Compositions, Densities, and Refractive Indices for the Ternary Systems Ethylene Glycol + NaCl + H_2O, Ethylene Glycol + KCl + H_2O, Ethylene Glycol + RbCl + H_2O, and Ethylene Glycol + CsCl + H_2O at 298.15 K

Yanhong Zhou, Shu'ni Li,* Quanguo Zhai, Yucheng Jiang, and Mancheng Hu*

Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an, Shaanxi, 710062, P R China

Solubilities, densities, and refractive indices have been measured for the four ternary systems, ethylene glycol + NaCl + H_2O, ethylene glycol + KCl + H_2O, ethylene glycol + RbCl + H_2O, and ethylene glycol + CsCl + H_2O, at T = 298.15 K, with mass fractions of ethylene glycol ranging from 0 to 1.0. Polynomial equations of fit are proposed for the solubility of the saturated solutions as a function of the mass fraction of ethylene glycol. The equations proposed also account for the density and refractive index for the saturated solutions. On the other hand, the density and refractive index of unsaturated solutions were also determined for the same ternary systems with varied undersaturated salt concentrations. Values for both the properties were also correlated with the salt concentrations and proportions of ethylene glycol in the undersaturated solutions. In all the cases, the presence of ethylene glycol significantly reduces the solubility of the salts in the aqueous solution.

Introduction

The addition of organic solvent to the aqueous solution of a salt normally decreases the solubility of the salt, which is termed "drowning out" and is usually employed in crystallization for producing supersaturation in a solution. 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 on.[1]

During the past decades, many studies are available in the literature on solubilities of various salts in water + organic solvents, the objectives of which have been to evaluate the potential applicability of the drowning-out procedure as a technique for separation of these salts.[2–15] For example, to control the precipitation process of the double salt $LiKSO_4$, Cartón et al. studied the solubility for the ternary systems Li_2SO_4 + CH_3OH + H_2O, $LiKSO_4$ + CH_3OH + H_2O, and $LiKSO_4$ + CH_3CH_2OH + H_2O at room temperature.[7–9] Similarly, Gomis et al. have investigated seven ternary aqueous systems including NaCl and KCl in 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol at 298.15 K.[10,11] These systems produced biphasic regions which showed the presence of a liquid−liquid equilibrium zone. They also reported five ternary aqueous systems[12] at 298.15 K of water + NaCl + 1-pentanol/2-pentanol/3-pentanol/2-methyl-2-butanol/2-methyl-1-butanol. Their experimental results show that the salting-out effect of the five pentanols is similar except for 2-methyl-2-butanol which presents the most significant decrease in the solubility of this ternary system. Moreover, Wagner et al.[13] determined solubilities of NaCl in different mixtures of solvents including water + cyclohexane, water + cyclohexanol, water + benzylalcohol, water + ethanol + cyclohexanol, and water + benzyl alcohol + cyclohexanol at 298.15 K. Furthermore, Taboada et al. measured liquid−liquid and liquid−liquid−solid equilibria for the ternary systems PEG 4000 + $NaNO_3$ + H_2O at 298.15 K.[14] They also measured PEG 4000 + KCl + H_2O and PEG 4000 + NaCl + H_2O at (298.15 and 333.15) K and the quaternary system NaCl + KCl + PEG + H_2O at 298.15 K.[15]

In our previous work, our research group has focused on the solubility of rare alkali metal (Rb and Cs) salts in water + organic solvent mixtures, which may be used to evaluate the potential applicability of the drowning-out procedure as a technique for separation of these valuable salts.[16–18] The organic solvents are mainly some aliphatic alcohols that are completely miscible or partly miscible with water, such as methanol, ethanol, 1-propanol, and 2-propanol, as well as PEG (poly(ethylene glycol)). To further investigate the influence of OH groups in organic solvents on the solubility of inorganic salts, ethylene glycol with two OH groups is selected. As far as we know, there is no report on the solubility data of the ternary systems ethylene glycol + NaCl + H_2O, ethylene glycol + KCl + H_2O, ethylene glycol + RbCl + H_2O, and ethylene glycol + CsCl + H_2O. Herein, to enrich our research project, we report the solubility, density, and refractive index data for these four ternary systems at 298.15 K.

