl + EC + H$_2$O systems, working solutions were obtained by the addition of solid inorganic salt to a previously prepared solution in each set of experiments (corresponding to a fixed solvent concentration). All samples were weighed with an analytical balance (Mettler Toledo-AL204, Switzerland) with accuracy ±0.0001 g. An electrometer/high resistance meter (Keithley-6517B, America) was used to measure the potentials. The whole experiment process was performed within 2 h.

The SLE and LLE were studied through the turbidity method utilizing laser monitoring. The known masses of water and EC were placed in the jacketed flask which was controlled by the thermostatic water bath. Then, a slightly excessive amount of RbCl/CsCl was added. Next, water was added cautiously to a stirred solution until the last portion of salts just disappeared. The intensity of the laser beam penetrating the vessel reached the maximum. The amount of water, EC and RbCl/CsCl are all recorded carefully. The binodal curve was obtained similarly. The known amount of aqueous RbCl/CsCl was placed in the flask and aqueous solution of EC was added until turbidity appeared which indicated the formation of two liquid phases. Solubility and binodal curve data for RbCl/CsCl + EC + H$_2$O systems at 298.15 K are given in Table 2. Moreover, the solubility of CsCl and RbCl in pure water was compared with literature [11] and showed good agreement. The solubility of EC in pure water was determined as 0.9190 at 298.2 K. It agrees well with the literature [1] of about 0.916. SLE and LLE for RbCl/CsCl in EC + H$_2$O mixtures are depicted in Fig. 1. The composition of the two liquid phases can be presented by the tie lines. For the determination of the tie lines, samples were prepared by mixing appropriate amounts of RbCl/CsCl, EC and H$_2$O in the corresponding syringes. Then the samples were fixed on the carrier plate and rotated for 48 h and settled for a further 24 h. After the equilibrium was achieved, the solution in the top and bottom phases were withdrawn and analyzed. In cases where excess solid salt was present, the sample was withdrawn gently and carefully. More details can be seen in the former work [12]. The concentrations of RbCl/CsCl and EC in both phases were determined by the titration method [13,14]. The concentration of the salt was determined by Mohr method with chromate ions as an indicator in the titration of chloride ions. The concentration of EC was determined after the alkaline hydrolysis of EC. Sodium carbonate was precipitated by barium chloride solution after the reaction of ethylene carbonate solution with excess sodium hydroxide standard solution at (80–100) °C. Then hydrochloric acid standard solution was used for back-titrating of the excess alkali standard solution with phenolphthalein as indicator. Data of the tie lines at 298.15 K of the studied systems are presented in Table 3.

3. Theoretical model

3.1. The Pitzer ion-interaction model

According to Pitzer, for the mean activity coefficients $\gamma_\pm$ of 1-1 type electrolytes the corresponding relations are [15,16]: