J. Chem. Eng. Data **2005,** *50,* 1299−1302

Multiphase Equilibrium Behaviors of Rubidium Salts (RbCl, $RbNO_3$, Rb_2SO_4, and Rb_2CO_3) in Aqueous Ethanol Mixture at 298.15 K

Jun Zhang,*,[†] Xian-Zhao Wang,[‡] Bang-Cai Song,[†] and Shu-Ping Xia[§]

Chemical Engineering Department, Henan University of Science and Technology, Luoyang 471003, People's Republic of China, Henan Xuchang Vocational and Technological College, Xuchang 461000, People's Republic of China, and Institute of Salt Lakes, Chinese Academy of Sciences, Xi'an 710043, People's Republic of China

---

Rubidium salts (RbCl, $RbNO_3$, Rb_2SO_4, and Rb_2CO_3) + water + ethanol systems have been comparatively investigated and discussed. The solubilities and mutual miscibilities decrease with increasing ethanol content in the systems. The equilibrium solid phases for the RbCl-, $RbNO_3$-, and Rb_2SO_4-containing systems are simple nonhydrates, but that of the Rb_2CO_3-containing system is $Rb_2CO_3 \cdot 2H_2O$. Rb_2CO_3 can make the miscible aqueous ethanol mixture split, and the three others cannot. An empirical formula was proposed to correlate the experimental data, and the phase diagrams were constructed. An explanation for the experimental results based on molecular structure is postulated.

Introduction

Adding organic solvents such as aliphatic alcohols methanol, ethanol, propanol, and butanol to aqueous inorganic salts mostly leads to an appreciable reduction in the solubility of the salts. This so-called salting-out effect plays an important role in the separation and purification of the inorganic salts and has already found many applications.[1−3] As is well known, rubidium belongs to rare and valuable alkali metals possessing extremely high chemical activities and unique optical and electrical properties, and it has been widely used in modern high-technology fields.[4] In the salt lake brine of western China, rubidium salt resources have been found. To exploit these valuable resources scientifically, extensive research on phase equilibrium relationships of aqueous and nonaqueous rubidium salt mixtures is necessary. Unfortunately, the published studies are not satisfactory.

Ethanol has been selected as a salting-out agent because of its nontoxicity and low cost. The phase equilibrium and isothermal mutual solubilities for similar alkali metal salts such as CsCl,[5] Cs_2SO_4,[6] and Rb_2CO_3[7] at different temperatures in ethanol and water mixed solvents have been investigated. However, a systematic and comparative study of common rubidium salts in mixed solvents is still lacking. As part of our effort to investigate and develop rubidium salts, we recently focused on a liquid−solid phase equilibrium study of (RbCl, $RbNO_3$, Rb_2SO_4, and Rb_2CO_3) in water + ethanol so as to provide basic reference data for further application and development.

Experimental Section

Materials. Rubidium chloride (RbCl), rubidium nitrate ($RbNO_3$), rubidium sulfate (Rb_2SO_4), and rubidium carbonate (Rb_2CO_3), purchased from Shanghai Chemical Company, were all analytical-grade reagents and were recrystallized from water until their mass fractions all exceeded 99.5 %. Analytical-grade ethanol (C_2H_5OH, purity >99.7 %) and potassium dichromate ($K_2Cr_2O_7$, purity >99.8 %) were directly used without further purification. Double-distilled water with a conductivity of less than 1.0×10^{-4} $S \cdot m^{-1}$ was used in all of the experiments.

Apparatus and Procedures. In view of the expensiveness and large solubility of the rubidium salts, a semimicro installation with a microsampling unit was designed and prepared in our laboratory (Figure 1). Transparent tubes (6 to 10, glass or PVC) with a volume of (10 to 20) cm^3 were employed as containers to carry out the phase equilibrium measurements. The tubes, fixed on the carrier plate, were put into the thermostat whose temperature was controlled at (298.15 ± 0.02) K. The carrier plate rotated at about 30 rpm. The mixtures, prepared by directly mixing a precalculated mass of rubidium salt, ethanol, and water, were put into the tubes up to about 70 % content. After the tubes rotated for 24 h, the equilibrium state was established, and then the solutions were allowed to settle down for 10 h to ensure that the interfaces between different phases were visible. During sampling, care was taken to ensure that turbidity did not appear, especially when the liquid phase was divided into two phases.

