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Phase equilibria of alkali metal salt ($NaNO_3$,KNO_3,$RbNO_3$,$CsNO_3$) in system $HOCH_2CH(OH)CH_2OH$ - H_2O at various temperatures

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ABSTRACT

By using a self-made research device for phase equilibrium, the equilibrium solubility of the saturation ternary system of $NaNO_3$/KNO_3/$RbNO_3$/$CsNO_3$ - $HOCH_2CH (OH)CH_2OH$ - H_2O at 35 and 45 °C was measured, and simultaneously the density and refractive index of this system was determined. The experimental results showed that, in all systems, with the increase of weight percentage of glycerol, the solubility and density of the salt in mixed solvent were reduced, while the refractive index was increased gradually. The solubility, refractive index and density data in all the saturation systems were fitted by the four-parameter empirical correlation equation.

KEYWORDS

Alkali metal nitrate;
Glycerin;
Solubility;
Density;
Refractive index.

INTRODUCTION

Crystallization, separation and purification can be undertaken by means of several small molecular weight organic solvents which are mutually soluble with water to form a salt-mixture solvent system. This method has been widely applied in chemical, biochemical, pharmaceutical and chemical production process[1-3]. The investigation on the alkali metal salt-alcohol water mixed solvent system becomes more and more polular[4-7]. Based on the series of system in our research group[8-12], the experiment method is improved and this paper has a systematic study on the physical properties of the ternary system of $NaNO_3$/ KNO_3/$RbNO_3$/$CsNO_3$ - $CH_3CHOHCH_2OH$ - H_2O at 35 and 45°C, including equilibrium solubility, density of the saturation solution, and refractive index, which aims to provide the necessary basic reference data for the separation and purification of alkali metal nitrate.

EXPERIMENTAL SECTION

Reagents and instruments

Reagents

Sodium nitrate (99.5% purity, Sinopharm Chemical Reagent Co., Ltd), potassium nitrate (99.5% purity, Sinopharm Chemical Reagent Co., Ltd), rubidium nitrate (purity 99.5%, Shanghai China Lithium Industrial Co., Ltd), cesium nitrate (Sichuan State Lithium Materials Co., Ltd), all the reagents were put into the oven at 110 °C for drying, and then placed into a dryer after cooling and bottling; Glycerol (purity, 99.0%, Sinopharm Chemical Reagent Co., Ltd); what should be noted is that all the water used in the experiment are double-distilled water.

Instruments

Semi-micro phase equilibrium experiment device (self-made)[6]; electronic balance (AL 204, Mettler Toledo, accuracy of $\pm 1 \times 10^{-4}$ g); density - refractometers (DMA4500-RXA170 Anton Paar, accuracy of $\pm 1 \times 10^{-5}$ g • cm^{-3} and 4×10^{-5}); vacuum oven (DZ-2BC, Tianjin Taisite Instrument Co., Ltd). The density-refractometers was calibrated by the air and double-distilled water each time before use.

Experimental method

Analytic method for nitrate and glycerol

The content of nitrate and glycerol were analyzed by a density-refractive index approach. According to the literature[13,14], in a certain range of concentration, the density and the refractive index of the ternary system solution are related to the salt and alcohol content of this solution, in accordance with the following empirical equation:

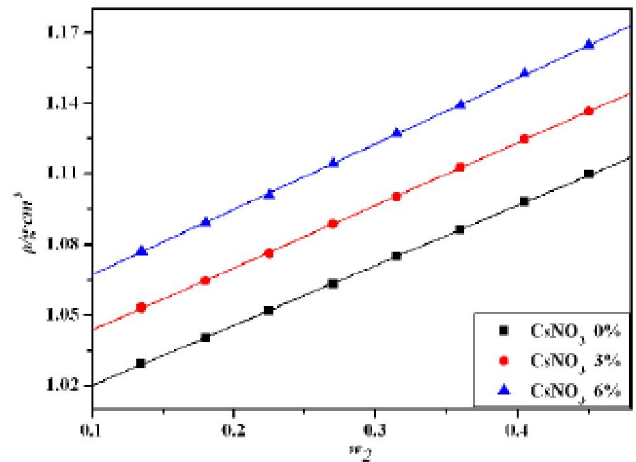
$$\rho = a_1 + b_1 w_1 + c_1 w_2 \quad (1)$$

