Solubility of Cesium Nitrate in Aqueous Alcohol Solutions at (25, 35, and 45) °C

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Solubility and refractive index data have been measured for the saturated ternary systems CH_3OH + $CsNO_3$ + H_2O, C_2H_5OH + $CsNO_3$ + H_2O, 1-propanol + $CsNO_3$ + H_2O, 2-propanol + $CsNO_3$ + H_2O, and 2-methyl-2-propanol + $CsNO_3$ + H_2O at (25, 35, and 45) °C. In all cases, the presence of alcohol significantly reduces the solubility of cesium nitrate in aqueous solution. The solubility data and the alcohol content in the mixtures were correlated to an empirical equation.

Introduction

The salting-out effect in aliphatic alcohol + water systems is of industrial interest. The addition of an organic solution to the aqueous solution of a salt normally decreases the solubility of the salt. These systems have been used in the extractive crystallization of inorganic salts. This crystallization technique has a series of advantages in comparison with the traditional procedure of evaporation and cooling, including operation at ambient temperature, producing crystals of high purity, increased yields, and so forth.[1]

In recent years, research groups have focused on the solubility of various salts in water + aliphatic alcohols, which may be used to evaluate the potential applicability of the drowning-out procedure as a technique for the separation of these salts.[2−11] As far as we know, the solubility data found in the literature for cesium nitrate in aqueous aliphatic alcohols are scarce but are of interest in the design of purification methods for cesium nitrate. In this study, solubility and refractive index data have been measured for these ternary systems at (25, 35, and 45) °C.

Experimental Section

Materials. Reagents utilized include methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-2-propanol (A. R. purity >99.5 %, Xi'an), and cesium nitrate (A. R. purity >99.5 %, Jiangxi). All reagents were used without further purification. Double-distilled water was used in all experiments.

Apparatus and Procedure. The phase equilibrium study was carried out by mixing known masses of aliphatic alcohols and water with excess salt. A detailed description of the equipment used in this experiment has been presented in former work.[12]

The solubility equilibrium was carried out by adding excess salt to the known alcohol/water ratio solution. All of the samples were prepared by mass using an analytical balance with a precision of $\pm 1 \times 10^{-4}$ g (Shanghai, FA-1104). The thermostat was set at a desired temperature. The samples were fixed on the carrier plate and were stirred for 24 h, and then the solution was allowed to settle for an additional 24 h to ensure that equilibrium had been established.

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After equilibrium was achieved, solutions were withdrawn using syringes that were maintained at a slightly increased temperature to avoid the precipitation of salts from the solutions under study. The refractive index of the sample was measured immediately after the sample was withdrawn. The refractive index of each solution was determined using a ZAW-J refractometer (Shanghai) with a precision of 1×10^{-4}, and temperature was controlled to ±0.1 K. The measurements were repeated at least three times.

The concentration of the salt in the solution was determined by evaporation. Approximately 3 cm^3 of sample was withdrawn from the saturated solutions. Then the solution was dried in an oven at 150 °C. The mass of the anhydrous salt was considered constant only when successive measurements of the same sample differed by less than 5×10^{-4} g. The uncertainty in the measurement of the mass fraction of the salt was estimated to be ±0.5 %. For those samples in which the mass fraction of alcohol was more than 80 %, the concentration of the salt was determined using atomic absorption spectrometry (AAS). The AAS measurements were performed using a TAS-986 (Beijing) atomic absorption spectrometer at a wavelength of 852.1 nm. The calibration line was obtained using an aqueous solution of CsCl from 0 to 20 ppm, so before the AAS measurements, it was necessary to dilute the samples to this concentration range. The measurements were carried out three times, and the uncertainty of the mass fraction of the salt was estimated to be ±0.2 %.

Results and Discussion

The solubility and refractive index data for the CH_3OH + $CsNO_3$ + H_2O, C_2H_5OH + $CsNO_3$ + H_2O, 1-propanol + $CsNO_3$ + H_2O, 2-propanol + $CsNO_3$ + H_2O, and 2-methyl-2-propanol + $CsNO_3$ + H_2O ternary systems are listed in Tables 1 to 5, respectively. Figure 1 presents the solubility diagram for the CH_3OH + $CsNO_3$ + H_2O system at (25, 35, and 45) °C. It can be observed that at a fixed temperature the solubility of the salt decreased with the addition of methanol and the salting-out effect increased with temperature. This tendency is similar for other ternary systems.