The concentration of rubidium salt in the equilibrium solid or liquid phases was determined by tetraphenylboron rubidium gravimetrical analysis[7] or alternatively by evaporating the solution to dryness at a temperature that was lower than the decomposition temperature of each rubidium salt. The potassium dichromate oxidation method[8,9] was adopted to measure the ethanol content in the equilibrium phases. The uncertainties in the mass fraction measurements of the rubidium salt and ethanol were estimated to be ±0.1 % and ±0.5 %, respectively.

Results and Discussion

For the four ternary systems (1) RbCl + C_2H_5OH + H_2O, (2) $RbNO_3$ + C_2H_5OH + H_2O, (3) Rb_2SO_4 + C_2H_5OH + H_2O, and (4) Rb_2CO_3 + C_2H_5OH + H_2O, the solubility or mutual miscibility and phase relationship at (298.15 ± 0.02) K were measured separately.

Solubility and Mutual Miscibility. Tables 1 to 3 give the experimental results of the solubilities and wet solid

---

* Corresponding author. E-mail: zhjabc@mail.haust.edu.cn.

[†] Henan University of Science and Technology.

[‡] Henan Xuchang Vocational and Technological College.

[§] Chinese Academy of Sciences.

10.1021/je050038x CCC: \$30.25

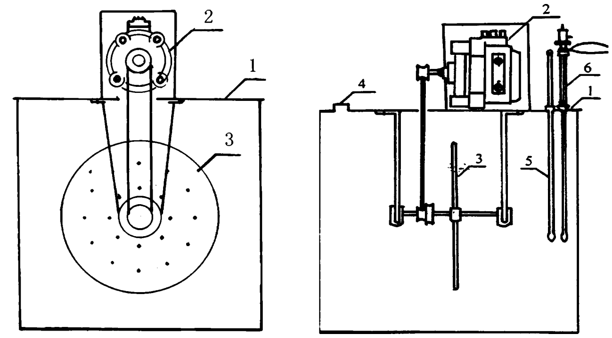

Figure 1. Semimicro apparatus used for phase equilibrium measurements: 1, thermostat; 2, motor; 3, carrier plate; 4, hole for the heating unit; 5, microthermometer; 6, contact thermometer.

Table 1. Mass Fractions of Saturated Solutions and the Wet Solid Phase of C_2H_5OH (1) + RbCl (2) + H_2O (3) at 298.15 K

saturated solution		wet solid phase		equilibrium solid phase
$100w_1$	$100w_2$	$100w_1$	$100w_2$	
0.00	45.58			RbCl
5.66	42.33	4.28	57.35	RbCl
13.02	35.65	7.66	62.67	RbCl
20.08	29.70	14.13	53.56	RbCl
30.98	22.03	14.78	62.94	RbCl
41.84	15.97	36.37	27.50	RbCl
60.96	6.98	30.51	52.34	RbCl
77.57	1.08	29.38	62.45	RbCl
93.88	0.17	30.97	67.64	RbCl

Table 2. Mass Fractions of Saturated Solutions and the Wet Solid Phase of C_2H_5OH (1) + $RbNO_3$ (2) + H_2O (3) at 298.15 K

saturated solution		wet solid phase		equilibrium solid phase
$100w_1$	$100w_2$	$100w_1$	$100w_2$	
0.00	39.95			$RbNO_3$
7.93	28.72	3.72	68.27	$RbNO_3$
18.93	17.88	12.23	46.97	$RbNO_3$
28.53	12.38	16.98	47.50	$RbNO_3$
34.89	9.73	25.37	34.35	$RbNO_3$
40.98	8.17	16.08	63.86	$RbNO_3$
54.17	4.84	34.81	38.74	$RbNO_3$
66.25	2.45	32.37	52.61	$RbNO_3$
74.26	1.19	47.66	36.52	$RbNO_3$
82.41	0.42	43.39	46.87	$RbNO_3$
94.33	0.04	65.34	29.08	$RbNO_3$