Experimental Section

Materials. Ethylene glycol, sodium chloride, and potassium chloride were supplied by the Xi'an Chemical Reagent Factory with purity of 99.8 %, 99.5 %, and 99.5 %, respectively. Rubidium chloride and cesium chloride were supplied by the Shanghai China Lithium Industrial Co. with purity of 99.5 %. All of the chemicals used in this study were used without further purification. Salts were dried to constant weight for 48 h at 375.15 K prior to use. Double distilled water was used in all the experiments.

* Corresponding authors. Tel.: +86-29-85307765. Fax: +86-29-85307774. E-mail: lishuni@snnu.edu.cn and hmch@snnu.edu.cn.

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Apparatus and Procedure. The phase equilibrium study was carried out by mixing of known masses of ethylene glycol and water with excess salt. The equipment used in the experiment is similar to what is described in a former work.[16] All of the samples were prepared by mass using an analytical balance with a precision of $\pm 1 \cdot 10^{-4}$ g (Shanghai, FA-1104). The solutions were prepared within an accuracy of $\pm 2 \cdot 10^{-4}$ g. The resultant supersaturated solutions were contained in suitably sealed plastic tubes. The thermostat was set at 298.15 K. 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. After equilibrium was achieved, the solutions were withdrawn using syringes, which were maintained at a slightly elevated temperature to avoid precipitation of salts from the solutions under study. The refractive index and density of each sample were measured immediately after the sample was withdrawn.

The densities of the saturated solutions were measured using a DMA4500 (Anton Paar) vibrating tube densimeter, and the temperature was controlled to $\pm$ 0.01 K. A minimum of three independent measurements was made for each sample, producing a precision of $\pm 3 \cdot 10^{-5}$ $g \cdot cm^{-3}$. The refractive index of each solution was determined using a RXA170 (Anton Paar) refractometer, and the temperature was controlled to $\pm$ 0.03 K. A minimum of three readings was obtained for each sample, obtaining a precision of $\pm 4 \cdot 10^{-5}$. Both the instruments were calibrated prior to initiation of each series of measurements, using air and deionized distilled water as reference substances. The undersaturated solutions were also prepared by mass using an analytical balance. Measurements of density and refractive index were carried out using the same methodology as described above for the saturated solutions.

The concentration of the salt in the solution was determined by the titration method with mercury nitrate as the precipitator, and the accuracy in the measurement of the mass fraction of the salt was estimated to be $\pm$ 0.5 %.[19] The concentration of ethylene glycol was determined by using $K_2Cr_2O_7$ as oxidant, and the uncertainty of the determination of ethylene glycol mass fraction was within $\pm$ 0.5 %.[20,21] Finally, the water concentration was computed using mass-balance equations.

Results and Discussion

Data for the solubility, density, and refractive index for the ethylene glycol + NaCl + H_2O, ethylene glycol + KCl + H_2O, ethylene glycol + RbCl + H_2O, and ethylene glycol + CsCl + H_2O saturated ternary systems are listed in Table 1. From Table 1, it can be observed that the solubility of the salt decreased with the addition of ethylene glycol in the mixed solvents at 298.15 K. In the ethylene glycol + NaCl/KCl + H_2O systems, the difference in solubility between the salts is appreciable only at intermediate values of ethylene glycol concentrations [(20 to 100) %], but as for the ethylene glycol + CsCl/RbCl + H_2O systems, the difference in solubility between the salts is appreciable over the entire interval of concentrations of ethylene glycol in the saturated solutions. The values for solubility of the four systems at 298.15 K in the absence of ethylene glycol when compared with those reported in the literature showed an average mean absolute deviation of $\pm$ 0.5 %, which are listed in Table 2.