The solubility data for the ternary systems at 25 °C are plotted together in Figure 2. Figure 2 shows that at the same temperature the solubility diagram for the five

10.1021/je050072b CCC: $30.25
Published on Web 06/04/2005

Table 1. Solubility (S) in Terms of the Molality and Refractive Index (n_D) for the CH_3OH (1) + $CsNO_3$ (2) + H_2O (3) System at (25, 35, and 45) °C

w_1'[a]	S/mol·kg^{-1}	n_D	w_1'[a]	S/mol·kg^{-1}	n_D
		25 °C			
0	1.396	1.3475	0.5336	0.2301	1.3387
0.1235	0.8876	1.3455	0.7357	0.08384	1.3362
0.1640	0.7855	1.3453	0.8170	0.05244	1.3325
0.2288	0.6367	1.3440	0.9052	0.02419	1.3319
0.4020	0.3686	1.3414	1	0.0119	1.3283
0.4657	0.2972	1.3403			
		35 °C			
0	2.006	1.3530	0.4080	0.5449	1.3426
0.05124	1.708	1.3510	0.5261	0.3545	1.3407
0.1271	1.328	1.3486	0.5935	0.2701	1.3404
0.1481	1.243	1.3482	0.6711	0.1825	1.3370
0.1878	1.104	1.3476	0.7251	0.1402	1.3360
0.2186	0.9979	1.3475	0.7617	0.1135	1.3346
0.2815	0.8219	1.3445	0.8148	0.0803	1.3332
0.3391	0.6829	1.3466	1	0.0279	1.3239
		45 °C			
0	2.797	1.3582	0.5375	0.4754	1.3390
0.04855	2.415	1.3555	0.6182	0.3451	1.3382
0.09886	2.061	1.3520	0.6306	0.3099	1.3376
0.2334	1.389	1.3494	0.6612	0.2726	1.3347
0.2515	1.286	1.3472	0.7084	0.2198	1.3334
0.3492	0.9446	1.3447	0.8823	0.07352	1.3275
0.3635	0.9071	1.3455	1	0.02997	1.3195
0.4684	0.6321	1.3426			

[a] w_1' − mass fraction of component 1 on a salt-free basis.

Table 2. Solubility (S) in Terms of the Molality and Refractive Index (n_D) for the C_2H_5OH (1) + $CsNO_3$ (2) + H_2O (3) System at (25, 35, and 45) °C

w_1'[a]	S/mol·kg^{-1}	n_D	w_1'[a]	S/mol·kg^{-1}	n_D
		25 °C			
0	1.396	1.3475	0.4176	0.3897	1.3593
0.05801	1.062	1.3477	0.4773	0.2695	1.3610
0.1415	0.7953	1.3506	0.5413	0.2149	1.3623
0.2073	0.6059	1.3529	0.6132	0.1435	1.3624
0.2870	0.5700	1.3560	0.6852	0.08291	1.3627
0.3495	0.4047	1.3581	0.8346	0.02708	1.3630
		35 °C			
0	2.006	1.3530	0.5635	0.2956	1.3587
0.1367	1.267	1.3535	0.5828	0.2703	1.3595
0.1908	1.058	1.3550	0.7034	0.1445	1.3600
0.2864	0.7824	1.3560	0.7877	0.0826	1.3597
0.2532	0.8779	1.3565	0.8651	0.04578	1.3591
0.4625	0.4474	1.3586	0.9156	0.0358	1.3584
		45 °C			
0	2.797	1.3582	0.6117	0.3097	1.3577
0.04503	2.271	1.3580	0.6715	0.2119	1.3578
0.1541	1.508	1.3579	0.7479	0.1249	1.3561
0.2454	1.072	1.3580	0.8353	0.04777	1.3555
0.3928	0.6552	1.3582	1	0.01498	1.3519
0.4194	0.6044	1.3575			

[a] w_1' − mass fraction of component 1 on a salt-free basis.

systems shows no significant difference. It is the same for other temperatures.

The experimental solubility data for these ternary systems can be described by the following expression that is valid at all temperatures[13]

$$\ln(S/\text{mol·kg}^{-1}) = A + Bw_1' + C(w_1')^2 + D(w_1')^3 \quad (1)$$

where S represents the salt solubility, as molality; $w_1' = w_1/(w_1 + w_3)$, where w_1' is the mass fraction of aliphatic alcohol in the salt-free mixed solvent; w_1 and w_3 represent the mass fractions of alcohol and water, respectively; and $A = \ln S_0$, where S_0 is the solubility of salt in pure water. The coefficients of eq 1 (B, C, and D) along with the corresponding standard deviations for the investigated systems are given in Table 6. On the basis of the obtained standard deviations, we conclude that eq 1 can be satis-