Table 3. Mass Fractions of Saturated Solutions and the Wet Solid Phase of C_2H_5OH (1) + Rb_2SO_4 (2) + H_2O (3) at 298.15 K

saturated solution		wet solid phase		equilibrium solid phase
$100w_1$	$100w_2$	$100w_1$	$100w_2$	
0.00	33.41			Rb_2SO_4
2.92	28.01	1.85	55.70	Rb_2SO_4
6.08	22.13	4.69	43.38	Rb_2SO_4
9.77	17.74	5.48	52.63	Rb_2SO_4
14.39	12.85	9.67	47.26	Rb_2SO_4
21.94	7.01	16.90	28.89	Rb_2SO_4
27.31	4.47	13.42	55.54	Rb_2SO_4
33.86	2.48	24.09	31.47	Rb_2SO_4
40.05	1.19	22.74	43.61	Rb_2SO_4
51.34	0.47	38.42	26.95	Rb_2SO_4
66.78	0.13	37.06	43.42	Rb_2SO_4

Table 4. Mass Fraction of Different Liquid Phases for C_2H_5OH (1) + Rb_2CO_3 (2) + H_2O (3) at 298.15 K

upper layer		lower layer	
$100w_1$	$100w_2$	$100w_1$	$100w_2$
88.52	0.11	0.38	64.75
85.03	0.47	2.49	54.88
81.38	0.96	4.37	47.41
67.95	1.94	4.60	42.33
54.56	4.02	6.84	40.59
38.91	11.10	9.76	35.07
19.35	24.03[a]		

[a] Miscible point.

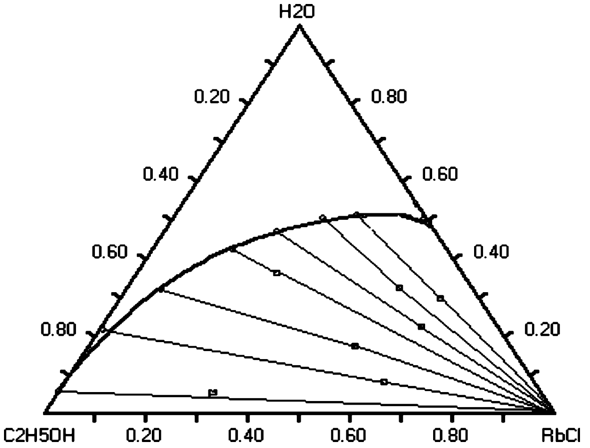

Figure 2. RbCl + C_2H_5OH + H_2O phase diagram at 298.15 K.

phase compositions (given in mass fraction here and in the rest of the article) for systems 1 to 3, respectively. Here, the wet solid phase stands for the corresponding equilibrium solid phase containing a small amount of mother liquid. This is, after sampling from the saturated solution in the top layer, the corresponding equilibrium solid phase in the bottom layer was withdrawn using a sampler. The solid phase was mingled with some water and ethanol to form a wet solid phase, and the exact composition of the wet solid phase, or w_1, w_2, or w_3, $w_3 = 1 - w_1 - w_2$, has been determined by chemical analysis, as shown in Tables 1 to 3. For these three ternary systems, no demixing phenomena were observed in the saturated solutions over the whole concentration range.

As for the Rb_2CO_3 + C_2H_5OH + H_2O ternary system, two marked features are quite different from those of the other three systems. First, the splitting phenomenon of the saturated solution phase appears. In accordance with the phase rule, the coexisting state for liquid−liquid−solid phases should be unique at the given temperature and pressure. In this state, it was found that the upper layer's mass fractions are 92.83 % (Rb_2CO_3) and 0.55 % (C_2H_5OH) and the lower layer's are 73.34 % (Rb_2CO_3) and 0.43 % (C_2H_5OH); the corresponding mass fractions of the wet solid phases are 83.09 % (Rb_2CO_3) and 0.27 % (C_2H_5OH). Therefore, Table 4 implies that either the solutions are not saturated or no solid phase exists. Second, the equilibrium solid phase is a hydrate but not simple rubidium salt as in the other three systems at the temperature studied; the solid phase is affirmed to be $Rb_2CO_3 \cdot 2H_2O$. It is worth noting that in Tables 1 to 4 the water content has been omitted because the total mass fraction for the rubidium salt, ethanol, and water in the system is 100 %.