$$n_D = a_2 + b_2 w_1 + c_2 w_2 \quad (2)$$

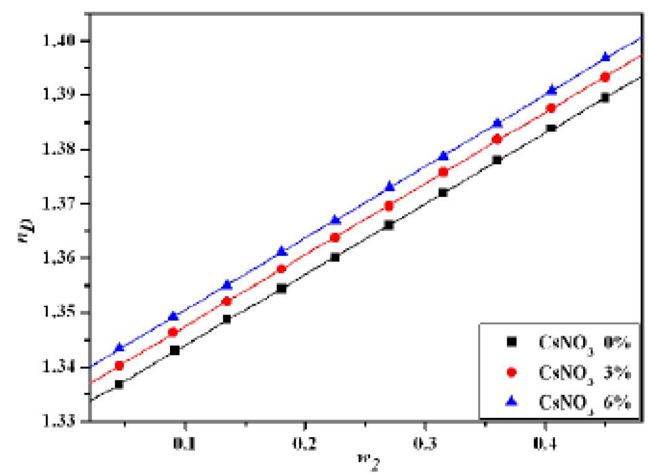
Whereas ρ (g/cm^{-3}) is density, n_D is the refractive index, w_1 is the weight percentage of the nitrates in the solution, w_2 is the weight percentage of the glycerol in the solution, and a_1, b_1, c_1, a_2, b_2 *and* c_2 are parameters of the equation respectively. For example, in the ternary system of $CsNO_3$ (w_1)+ $CH_2CHOHCH_2OH$ (w_2)+ H_2O (w_3), three standard solutions were prepared, in which the content of cesium nitrate was 0%, 3%, 6% respectively and the content of glycerol was increased gradually, then the density and the refractive index of these solutions were measured at 25 °C. The density (ρ) and refractive index (n_D) were plotted with the content of glycerin (w_2) respectively, as shown in Figure 1, the linear fits well within the studied range ($w_1 < 0.06$, $w_2 < 0.45$), and the formula for w_1, w_2 was deduced by the determined parameters (TABLE 1) and combined with equation (1) and (2).

Phase equilibrium determination in saturated system

7 g mixed solvents of different alcohol/water ratio were added into a 10ml balance tube, respectively, and then salts were added to an excess. The balance tube was packaged well, fixed on the turntable of the semi-micro phase equilibrium experimental device, and then placed into a constant temperature water bath (accuracy ± 0.05) for automatic rotation lasting for 48 h. The whole process should be observed at all times to ensure that there was a appropriate amount of crystal in the balance tube otherwise salts need to add, and after repeating the above process, the tube was kept at a



(a)



(b)

Figure 1 : The density (a) and refractive index (b) calibration curves for the $CsNO_3$ - $HOCH_2CH(OH)CH_2OH$ - H_2O system at 25 °C (■, 0 % $CsNO_3$; •, 3% $CsNO_3$; ▲, 6% $CsNO_3$)

TABLE 1 : The parameters of equation 1 and 2

Salts	a_1	b_1	c_1	a_2	b_2	c_2
KNO_3	0.99447	0.67367	0.26012	1.33091	0.11600	0.13194
NaNO	0.99447	0.60433	0.26111	1.33091	0.07750	0.13303
$RbNO_3$	0.99447	0.71633	0.26233	1.33091	0.06700	0.13265
$CsNO_3$	0.99440	0.74667	0.26054	1.33102	0.05233	0.13233

static temperature for 24 h. The saturated solution was removed and diluted, then the density and refractive index of the solution was measured at 25 °C, and the weight percentage of the salts and alcohols were calculated by a density-refractive index approach. The content of water was calculated by the subtraction method.