The density for the ethylene glycol + CsCl/RbCl + H_2O systems significantly decreased with increasing mass fraction of ethylene glycol in the solvent, but for the ethylene glycol + NaCl/KCl + H_2O systems, the density decreases are slight with the addition of ethylene glycol. Moreover, for the ethylene glycol + KCl + H_2O system, the density slightly increased when the mass fraction of ethylene glycol was larger than 90 %. In our opinion, this phenomenon is mainly

Table 1. Mass Fraction, Density (ρ), and Refractive Index (n_D) for the Ethylene Glycol (1) + NaCl (2) + H_2O (3), Ethylene Glycol (1) + KCl (2) + H_2O (3), Ethylene Glycol (1) + RbCl (2) + H_2O (3), and Ethylene Glycol (1) + CsCl (2) + H_2O (3) Systems at 298.15 K[a]

w_1'	w_2	n_D	ρ ($g \cdot cm^{-3}$)	w_1'	w_2	n_D	ρ ($g \cdot cm^{-3}$)
Ethylene Glycol (1) + NaCl (2) + H_2O (3)							
0.0000	0.2641	1.37964	1.19826	0.6009	0.1307	1.41030	1.16130
0.1026	0.2393	1.38358	1.18990	0.7001	0.1137	1.41652	1.15770
0.2046	0.2138	1.38805	1.18286	0.8014	0.0930	1.42324	1.15453
0.2994	0.1919	1.39350	1.17582	0.8894	0.0809	1.43026	1.15244
0.3985	0.1733	1.39854	1.17110	1.0000	0.0669	1.43731	1.15053
0.5012	0.1518	1.40434	1.16602				
Ethylene Glycol (1) + KCl (2) + H_2O (3)							
0.0000	0.2662	1.36884	1.17690	0.6000	0.1136	1.40310	1.14110
0.1048	0.2322	1.37319	1.16779	0.7006	0.0958	1.41090	1.13880
0.2152	0.2038	1.37816	1.16000	0.7992	0.0785	1.41850	1.13754
0.2997	0.1799	1.38369	1.15353	0.8993	0.0675	1.42600	1.13733
0.4053	0.1544	1.38986	1.14812	1.0000	0.0528	1.43410	1.13847
0.5001	0.1365	1.39644	1.14403				
Ethylene Glycol (1) + RbCl (2) + H_2O (3)							
0.0000	0.4858	1.38841	1.49651	0.6003	0.2552	1.41171	1.29555
0.0998	0.4490	1.39104	1.46381	0.6998	0.2178	1.41632	1.25825
0.2004	0.4217	1.39409	1.42708	0.8001	0.1771	1.42370	1.23930
0.3003	0.3735	1.39769	1.39490	0.8999	0.1460	1.42995	1.21871
0.4996	0.2951	1.40647	1.32306	1.0000	0.0958	1.43742	1.20184
Ethylene Glycol (1) + CsCl (2) + H_2O (3)							
0.0000	0.6563	1.41952	1.92072	0.5983	0.4387	1.42845	1.55257
0.1052	0.6210	1.41989	1.86327	0.6963	0.3799	1.43136	1.48585
0.1982	0.5953	1.42089	1.80765	0.7953	0.3292	1.43490	1.42088
0.3025	0.5575	1.42212	1.74678	0.8895	0.2809	1.43752	1.35520
0.4021	0.5175	1.42383	1.68383	1.0000	0.2228	1.44383	1.31475
0.5037	0.4572	1.42592	1.61847				

[a] w_1' is the mass fraction of ethylene glycol in the salt-free mixed solvent.

Table 2. Solubility in Pure Water (w %) at 298.15 K

salt	our result	reference result	deviation
NaCl	26.41	26.28[22]	+0.13
KCl	26.62	26.67[22]	+0.05
RbCl	48.58	48.51[23]	+0.07
CsCl	65.63	65.56[23]	+0.07

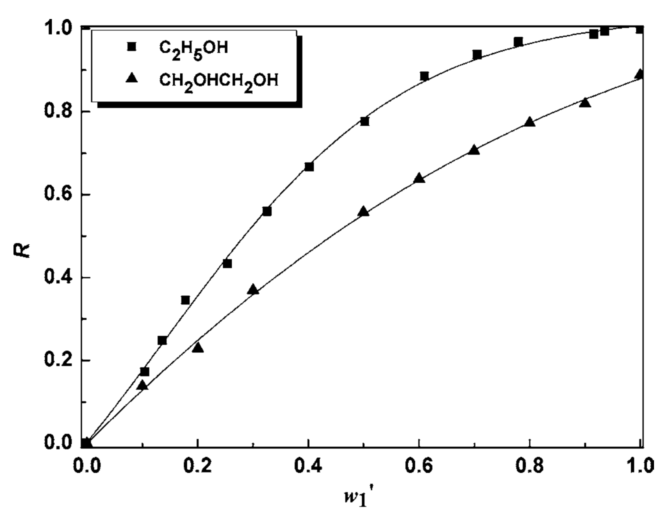

Figure 1. Salting-out effect for the ethylene glycol + RbCl + H_2O and ethanol + RbCl + H_2O[22] systems at 298.15 K (■, C_2H_5OH; ▲, CH_2OHCH_2OH).