Phase Diagram. The triangular phase diagrams for (1) RbCl + C_2H_5OH + H_2O, (2) $RbNO_3$ + C_2H_5OH + H_2O, (3) Rb_2SO_4 + C_2H_5OH + H_2O, and (4) Rb_2CO_3 + C_2H_5OH + H_2O at 298.15 K were separately drawn using the computer drawing program developed in our laboratory and are shown in Figures 2 to 4.

The phase diagram of ternary system Rb_2CO_3 + C_2H_5OH + H_2O is quite distinct and different from the other three figures because of its demixing characteristics (Figure 5).

Table 5. Parameters Values and Standard Deviation of the Correlation Equation

system	k_0	10^2k_1	10^4k_2	10^5k_3	10^8k_4	10^3D^a
$RbCl-C_2H_5OH-H_2O$	3.878	−3.946	11.982	−2.439	9.841	9.505
$RbNO_3-C_2H_5OH-H_2O$	3.692	−4.175	−2.715	1.490	−16.50	8.577
$Rb_2SO_4-C_2H_5OH-H_2O$	3.522	−1.091	2.224	6.853	−10.303	3.996
$Rb_2CO_3-C_2H_5OH-H_2O$	4.169	3.242	7.053	−8.428	1.999	6.830

[a] $D = \sqrt{\{\sum_{i=1}^{n}[(w_s(e)-w_s(c))/w_s(e)]^2/N\}}$, where w_s(e) and w_s(c) refer to experimental and calculated solubilities, respectively, and N is the number of experimental data points.

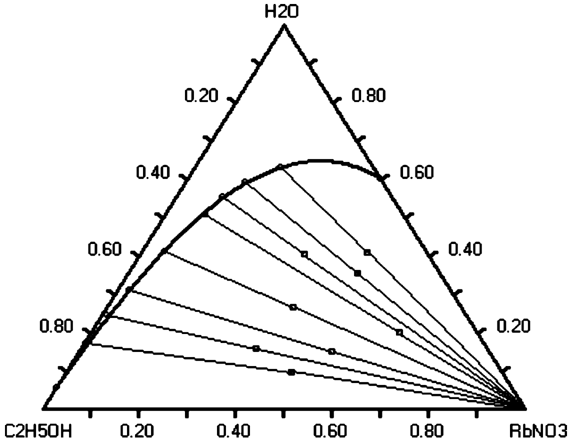

Figure 3. $RbNO_3 + C_2H_5OH + H_2O$ phase diagram at 298.15 K.

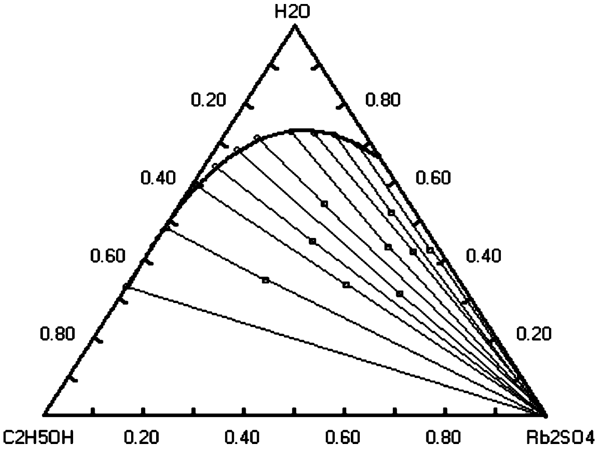

Figure 4. $Rb_2SO_4 + C_2H_5OH + H_2O$ phase diagram at 298.15 K.