RESULTS AND DISCUSSION

The solubility, density and refractive index data of the ternary saturated solution system $NaNO_3$/ KNO_3/ $RbNO_3$/$CsNO_3$ (w_1)+ $HOCH_2CH(OH)CH_2OH$ (w_2)+ H_2O (w_3) at 35 °C and 45 °C are listed in TABLE 2. TABLE 3 has presented the solubility and refractive index data of alkali metal nitrates at 45 °C in

TABLE 2 : Weight percentage, density (ρ), and refractive Index (n_D) for the glycerin (1) - MNO_3 (2) - H_2O (3) systems (M=Na, K, Rb, Cs) at 35 and 45 °C

w_1	w_2	ρ/(g·cm^{-3})	n_D	w_1	w_2	ρ/(g·cm^{-3})	n_D
35 °C $NaNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)							
0.0000	0.4999	1.40465	1.39039	0.4724	0.2677	1.33232	1.42614
0.0752	0.4629	1.39390	1.39471	0.5629	0.2343	1.32276	1.43443
0.1385	0.4237	1.38104	1.39943	0.6521	0.2020	1.31884	1.44481
0.2236	0.3833	1.36927	1.40482	0.7556	0.1677	1.31542	1.45660
0.2975	0.3465	1.35579	1.41077	0.8695	0.1349	1.31444	1.47066
0.3871	0.3047	1.34292	1.41755				
35 °C KNO_3 (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)							
0.0000	0.3320	1.24458	1.36549	0.5246	0.1283	1.22066	1.41505
0.0702	0.2951	1.23327	1.37088	0.6283	0.1030	1.23049	1.42719
0.1489	0.2578	1.22308	1.37734	0.7315	0.0829	1.24295	1.44018
0.2336	0.2194	1.21656	1.38498	0.8406	0.0654	1.25838	1.45425
0.3244	0.1850	1.21468	1.39404	0.9511	0.0500	1.27912	1.47076
0.4234	0.1517	1.21593	1.40409				
35 °C $RbNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)							
0.0000	0.4936	1.48389	1.37078	0.4884	0.1878	1.31572	1.41526
0.0562	0.4389	1.45091	1.37421	0.5967	0.1487	1.30861	1.42685
0.1255	0.3739	1.41807	1.37995	0.7051	0.1195	1.30411	1.43987
0.2031	0.3242	1.38099	1.38617	0.8171	0.0927	1.30296	1.45294
0.2906	0.2748	1.34956	1.39497	0.9310	0.0694	1.30209	1.46608
0.3885	0.2243	1.32745	1.40424				
35 °C $CsNO_3$ (1)- $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)							
0.0000	0.2904	1.23655	1.35122	0.5239	0.5239	1.24377	1.41446
0.0744	0.2560	1.23283	1.35862	0.6282	0.1025	1.25161	1.42657
0.1543	0.2282	1.23181	1.36853	0.7337	0.0828	1.26282	1.43978
0.2394	0.2019	1.23153	1.37861	0.8412	0.0652	1.27565	1.45708
0.3310	0.1725	1.23399	1.38996	0.9499	0.0501	1.28974	1.46953
0.4252	0.1494	1.23908	1.40159				
45 °C $NaNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)							
0.0000	0.5223	1.42192	1.39141	0.4711	0.2882	1.34263	1.42667
0.0722	0.4862	1.40778	1.39533	0.5537	0.2519	1.33215	1.43382
0.1375	0.4460	1.39485	1.40029	0.6502	0.2122	1.32496	1.44352
0.2204	0.4049	1.38015	1.40617	0.7559	0.1781	1.32034	1.45311
0.2930	0.3654	1.36723	1.41196	0.8656	0.1460	1.31775	1.46483
0.3848	0.3253	1.35423	1.41879				
45 °C KNO_3 (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)							
0.0000	0.4202	1.28548	1.37064	0.5077	0.1527	1.22971	1.41212
0.0653	0.3580	1.26843	1.37369	0.6152	0.1230	1.23706	1.42380
0.1360	0.3021	1.25489	1.37874	0.7221	0.0968	1.24875	1.43781
0.2210	0.2616	1.24286	1.38495	0.8294	0.0786	1.26231	1.45365
0.3156	0.2210	1.23349	1.39288	0.9410	0.0595	1.27849	1.46839
0.4077	0.1828	1.22995	1.40048				
45 °C $RbNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)							
0.0000	0.5794	1.58932	1.38174	0.4654	0.2256	1.34156	1.41549
0.0479	0.5216	1.53699	1.38373	0.5741	0.1813	1.32507	1.42592
0.1081	0.4612	1.49599	1.38702	0.6861	0.1432	1.31653	1.43937
0.1810	0.3981	1.44888	1.39218	0.8021	0.1092	1.31322	1.45167
0.2657	0.3374	1.40508	1.39761	0.9208	0.0795	1.31035	1.46592
0.3626	0.2760	1.36723	1.40634				
45 °C $CsNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)							
0.0000	0.3585	1.31475	1.35598	0.5095	0.1507	1.26886	1.41290
0.0692	0.3086	1.29815	1.36131	0.6096	0.1290	1.27009	1.42742
0.1466	0.2673	1.28645	1.36963	0.7176	0.1028	1.27699	1.44125
0.2300	0.2333	1.27714	1.37881	0.8260	0.0821	1.28407	1.45529
0.3174	0.2063	1.27233	1.38842	0.9348	0.0651	1.29468	1.47009
0.4115	0.1769	1.26901	1.40027				

