Phase Equilibrium of $NaNO_3/KNO_3$ in Glycerol + H_2O Mixed Solvent System at 288.15 K and 298.15 K

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H.-Y. Zhang, W.-W. Zhu, G.-L. Qin*, and *Z. Wei*
School of Chemical and Biological Engineering, Hechi University, 546 300 Yizhou, Guangxi, PR China

Solubility, density, and refractive index were determined for the ternary systems of $NaNO_3/KNO_3$ + glycerol + H_2O at 288.15 K and 298.15 K. The solubility of the salts was calculated by the method of combining density and refractive index. In all cases the solubility of the salts decreased with the increase in glycerol content. A reverse trend for the refractive indices was observed. However, $NaNO_3$ density tended to decrease and KNO_3 density tended to increase with the addition of glycerol in the solution. Moreover, the experimental data were correlated using a four-parameter and seven-parameter empirical equation for the saturated and unsaturated solutions, respectively. Therefore, research of such kind of system has potential theoretical and practical application for the purification process and thermodynamic chemistry.

Key words: *Sodium nitrate, potassium nitrate, glycerol, solubility, density, refractive index*

Introduction

"Salting out effect" means that the addition of an organic solvent to an aqueous solution of a salt will reduce the solubility of salts and thus induce its precipitation.[1] Therefore, the investigations of the physicochemical properties of inorganic salts in organic solvents – water, such as solubility data together with density, refractive index and so on, are of great scientific importance. Various systems of salt and mixed solvent systems have been investigated to assess the potential applicability of such method as a technique for separation of salts. Many of the reports focus on systems composed of alkaline metal chlorides, alcohols, and water. For example, the properties of systems of alcohol (propan-1-ol, propan-2-ol, pentan-2-ol, pentan-3-ol, 2-methylbutan-2-ol, 2-methylbutan-1-ol, and pentan-1-ol) + MCl (M = Na, K) + water were systematically studied by *Gomis et al.*[2–5] Moreover, physicochemical properties of $NaNO_3$ + H_2O + poly(ethylene glycol),[6] KNO_3 + H_2O + propan-2-ol,[7] and $LiNO_3$ in organic solvent (methanol, ethanol, propan-1-ol, propan-2-ol and butan-1-ol)[8] were reported.

In previous work, our research groups have focused on the solubility of alkali metal (Na, K, Rb and Cs) salts in water + organic solvent.[9–11] In this work, the equilibrium solubility of $NaNO_3$ and KNO_3 in the mixed solvent $HOCH_2CH(OH)CH_2OH$ + H_2O were determined by the density-refractive index method. The density and refractive index of the saturated and unsaturated solutions were also measured.

* Corresponding author: Dr Hui-Ying Zhang
e-mail: zhy5158@126.com

Experimental Section

Materials. All the chemicals (purity > 99.5 %), including sodium nitrate, potassium nitrate, and glycerol were purchased from Sinopharm Chemical Reagent Co. Ltd., and used without further purification. The salt was dried to constant weight for 48 h at 110 °C and stored in desiccators prior to use. Double-distilled water was used throughout this work.

Apparatus and Procedure. All samples were prepared by mass with electronic balance (AL204, Mettler Toledo, accuracy of $\pm 1 \cdot 10^{-4}$ g). The experimental apparatus and process are the same as those reported in our former work.[9–11] The mixed solvent (glycerol and water) was firstly placed in a 10 ml syringe (the mass fraction of glycerol in the mixed solvent varied from 0.0 to 1.0). Excessive amounts of $NaNO_3$ and KNO_3 were then added into the mixed solvent. Next, the samples were stirred for 48 h and settled for a further 24 h to ensure that equilibrium was established. The temperature was controlled within an accuracy of ±0.1 K. After equilibrium was achieved, the solutions were withdrawn and analysed. The unsaturated solutions were prepared by adding salt to the mixtures of glycerol – water at a certain ratio.

Refractive index and density of both saturated and unsaturated solutions were determined using RXA 170 refractometer (Anton Paar) and DMA 4500 vibrating tube densimeter (Anton Paar) with a precision of $4 \cdot 10^{-5}$ and $\pm 1 \cdot 10^{-5}$ g cm^{-3}, respectively. Both the instruments were calibrated prior to initiation of each series of measurements, using air and double-distilled water as reference substances.

The content of the salts and glycerol was analysed using density–refractive index method,[9] because refractive index and

density both depend on quantity of dissolved salts and concentration of glycerol in ternary systems $NaNO_3/KNO_3$ (1) + glycerol (2) + H_2O (3), based on the following equations:

$$\rho/\mathrm{g\,cm^{-3}} = a_1 + b_1 w_1 + c_1 w_2 \quad (1)$$

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

where ρ is the density, n_D is the refractive index, w_1 and w_2 are the mass fraction of the salts and glycerol in the mixed solution, respectively. The samples for calibration were prepared containing the salt with mass fraction of 0 %, 3 %, 6 %, and glycerol with known varying content. The density and refractive index of the samples were then determined at 298.15 K and plotted against the mass fraction of glycerol. The values of parameters of equations 1 and 2 were obtained by the calibration curves listed in Table 1. However, it should be noted that this equation is only valid for dilute solutions of glycerol and salt ($w_1 < 0.06$, $w_2 < 0.45$). Therefore, it was necessary to dilute the samples before measurement of refractive index and density. The combined equations 1 and 2 can then be solved, and w_1 and w_2 in the ternary systems can be determined.