Table 3. Values of Parameters of Equation[a] 1

system	A	B	C	D	δ
		Mass Fraction			
ethylene glycol (1) + NaCl (2) + H_2O (3)	−1.3351	−0.8721	−0.4631	−0.0412	0.0100
ethylene glycol (1) + KCl (2) + H_2O (3)	−1.3250	−1.1932	−0.2642	−0.1480	0.0110
ethylene glycol (1) + RbCl (2) + H_2O (3)	−0.7282	−0.5043	−1.0792	0.2090	0.0120
ethylene glycol (1) + CsCl (2) + H_2O (3)	−0.4221	−0.4744	−0.0216	−0.5831	0.0050
		Density			
ethylene glycol (1) + NaCl (2) + H_2O (3)	0.1801	−0.0701	0.0323	−0.0027	0.0002
ethylene glycol (1) + KCl (2) + H_2O (3)	0.1622	−0.0828	0.0555	−0.0062	0.0001
ethylene glycol (1) + RbCl (2) + H_2O (3)	0.4036	−0.2180	−0.1123	0.1182	0.0017
ethylene glycol (1) + CsCl (2) + H_2O (3)	0.6504	−0.2301	−0.2944	0.1443	0.0027
		Refractive Index			
ethylene glycol (1) + NaCl (2) + H_2O (3)	0.3211	0.0276	0.0173	−0.00389	0.0001
ethylene glycol (1) + KCl (2) + H_2O (3)	0.3130	0.0282	0.0278	−0.00951	0.0001
ethylene glycol (1) + RbCl (2) + H_2O (3)	0.3281	0.0172	0.0161	0.0011	0.0002
ethylene glycol (1) + CsCl (2) + H_2O (3)	0.3502	0.0048	0.0064	0.00566	0.0003

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

Table 4. Density (ρ) and Refractive Index (n_D) for the Ethylene Glycol (1) + NaCl (2) + H_2O (3) Undersaturated System at 298.15 K

w_1	w_2	n_D	ρ (g·cm^{-3})	w_1	w_2	n_D	ρ (g·cm^{-3})
			$w_1/w_3 = 0.1111$				
0.0979	0.0232	1.02567	1.34574	0.0885	0.1246	1.09834	1.36297
0.0953	0.0478	1.04256	1.34977	0.0859	0.1428	1.11063	1.36567
0.0934	0.0664	1.05620	1.35306	0.0874	0.1594	1.12538	1.36938
0.0923	0.0868	1.06969	1.35617	0.0826	0.1764	1.13673	1.37169
0.0898	0.1060	1.08436	1.35966	0.0825	0.1918	1.14878	1.37450
			$w_1/w_3 = 0.4285$				
0.2942	0.0197	1.04883	1.36447	0.2687	0.1042	1.10779	1.37806
0.2895	0.0369	1.06078	1.36736	0.2652	0.1167	1.11605	1.37968
0.2841	0.0562	1.07395	1.37035	0.2605	0.1315	1.12711	1.38224
0.2787	0.0713	1.08514	1.37302	0.2567	0.1454	1.13583	1.38389
0.2741	0.0875	1.09670	1.37568	0.2515	0.1656	1.14735	1.38635
			$w_1/w_3 = 1.0000$				
0.4921	0.0150	1.07181	1.38433	0.4590	0.0831	1.11564	1.39313
0.4858	0.0293	1.08069	1.38602	0.4522	0.0961	1.12522	1.39536
0.4778	0.0432	1.08915	1.38750	0.4395	0.1204	1.14134	1.39857
0.4713	0.0573	1.09907	1.38981	0.4473	0.1080	1.13362	1.39714
0.4672	0.0687	1.10709	1.39172	0.4346	0.1318	1.14871	1.39997
			$w_1/w_3 = 2.3333$				
0.6919	0.0111	1.09089	1.40267	0.6555	0.0641	1.12473	1.40907
0.6843	0.0222	1.09781	1.40389	0.6480	0.0725	1.13034	1.41016
0.6745	0.0328	1.10457	1.40521	0.6393	0.0830	1.13703	1.41138
0.6693	0.0434	1.11147	1.40667	0.6351	0.0927	1.14369	1.41280
0.6623	0.0536	1.11786	1.40778	0.6266	0.1012	1.14782	1.41320
			$w_1/w_3 = 9.0000$				
0.8907	0.0084	1.10789	1.42213	0.8557	0.0462	1.13056	1.42555
0.8853	0.0157	1.11208	1.42286	0.8511	0.0541	1.13591	1.42675
0.8782	0.0238	1.11722	1.42362	0.8437	0.0614	1.13937	1.42707
0.8704	0.0319	1.12238	1.42471	0.8387	0.0672	1.14424	1.42805
0.8607	0.0389	1.12616	1.42483	0.8328	0.0744	1.14884	1.42886