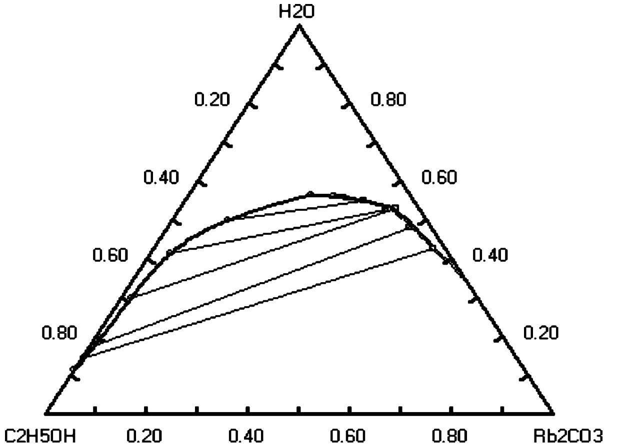

Figure 5. $Rb_2CO_3 + C_2H_5OH + H_2O$ phase diagram at 298.15 K.

Correlation of Experimental Data. In consideration of the binodal curve's features in these phase diagrams, a nonlinear polynomial equation was proposed to correlate the solubility and mutual miscibility

$$\ln(w_s) = \sum(k_n w_e^n) \qquad n = 0, 1, 2, 3, 4$$

where w_s and w_e refer to the mass fractions of rubidium salts and ethanol in the various mixtures, respectively. k_n stands for adjustable parameters that can be obtained by regressing the experimental data. Table 5 lists the k_n values for the four systems, together with the standard deviations (D). Here, $D = \sqrt{\{\sum_{i=1}^{n}[(w_s(e)-w_s(c))/w_s(e)]^2/N\}}$, where w_s(e) and w_s(c) refer to experimental and calculated solubilities, respectively, and N is the number of experimental data points.

Identification of the Equilibrium Solid Phase. As seen from Figures 2 to 4, the tie line between the liquid and solid phase points directly to the vertexes indicating the rubidium salts (RbCl, $RbNO_3$, Rb_2SO_4) in the phase diagram. These effects show that at 298.15 K the equilibrium solid phases for these systems are neither hydrates nor any new compounds. The principle for this judgment method is based on Schrainemakers' wet residual tie line technique.[10] According to Schrainemakers, if the tie lines between the composition points of the saturated solution and the wet solid phase intersect at the same point on the side line of triangular phase diagram, then the intersection point can represent the composition of the solid phase. At the same time, corresponding XRD analyses of these equilibrium solid phases have also verified the reliability of the above results. (The XRD patterns were omitted here).

Comparative Analysis and Discussion. Tables 1 to 4 and Figures 2 to 5 show that the solubilities and mutual miscibilities all display a marked reduction with an increase in ethanol content in the ternary systems (e.g., ethanol has an strong salting-out effect on the rubidium salts). Different rubidium salts (RbCl, $RbNO_3$, Rb_2SO_4, and Rb_2CO_3) have different abilities to split the wholly miscible $C_2H_5OH + H_2O$ binary liquid system. For these phenomena, a trial explanation may be given by way of a microstructure and microinteraction mechanism of the solution.

On one hand, water and ethanol are both polar molecules with similar microstructures, each having one OH group to form H bonds. Both can form associated molecules. However, the "bulk" of the single H_2O molecule is much smaller than that of the C_2H_5OH molecule, so the spatial steric hindrance of the H_2O molecule is correspondingly much smaller than that of the C_2H_5OH molecule. In addition, the relative permittivity of water is 3 times that of ethanol at 298.15 K (the former is 78.13; the latter is 23.8). When ethanol is added to an aqueous rubidium salt solution, the ethanol molecules will attract the water molecules via hydrated cations and anions. The gradual decrement of the relative permittivity of the mixed solvents with increasing ethanol content directly results in the increment of the static electric attracting force between cations and anions. As a result, the solubilities of rubidium salts decrease with the addition of ethanol.