Table 3. Solubility (S) in Terms of the Molality and Refractive Index (n_D) for the 1-Propanol (1) + $CsNO_3$ (2) + H_2O (3) System at (25, 35, and 45) °C

w_1'[a]	S/mol·kg^{-1}	n_D	w_1'[a]	S/mol·kg^{-1}	n_D
		25 °C			
0	1.396	1.3475	0.4779	0.3520	1.3700
0.0167	1.301	1.3480	0.5567	0.2566	1.3726
0.05741	1.131	1.3499	0.6892	0.1097	1.3766
0.1654	0.8276	1.3555	0.7752	0.05849	1.3794
0.2280	0.7008	1.3590	0.8418	0.02496	1.3805
0.2808	0.6254	1.3602	0.9271	0.007717	1.3830
0.3645	0.5131	1.3646	1	0.005972	1.3830
		35 °C			
0	2.006	1.3530	0.4648	0.5521	1.3660
0.09983	1.478	1.3557	0.4966	0.4897	1.3678
0.1189	1.408	1.3565	0.5321	0.4210	1.3685
0.1554	1.275	1.3568	0.6164	0.2822	1.3716
0.2913	0.9194	1.3610	0.6667	0.2146	1.3727
0.3299	0.8327	1.3622	0.7505	0.1096	1.3750
0.4216	0.6357	1.3656	0.8052	0.06147	1.3765
0.4565	0.5680	1.3666	0.9188	0.01775	1.3785
		45 °C			
0	2.797	1.3582	0.6264	0.3712	1.3685
0.1620	1.812	1.3600	0.6811	0.2589	1.3689
0.2347	1.508	1.3605	0.7401	0.1663	1.3709
0.2987	1.282	1.3616	0.7889	0.09902	1.3722
0.4226	0.8994	1.3643	0.8663	0.03891	1.3735
0.4580	0.7881	1.3660	1	0.01111	1.3747
0.5479	0.5490	1.3672			

[a] w_1' − mass fraction of component 1 on a salt-free basis.

Table 4. Solubility (S) in Terms of the Molality and Refractive Index (n_D) for the 2-Propanol (1) + $CsNO_3$ (2) + H_2O (3) System at (25, 35, and 45) °C

w_1'[a]	S/mol·kg^{-1}	n_D	w_1'[a]	S/mol·kg^{-1}	n_D
		25 °C			
0	1.396	1.3475	0.4152	0.3577	1.3659
0.01587	1.277	1.3489	0.4740	0.2921	1.3675
0.1389	0.8194	1.3530	0.5360	0.2253	1.3697
0.1914	0.6921	1.3559	0.6040	0.1597	1.3725
0.2213	0.6295	1.3585	0.7577	0.05073	1.3732
0.2508	0.5787	1.3589	0.8320	0.01951	1.3755
0.2799	0.5346	1.3611	0.9068	0.008389	1.3760
0.3362	0.4526	1.3635			
		35 °C			
0	2.006	1.3530	0.4895	0.4131	1.3660
0.05957	1.597	1.3535	0.5249	0.3526	1.3674
0.1246	1.306	1.3558	0.5910	0.2549	1.3678
0.1780	1.094	1.3585	0.6652	0.1712	1.3686
0.2359	0.9286	1.3607	0.7350	0.1050	1.3704
0.2919	0.7865	1.3610	0.7734	0.07378	1.3710
0.3454	0.6757	1.3620	0.8750	0.01927	1.3708
0.3876	0.5885	1.3637	1	0.002477	1.3707
0.4376	0.5096	1.3653			
		45 °C			
0	2.797	1.3582	0.4766	0.6121	1.3638
0.1272	1.857	1.3580	0.5122	0.5320	1.3640
0.1611	1.663	1.3589	0.6100	0.3290	1.3653
0.2785	1.180	1.3601	0.6607	0.2430	1.3665
0.3211	1.035	1.3616	0.7260	0.1503	1.3670
0.4193	0.7527	1.3631	0.8455	0.0383	1.3671
0.4501	0.6726	1.3630	1	0.002747	1.3670

[a] w_1' − mass fraction of component 1 on a salt-free basis.