ascribed to the smallest solubility of KCl in the mixed solvent with a larger content of ethylene glycol. The trend of the refractive index increasing with increasing mass fraction of ethylene glycol in the solvent is different from that of densities and a behavior observed for all the saturated ternary systems. It should be noted that this phenomenon tends to be completely different from the ethanol + MCl (M = Na, K, Rb, Cs) + H_2O systems.[22,23] The refractive index increases with the increasing mass fraction of ethylene glycol but decreases with increasing ethanol. The behavior can be explained by the fact that the refractive index for the mixed solution is mainly influenced by two factors: mixed solvent composition and salt content. The refractive index increased with increasing salt content and organic-phase content. However, the salt content decreases with the enhancement of organic solvent, so the two factors are contradictory. Consequently, the salt content should be the key factor that influenced the refractive index for the ethanol + MCl + H_2O ternary systems, but as for the ethylene glycol + MCl + H_2O systems, mixed solvent composition should be the key factor.

To compare the salting-out effect of ethylene glycol and ethanol, we defined $R = (S_0 - S)/S_0$, where S_0 is the solubility of salts in pure water and S is the solubility of salts in mixed solvents. The R values as a function of the organic solvent mass fractions for the two ternary systems ethylene glycol + RbCl + H_2O and ethanol + RbCl + H_2O[23] at 298.15 K are plotted together in Figure 1. Figure 1 shows that the salting-out effect of ethanol on the same aqueous solution is greater than that of ethylene glycol, a similar behavior observed for other systems with NaCl, KCl, or CsCl as inorganic salts at 298.15 K, this being mainly due to the fact

Table 5. Density (ρ) and Refractive Index (n_D) for the Ethylene Glycol (1) + KCl (2) + H_2O (3) Undersaturated System at 298.15 K