On the other hand, why do different rubidium salts have different abilities to split the miscible ethanol + water system? According to Timmermans,[11] if a salt dissolves in one solvent more easily than in another solvent, then the salt can reduce the miscibility of the binary liquid system. For the four rubidium salts studied, their solubilities (mass fractin) in water are 48.6 % (RbCl), 39.9 % ($RbNO_3$), 33.7 % (Rb_2SO_4), and 71.2 % (Rb_2CO_3), respectively, but they can hardly dissolve in pure ethanol. Rb_2CO_3 has the highest demixing ability of the aqueous ethanol mixture. The static electric attracting force and spatial steric hindrance are the two most important factors that decide the splitting ability of rubidium salts. RbCl and $RbNO_3$ are 1−1-type electrolytes, having relatively weak and similar demixing abilities. However, Rb_2SO_4 and Rb_2CO_3 are the same 1−2-type salts, but they have quite different demixing abilities. The reason is that their static electric attracting forces are equivalent but their spatial steric hindrances are different. SO_4^{2-} and CO_3^{2-} adopt tetrahedron and planar triangle spatial configurations, respectively. Therefore, the spatial steric hindrance of SO_4^{2-} is larger than that of CO_3^{2-}, and the corresponding solvated ability of CO_3^{2-} is stronger than that of SO_4^{2-}. Therefore, in the ethanol + water mixed solvent, Rb_2CO_3 reveals the largest demixing ability.

Conclusions

For the four rubidium salts involved, the solubility, mutual miscibility, and phase relationship in RbCl ($RbNO_3$, Rb_2SO_4, and Rb_2CO_3) + water + ethanol ternary systems have been comparatively investigated and discussed. At 298.15 K, RbCl and $RbNO_3$, as 1−1-type salts, cannot split the miscible ethanol + water system, and the equilibrium solid phases are all simple nonhydrates. As the same 1−2-type rubidium salts, Rb_2SO_4 cannot demix an aqueous ethanol mixture, but Rb_2CO_3 can. This reveals the large differences between their microstructures. In summary, ethanol can be used as an effective salting-out reagent to separate and purify rubidium salts. On the contrary, rubidium salts should be helpful in the enriching distillation or extraction of ethanol.

Literature Cited

(1) Diego, B.; Vincenzo, B.; Gabriele, D. G. Salting-out Effect in the Separation of Water-Alcohol Systems. *Chim. Ind*. **1984**, *66*, 319−326.

(2) Aznar, M.; Araujo, R. N.; Romanato, J. F.; Santos, G. R.; d'Avila, S. G. Salt Effects on Liquid−Liquid Equilibrium in Water + Ethanol + Alcohol + Salt Systems. *J. Chem. Eng. Data* **2000**, *45*, 1055−1059.

(3) Gomis, V.; Ruiz, F.; Asensi, J. C.; Cayvela, P. Liquid-Liquid-Solid Equilibria for the Ternary Systems Water-Lithium Chloride-1-Propanol or 2-Propanol at 298.15 K. *Fluid Phase Equilib.* **1996**, *119*, 191−195.

(4) Perel'man, F. M. *Rubidium and Cesium*; Pergamon Press: London, 1985.

(5) Hu, M-c.; Liu, Z-h. Study on the Phase Diagram of CsCl-C_2H_5-OH-H_2O Ternay System at 30, 40, 50 °C. *Chem. J. Chin. Univ.* **2000**, *21*, 1717−1719.

(6) Zhai, Q-g.; Hu, M-c.; Liu, Z-h. Phase Equilibrium of the Cs_2SO_4-C_2H_5OH-H_2O Ternary System. *Acta Phys.-Chim. Sin.* **2003**, *19*(11), 1089−1092.

(7) Yue, T.; Gao, S-y. Phase Diagram of Rubidium Carbonate + Ethanol + Water Ternary Syatem. *Indian J. Chem.* **2003**, *42A*, 1031−1034.

(8) Barnard, J. A.; Karayannis, N. The Determination of Some Alcohols and Aldehydes by Oxidation with Acid Potassium Dichromate. *Anal. Chim. Acta* **1962**, *26*, 253−258.

(9) Xia, S-p.; Wang, G-f. Analysis of Salt-Containing Aliphatic Alcohols. *J. Salt Lakes* **1987**, *1*, 14−17 (in Chinese).

(10) Chen, Y-s. *Physico-Chemical Analysis*; Higher Education Press: Beijing, 1985; p 56.

(11) Timmermans, J. Die Kritische Lösungstemperatur von Ternären Gemengen. *Z. Phys. Chem.* **1907**, *68*, 129−213.

Received for review January 25, 2005. Accepted May 13, 2005.

JE050038X