Table 5. Solubility (S) in Terms of the Molality and Refractive Index (n_D) for the 2-Methyl-2-propanol (1) + $CsNO_3$ (2) + H_2O (3) System at (25, 35, and 45) °C

w_1'[a]	S/mol·kg^{-1}	n_D	w_1'[a]	S/mol·kg^{-1}	n_D
		25 °C			
0	1.396	1.3475	0.2486	0.6044	1.3619
0.02188	1.215	1.3470	0.3037	0.5238	1.3641
0.08703	0.9702	1.3519	0.3425	0.4733	1.3660
0.1124	0.8917	1.3530	0.4694	0.3206	1.3726
0.1307	0.8322	1.3540	0.5859	0.1993	1.3765
0.1689	0.7439	1.3556	0.7784	0.05402	1.3823
0.2132	0.6639	1.3594			
		35 °C			
0	2.006	1.3530	0.5599	0.3542	1.3719
0.09707	1.467	1.3560	0.6585	0.2082	1.3741
0.1527	1.252	1.3584	0.7425	0.1017	1.3750
0.1996	1.112	1.3606	0.8264	0.03907	1.3765
0.2639	0.9425	1.3640	0.9073	0.01142	1.3786
0.4328	0.5372	1.3670	1	0.006947	1.3789
0.4981	0.4556	1.3700			
		45 °C			
0	2.797	1.3582	0.5912	0.4114	1.3705
0.1320	1.899	1.3607	0.6521	0.2974	1.3710
0.2381	1.440	1.3636	0.6900	0.2235	1.3717
0.3818	0.7953	1.3666	0.7893	0.07501	1.3726
0.5281	0.4867	1.3702	1	0.007198	1.3755

[a] w_1' − mass fraction of component 1 on a salt-free basis.

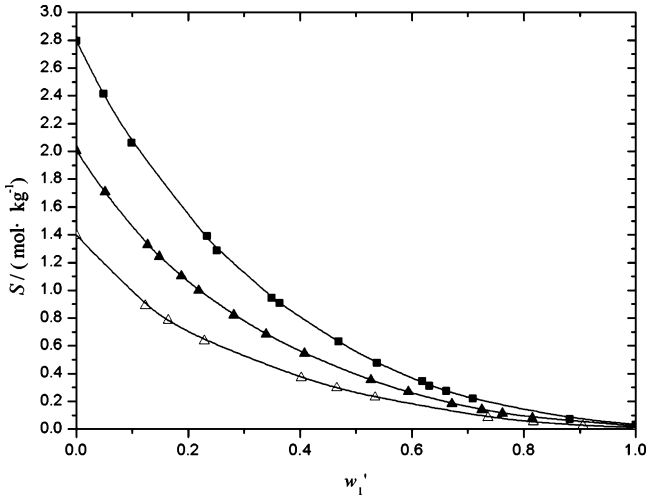

Figure 1. Solubility (S) in terms of molality for the CH_3OH (1) + $CsNO_3$ (2) + H_2O (3) system at (25, 35, and 45) °C as a function of the methanol mass fraction in the salt-free solvent: △, 25 °C; ▲, 35 °C; ■, 45 °C; —, calculated from eq 1.

factorily used to correlate the solubility data of the investigated systems.

Table 1 shows that the refractive index for CH_3OH (1) + $CsNO_3$ (2) + H_2O (3) saturated ternary systems decreased with increasing mass fraction of methanol in the solvent at three temperatures. The refractive index data at 25 °C and 45 °C are given in Figure 3. A point of intersection ($w_1 \approx 0.6$) is observed in Figure 3. Before the point of intersection ($w_1 < 0.6$), the curve at 45 °C is above that at 25 °C; however, after the point ($w_1 > 0.6$), the curve at 45 °C is below that at 25 °C. Similar behavior is also observed between the curve at 25 °C and that at 35 °C and the curve at 35 °C and that at 45 °C.

Table 2 shows that the trend in refractive index for the aqueous ethanol system at the three temperatures given is erratic.

However, the refractive index increased with increasing mass fraction of 1-propanol, 2-propanol, or 2-methyl-2-propanol at three temperatures in Tables 3 to 5. This tendency is similar to that of the data available in the literature.[14]