TABLE 3 : Solubility (S) and refractive index (n_D) in pure water (w %) at 45 °C

salt	this work		literature	
	S (w %)	n_D	S (w %)	n_D
$NaNO_3$	52.23	1.39141	52.25[16]	1.3911[16]
KNO_3	42.02	1.37064	-	-
$RbNO_3$	57. 94	1.38174	57.48[17]	1.3837[17]
$CsNO_3$	35.85	1.35598	35.28[18]	1.3582[18]

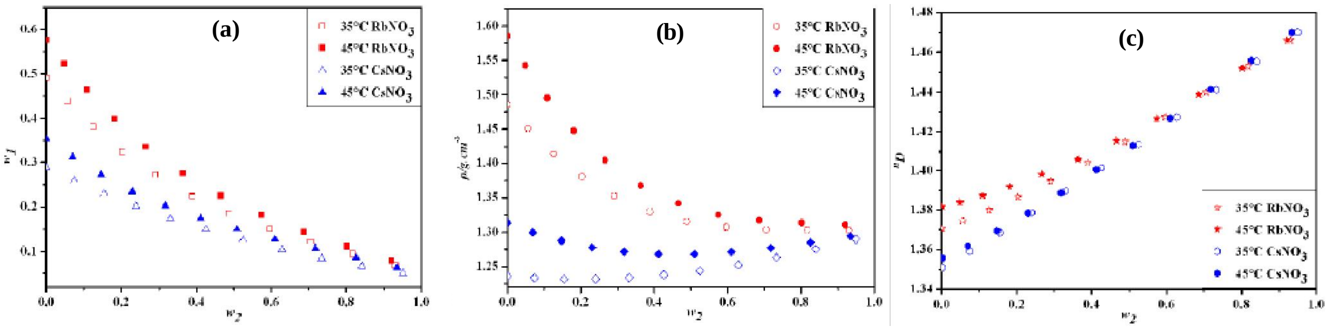


Figure 2 : The solubility, densities (a) and refractive indices (b) for the ternary systems $RbNO_3/CsNO_3$ (1) + $HOCH_2CH(OH)CH_2OH$ (2) + H_2O (3) at 35 °C and 45 °C

TABLE 4 : Values of parameters of eq (3)

systems	A_0	A_1	A_2	A_3	δ
Weight percentage					
35 °C $NaNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	0.5014	-0.5686	0.1550	0.0167	0.0014
45 °C $NaNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	0.5233	-0.5649	0.1056	0.0495	0.0017
35 °C KNO_3 (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	0.3328	-0.5716	0.4028	-0.1202	0.0011
45 °C KNO_3 (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	0.4139	-0.8636	0.8657	-0.3732	0.0043
35 °C $RbNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	0.4910	-0.9914	0.9292	-0.3788	0.0027
45 °C $RbNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	0.5766	-1.1580	1.0583	-0.4217	0.0016
35 °C $CsNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	0.2885	-0.4215	0.2466	-0.0715	0.0013
45 °C $CsNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	0.3538	-0.6438	0.6201	-0.2835	0.0032
Density					
35 °C $NaNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.4056	-0.1737	-0.0026	0.0955	0.0011
45 °C $NaNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.4220	-0.2041	0.0464	0.0586	0.0005
35 °C KNO_3 (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.2444	-0.1838	0.3059	-0.0787	0.0005
45 °C KNO_3 (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.2855	-0.2788	0.3958	-0.1135	0.0006
35 °C $RbNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.4859	-0.6721	0.8273	-0.3407	0.0018
45 °C $RbNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.5857	-0.9506	1.1274	-0.4561	0.0021
35 °C $CsNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.2361	-0.0474	0.1308	-0.0225	0.0005
45 °C $CsNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3134	-0.2214	0.3145	-0.1067	0.0009
Refractive index					
35 °C $NaNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3905	0.0554	0.0400	0.0029	0.0003
45 °C $NaNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3912	0.0604	0.0342	-0.0068	0.0003
35 °C KNO_3 (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3653	0.0777	0.0297	0.0051	0.0002
45 °C KNO_3 (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3706	0.0481	0.0711	-0.0120	0.0005
35 °C $RbNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3706	0.0659	0.0649	-0.0274	0.0002
45 °C $RbNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3816	0.0432	0.0749	-0.0244	0.0004
35 °C $CsNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3508	0.1125	0.0164	-0.0028	0.0008
45 °C $CsNO_3$ (1) - $HOCH_2CH(OH)CH_2OH$ (2) - H_2O (3)	1.3558	0.0821	0.0812	-0.0411	0.0004