w_1	w_2	n_D	ρ $(g \cdot cm^{-3})$	w_1	w_2	n_D	ρ $(g \cdot cm^{-3})$
			$w_1/w_3 = 0.1111$				
0.0991	0.0246	1.02518	1.34520	0.0887	0.1308	1.09399	1.35904
0.0963	0.0477	1.03975	1.34817	0.0850	0.1493	1.10637	1.36132
0.0930	0.0708	1.05345	1.35086	0.0877	0.1672	1.11945	1.36419
0.0926	0.0911	1.06740	1.35371	0.0816	0.1841	1.13073	1.36602
0.0889	0.1120	1.08131	1.35644	0.0806	0.2001	1.14203	1.36820
			$w_1/w_3 = 0.4285$				
0.2971	0.0179	1.04745	1.36395	0.2742	0.0991	1.09896	1.37395
0.2900	0.0356	1.05479	1.36508	0.2659	0.1140	1.10726	1.37502
0.2858	0.0521	1.06777	1.36767	0.2620	0.1284	1.11642	1.37680
0.2822	0.0679	1.07745	1.36965	0.2580	0.1417	1.12511	1.37845
0.2752	0.0842	1.08813	1.37146	0.2536	0.1553	1.13431	1.38004
			$w_1/w_3 = 1.0000$				
0.4934	0.0134	1.06813	1.38327	0.4649	0.0717	1.10529	1.38988
0.4875	0.0251	1.07710	1.38476	0.4589	0.0822	1.11190	1.39073
0.4807	0.0362	1.08335	1.38579	0.4540	0.0927	1.11842	1.39185
0.4764	0.0482	1.08997	1.38717	0.4483	0.1038	1.12414	1.39291
0.4713	0.0597	1.09790	1.38845	0.4434	0.1139	1.13085	1.39416
			$w_1/w_3 = 2.3333$				
0.6903	0.0086	1.08913	1.40250	0.6648	0.0497	1.11427	1.40702
0.6888	0.0163	1.09525	1.40402	0.6618	0.0559	1.11878	1.40792
0.6819	0.0250	1.09950	1.40461	0.6502	0.0625	1.12031	1.40747
0.6781	0.0642	1.10509	1.40577	0.6508	0.0706	1.12694	1.40901
0.6688	0.0398	1.10906	1.40599	0.6451	0.0784	1.12757	1.40912
			$w_1/w_3 = 9.0000$				
0.8965	0.0038	1.10491	1.42162	0.8797	0.0223	1.11567	1.42315
0.8927	0.0077	1.10723	1.42196	0.8757	0.0261	1.11759	1.42320
0.8891	0.0114	1.10920	1.42226	0.8718	0.0299	1.11944	1.42330
0.8857	0.0151	1.11141	1.42251	0.8702	0.0330	1.12116	1.42336
0.8828	0.0178	1.11222	1.42289	0.8654	0.0381	1.12464	1.42416

Table 6. Density (ρ) and Refractive Index (n_D) for the Ethylene Glycol (1) + RbCl (2) + H_2O (3) Undersaturated System at 298.15 K

w_1	w_2	n_D	ρ $(g \cdot cm^{-3})$	w_1	w_2	n_D	ρ $(g \cdot cm^{-3})$
			$w_1/w_3 = 0.1111$				
0.0960	0.0439	1.04257	1.34599	0.0783	0.2157	1.19061	1.36260
0.0931	0.0840	1.07422	1.34977	0.0754	0.2441	1.21781	1.36552
0.0888	0.1204	1.10417	1.35311	0.0747	0.2688	1.24382	1.36852
0.0853	0.1554	1.13454	1.35648	0.0718	0.2923	1.26866	1.37086
0.0816	0.1873	1.16351	1.35967	0.0691	0.3149	1.29300	1.37363
			$w_1/w_3 = 0.4285$				
0.2887	0.0379	1.06127	1.36451	0.2427	0.1885	1.19087	1.37803
0.2788	0.0721	1.09106	1.36779	0.2357	0.2131	1.20703	1.37957
0.2687	0.1039	1.11660	1.37045	0.2295	0.2366	1.23611	1.38254
0.2590	0.1350	1.14286	1.37313	0.2236	0.2576	1.24890	1.38353
0.2551	0.1614	1.16653	1.37590	0.2162	0.2792	1.28057	1.38690
			$w_1/w_3 = 1.0000$				
0.4861	0.0282	1.08270	1.38421	0.4266	0.1457	1.17737	1.39317
0.4704	0.0541	1.10228	1.38593	0.4161	0.1663	1.19649	1.39485
0.4605	0.0784	1.12166	1.38809	0.4072	0.1851	1.21329	1.39652
0.4489	0.1024	1.14124	1.38986	0.3971	0.2033	1.22852	1.39781
0.4368	0.1252	1.15995	1.39154	0.3983	0.2211	1.24651	1.39952
			$w_1/w_3 = 2.3333$				
0.6839	0.0202	1.09968	1.40353	0.6221	0.1104	1.16719	1.40932
0.6704	0.0389	1.11345	1.40460	0.6113	0.1256	1.18280	1.41060
0.6590	0.0580	1.12839	1.40617	0.6015	0.1412	1.19653	1.41199
0.6465	0.0767	1.14275	1.40743	0.5910	0.1550	1.20843	1.41264
0.6350	0.0918	1.15550	1.40841	0.5816	0.1696	1.22021	1.41343
			$w_1/w_3 = 9.0000$				
0.8845	0.0125	1.11165	1.42193	0.8322	0.0680	1.15307	1.42545
0.8751	0.0233	1.11947	1.42260	0.8356	0.0752	1.16291	1.42618
0.8676	0.0354	1.12923	1.42363	0.8193	0.0892	1.17035	1.42664
0.8547	0.0479	1.13849	1.42419	0.8091	0.1001	1.17987	1.42724
0.8482	0.0575	1.14622	1.42497	0.8005	0.1103	1.18475	1.42770