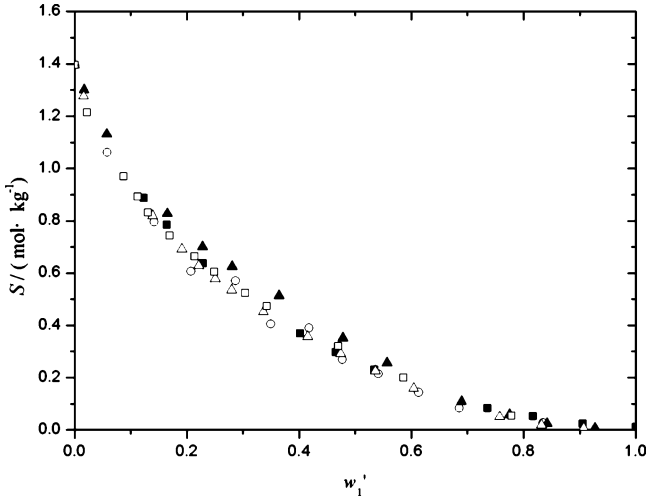

Figure 2. Solubility (S) in terms of molality for CH_3OH (1) + $CsNO_3$ (2) + H_2O (3), C_2H_5OH (1) + $CsNO_3$ (2) + H_2O (3), 1-propanol (1) + $CsNO_3$ (2) + H_2O (3), 2-propanol (1) + $CsNO_3$ (2) + H_2O (3), and 2-methyl-2-propanol (1) + $CsNO_3$ (2) + H_2O (3) systems at 25 °C as a function of the alcohol mass fraction in the salt-free solvent: ■, CH_3OH; ○, C_2H_5OH; ▲, 1-propanol; △, 2-propanol; □, 2-methyl-2-propanol.

Table 6. Values of the Parameters of Equation 1

temperature/°C	A[a]	B	C	D	δ[b]
		$CH_3OH + CsNO_3 + H_2O$			
25	0.3336	−3.992	3.455	−4.340	0.002203
35	0.6962	−3.367	1.424	−2.520	0.004807
45	1.028	−3.130	0.8882	−2.213	0.007324
		$C_2H_5OH + CsNO_3 + H_2O$			
25	0.3336	−5.222	9.585	−11.64	0.02472
35	0.6962	−3.722	2.811	−4.004	0.004974
45	1.028	−4.720	4.790	−5.261	0.01556
		1-$C_3H_7OH + CsNO_3 + H_2O$			
25	0.3336	−4.073	6.860	−9.049	0.003849
35	0.6962	−3.459	4.685	−6.920	0.003675
45	1.028	−3.153	3.748	−6.274	0.006857
		2-$C_3H_7OH + CsNO_3 + H_2O$			
25	0.3336	−4.756	7.262	−8.895	0.00635
35	0.6962	−4.041	4.890	−6.650	0.005852
45	1.028	−3.643	3.583	−5.592	0.008349
		2-methyl-2-$C_3H_7OH + CsNO_3 + H_2O$			
25	0.3336	−4.909	8.656	−10.19	0.01341
35	0.6962	−3.586	4.350	−6.469	0.01247
45	1.028	−2.876	0.2723	−2.086	0.03758

[a] $A = \ln S_0$, and S_0 is the solubility of salt in pure water. [b] $\delta = \sum((S^{calcd} - S^{exptl})^2/N)^{0.5}$, where N is the number of experimental points.

The refractive index for the solution was influenced by many factors, so the former behavior of the five investigated systems was complex. In our opinion, we should consider at least three factors: mixed solvent composition, salt content, and temperature. The refractive index increased with increasing salt content and organic-phase content. However, the salt content decreased with the enhancement of organic solvent, so the two factors were contradictory. The refractive index decreased with the enhancement of temperature, but the salt content increased with increasing temperature. Therefore, these two factors were also contradictory.

Finally, the systematized experimental study is an important contribution to existing data for salt solubility

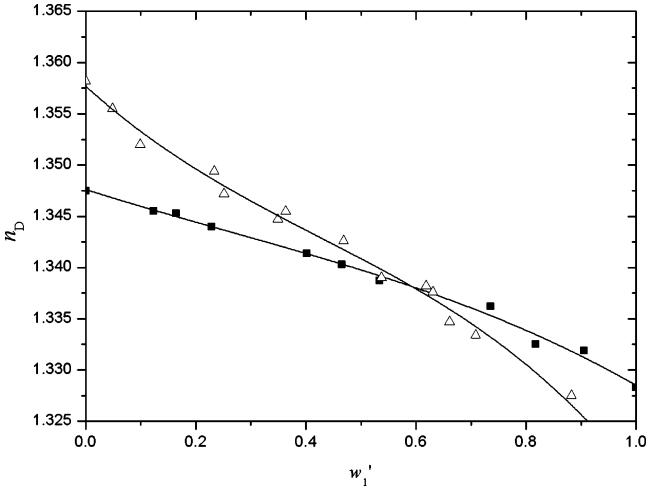

Figure 3. Refractive index (n_D) for the CH_3OH (1) + $CsNO_3$ (2) + H_2O (3) saturated system at (25 and 45) °C as a function of the methanol mass fraction in the salt-free solvent: ■, 25 °C; △, 45 °C.

in mixed solvent systems. The solubility and refractive index have been measured for the salt $CsNO_3$ in a series of aqueous alcohol systems at three different temperatures.

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Received for review February 21, 2005. Accepted May 11, 2005. This study was supported by the National Natural Science Foundation of China (no. 20471035).

JE050072B