$\delta = [\Sigma (Y_{cal} - Y_{exp})^2/N]^{0.5}$, where N is the number of experimental points

pure water, and it can be seen that the obtained experimental data is reliable when compared with the literature.

In order to detect the variation trend of the phase equilibrium of the research system clearly, the variation trend curve of the ternary system $RbNO_3/CsNO_3$ (w_1)+ $HOCH_2CH(OH)CH_2OH$ (w_2)+ H_2O (w_3) is presented as an example. As shown in Figure 2, with the increasing weight percentage of glycerol at the same temperature, the solubility of the salt in the mixed solvent (Figure 2 a) decreases gradually, while the solubility increases as the temperature rises. However, the density of the system (Figure 2 b) has appeared two kinds of variation trend at the same temperature, which means with the increasing weight percentage of glycerol, the density of the system $RbNO_3$ (w_1)+ $HOCH_2CH(OH)CH_2OH$ (w_2)+ H_2O (w_3) is reduced gradually, while the density of the system $CsNO_3$ (w_1)+ $HOCH_2CH(OH)CH_2OH$ (w_2)+ H_2O (w_3) is reduced then increased, mainly because of the less solubility of $CsNO_3$, so that the influence of glycerol density plays a dominant role and results in the increase of the present density. The variation trend of the density of system KNO_3 (w_1)+ $HOCH_2CH(OH)CH_2OH$ (w_2)+ H_2O (w_3) is the same with this system. At different temperatures, with the increase of the alcohol content, the temperature and the density of all studied systems increase.

The refractive index of the salt solution (Figure 2c) shows the contrary variation trend to the solubility and density, meaning that at the same temperature, the refractive index rises with the increase of the glycerin content, which shows a completely different trend according to the other systems in the literature[9,10]. And the refractive index curves at two different temperatures are almost coincidence, indicating that the temperature has rare influence on the refractive index of this system.

In the studied systems, the rate equation (3) is used for the fitting of solubility, density and refractive data, and the resulting parameter values and relative standard deviation δ are listed in TABLE 4.

$$Y = A_0 + A_1 w_2 + A_2 w_2^2 + A_3 w_2^3 \quad [15] \qquad (3)$$

Wherein Y represents the solubility, density, or refractive index in the studied systems, Ai means a fitting parameter, w_2 represents the weight percentage of glycerol.

CONCLUSIONS

In this paper, the solubility, density and refractive index of the ternary system $NaNO_3$/ KNO_3/$RbNO_3$/ $CsNO_3$ - $HOCH_2CHOHCH_2OH$ - H_2O were comprehensively investigated, which provided reference data for the application research of the corresponding system. A trend curve of the ternary system $RbNO_3$/ $CsNO_3$ - $HOCH_2CHOHCH_2OH$ - H_2O was plotted and illustrated on the basis of the data. The salt content calculated by the simultaneous equations of density and refractive index provided more accurate data. The data of solubility, refractive index and density via glycerol content variation in the studied systems was fitted by the four-parameter empirical correlation equation, which showed that the standard deviation was little and the results were satisfied.

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