that ethylene glycol dissolves water easily because of its higher polarity than that of ethanol, so the salting-out effect of ethylene glycol on the same aqueous solution is smaller than that of ethanol.

Table 7. Density (ρ) and Refractive Index (n_D) for the Ethylene Glycol (1) + CsCl (2) + H_2O (3) Undersaturated System at 298.15 K

w_1	w_2	n_D	ρ ($g\cdot cm^{-3}$)	w_1	w_2	n_D	ρ ($g\cdot cm^{-3}$)
			$w_1/w_3 = 0.1111$				
0.0943	0.0591	1.05674	1.34663	0.0730	0.2715	1.26481	1.36640
0.0895	0.1110	1.10153	1.35100	0.0699	0.3043	1.30397	1.37005
0.0844	0.1596	1.14668	1.35533	0.0666	0.3328	1.33892	1.37321
0.0804	0.1999	1.18689	1.35913	0.0643	0.3588	1.36690	1.37579
0.0761	0.2393	1.22875	1.36304	0.0625	0.3826	1.40575	1.37937
			$w_1/w_3 = 0.4285$				
0.2843	0.0527	1.07829	1.36577	0.2251	0.2498	1.26658	1.38218
0.2705	0.1000	1.11883	1.36945	0.2161	0.2786	1.30087	1.38522
0.2564	0.1428	1.15775	1.37278	0.2073	0.3083	1.33670	1.38826
0.2441	0.1870	1.20090	1.37663	0.2004	0.3335	1.36872	1.39101
0.2351	0.2178	1.23322	1.37950	0.1928	0.3575	1.40101	1.39375
			$w_1/w_3 = 1.0000$				
0.4773	0.0453	1.09807	1.38520	0.3894	0.2215	1.26381	1.39861
0.4565	0.0869	1.13344	1.38817	0.3721	0.2483	1.29224	1.40042
0.4377	0.1247	1.16746	1.39090	0.3612	0.2746	1.32299	1.40303
0.4205	0.1590	1.20005	1.39363	0.3500	0.3002	1.35373	1.40558
0.4046	0.1906	1.23139	1.39602	0.3990	0.3222	1.38124	1.40771
			$w_1/w_3 = 2.3333$				
0.6743	0.0370	1.11466	1.40455	0.5704	0.1847	1.24841	1.41441
0.6485	0.0704	1.14236	1.40677	0.5535	0.2091	1.27419	1.41642
0.6271	0.1026	1.17045	1.40897	0.5372	0.2328	1.29922	1.41816
0.6067	0.1321	1.19795	1.41111	0.5212	0.2542	1.32401	1.41996
0.5853	0.1593	1.22340	1.41252	0.5068	0.2752	1.34775	1.42142
			$w_1/w_3 = 9.0000$				
0.8745	0.0277	1.12446	1.42249	0.7691	0.1444	1.22839	1.43003
0.8516	0.0531	1.14601	1.42446	0.7515	0.1640	1.24756	1.43137
0.8292	0.0788	1.16828	1.42616	0.7342	0.1840	1.26820	1.43285
0.8066	0.1006	1.18749	1.42718	0.7186	0.2016	1.28593	1.43385
0.7885	0.1234	1.20784	1.42845	0.7022	0.2192	1.30438	1.43492

Table 8. Values of Parameters of Equation [2] for the Density and Refractive Index of the Undersaturated Ternary Systems at 298.15 K[a]

system	A_0	A_1	A_2	A_3	A_4	A_5	A_6	δ
Density								
ethylene glycol (1) + NaCl (2) + H_2O (3)	0.9936	0.7480	0.1454	−0.0409	0.0634	−0.0054	0.000362	0.0005
ethylene glycol (1) + KCl (2) + H_2O (3)	0.9939	0.6729	0.1334	0.0941	−0.1097	−0.0006	−0.000049	0.0007
ethylene glycol (1) + RbCl (2) + H_2O (3)	0.9780	0.9509	0.1690	−0.0800	0.0767	−0.0063	0.000403	0.0028
ethylene glycol (1) + CsCl (2) + H_2O (3)	0.9635	1.0882	0.1549	0.1283	−0.2672	0.0012	−0.000150	0.0057
Refractive Index								
ethylene glycol (1) + NaCl (2) + H_2O (3)	1.3314	0.1780	0.1017	0.0311	−0.0152	−0.0004	0.000036	0.0002
ethylene glycol (1) + KCl (2) + H_2O (3)	1.3335	0.1040	0.0764	0.3819	−0.5284	0.0063	−0.000520	0.0010
ethylene glycol (1) + RbCl (2) + H_2O (3)	1.3304	0.1092	0.1015	0.0503	0.0011	0.0002	−0.000030	0.0003
ethylene glycol (1) + CsCl (2) + H_2O (3)	1.3290	0.1065	0.1001	0.0879	−0.0330	0.0007	−0.000069	0.0005

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

The experimental data for the mass fraction of the salt, density, and the refractive index of the four saturated ternary systems can be expressed by the following expression[7,24]

$$\ln Y = A + Bw_1' + Cw_1'^2 + Dw_1'^3 \qquad (1)$$

where w_1' is the mass fraction of ethylene glycol in the salt-free mixed solvent and Y represents either the mass fraction of salts in the solution (w_2), the density (ρ), or the refractive index (n_D) of the ternary systems. The coefficients of eq 1 (A, B, C, D) along with the corresponding standard deviations for the investigated systems are given in Table 3. On the basis of the obtained standard deviations, we conclude that eq 1 can be satisfactorily used to correlate the solubility, density, and refractive index data of the investigated systems.

Densities and refractive indices in the four ternary systems were also measured in undersaturated solutions in our investigation. Work was carried out by varying the concentrations of salt in the solutions using the same mass ratios employed with the solubility equilibria. These values, which are listed in Tables 4 to 7, besides providing basic information on the behavior of these systems, may be useful for the operation of a crystallization process. From Tables 4 to 7, it can be observed that the values of the densities and refractive indices increased with the concentrations of salt. With an increase in the ethylene glycol/water ratio while maintaining the remaining variables constant, the density and the refractive index of the solutions also increased. No appreciable variation was observed in the development of any of the properties upon reaching the solubility equilibrium concentrations. This phenomenon is different from the ethanol + KCl + H_2O and ethanol + NaCl + H_2O ternary systems reported by Galleguillos and co-workers[22] since the density decreases with increasing ethanol/water ratio. It can be explained by the smaller density of ethanol than that of ethylene glycol.

Experimental values for density and refractive index for each ternary system in the undersaturated solutions fit the following expression[22]

$$Y = (A_0 + A_1w_1 + A_2w_2 + A_3w_1w_2 + A_4w_1w_2^2)\ \exp[A_5(w_2/w_3) + A_6(w_2/w_3)^2] \qquad (2)$$

where Y represents density ($g \cdot cm^{-3}$) or the refractive index, w_1, w_2, and w_3 represent the mass fractions of ethylene glycol, salt, and water in the solution, respectively. The A_i values together with the obtained standard deviation (δ) of the fit are listed in Table 8. The corresponding standard deviations (δ) show that eq 2 can be satisfactorily used to correlate the density and refractive index values for the investigated undersaturated systems.

Conclusions

In this work, we investigated the four ternary systems ethylene glycol + NaCl + H_2O, ethylene glycol + KCl + H_2O, ethylene glycol + RbCl + H_2O, and ethylene glycol + CsCl + H_2O at 298.15 K. Our analysis produced the solubility, density, and refractive index diagrams for the four ternary systems. We discussed the influences of the inorganic salts and ethylene glycol on the density and refractive index. Moreover, the density and the refractive index data of unsaturated solutions have also been determined for the four ternary systems and correlated with the proportions of ethylene glycol and the concentrations of salt. These values may be used to improve the yield and purity of the salts from aqueous solution.

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