Results and Discussion

The solubility, density, and refractive index of the saturated solution for $NaNO_3$/ KNO_3+ glycerol + H_2O at 288.15 K and 298.15 K are listed in Table 2. Moreover, the comparison of the solubility, refractive index, and density of sodium nitrate and potassium nitrate in pure water at 298.15 K with literatures[12–15] are given in Table 3, which shows good agreement.

Table 1 – *Parameters of equations 1 and 2*

Tablica 1 – *Parametri jednadžbi 1 i 2*

System Sustav	a_1	b_1	c_1	a_2	b_2	c_2
$NaNO_3$ (1) + glycerol (2) + H_2O (3)	0.99447	0.26012	0.67367	1.33091	0.13194	0.11600
KNO_3 (1) + glycerol (2) + H_2O (3)	0.99447	0.26111	0.60433	1.33091	0.13303	0.07750

Table 2 – *Solubility (w_1), density (ρ), and refractive index (n_D) for $NaNO_3/KNO_3$ (1) + glycerol (2) + H_2O (3) systems at 288.15 and 298.15 K*

Tablica 2 – *Topljivost (w_1), gustoća (ρ) i indeks loma (n_D) u sustavu $NaNO_3/KNO_3$ (1) + glicerol (2) + H_2O (3) pri 288,15 i 298,15 K*

	T = 288.15 K				T = 298.15 K			
T/K	w_1	w_2	n_D	ρ/g cm^{-3}	w_1	w_2	n_D	ρ/g cm^{-3}
	0.4538	0.0000	1.38910	1.37633	0.4797	0.0000	1.38855	1.39129
	0.4218	0.0578	1.39397	1.36727	0.4397	0.0560	1.39317	1.38162
	0.3856	0.1229	1.39856	1.35567	0.3997	0.1201	1.39811	1.37145
	0.3512	0.1946	1.40496	1.34496	0.3628	0.1911	1.40393	1.35902
	0.3144	0.2742	1.41152	1.33395	0.3251	0.2700	1.41052	1.34482
$NaNO_3$	0.2812	0.3594	1.41826	1.32481	0.2883	0.3559	1.41708	1.33331
	0.2444	0.4533	1.42757	1.31824	0.2533	0.4480	1.42558	1.32390
	0.2060	0.5558	1.43808	1.31419	0.2204	0.5457	1.43580	1.31741
	0.1741	0.6607	1.44946	1.31149	0.1864	0.6509	1.44735	1.31348
	0.1485	0.7664	1.45964	1.31001	0.1540	0.7614	1.45753	1.31262
	0.1282	0.8718	1.47482	1.30819	0.1304	0.8696	1.47282	1.31114

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Table 2 – *(continued) Solubility (w_1), density (ρ), and refractive index (n_D) for $NaNO_3/KNO_3$ (1) + glycerol (2) + H_2O (3) systems at 288.15 and 298.15 K*

Tablica 2 – *(nastavak) Topljivost (w_1), gustoća (ρ) i indeks loma (n_D) u sustavu $NaNO_3/KNO_3$ (1) + glicerol (2) + H_2O (3) pri 288,15 i 298,15 K*

	T = 288.15 K				T = 298.15 K			
T/K	w_1	w_2	n_D	ρ/g cm^{-3}	w_1	w_2	n_D	ρ/g cm^{-3}
	0.2127	0.0000	1.35356	1.14029	0.2751	0.0000	1.35923	1.18137
	0.1744	0.0819	1.36247	1.14718	0.2319	0.0762	1.36594	1.18209
	0.1429	0.1709	1.37194	1.15336	0.1978	0.1599	1.37302	1.18343
	0.1201	0.2635	1.38182	1.16137	0.1654	0.2499	1.38199	1.18578
	0.1013	0.3588	1.39262	1.17046	0.1375	0.3445	1.39275	1.19021
KNO_3	0.0859	0.4564	1.40393	1.18544	0.1137	0.4428	1.40373	1.19817
	0.0729	0.5558	1.41748	1.20297	0.0950	0.5555	1.41559	1.20893
	0.0607	0.6569	1.42998	1.21981	0.0787	0.6446	1.42866	1.22357
	0.0493	0.7602	1.44394	1.23807	0.0640	0.7485	1.44267	1.24067
	0.0402	0.8635	1.45910	1.25946	0.0525	0.8526	1.45648	1.25841
	0.0334	0.9664	1.47391	1.28141	0.0419	0.9578	1.47042	1.27775

Table 3 – *Comparison of solubility (S), density (ρ), and refractive index (n_D) of the salts in pure water at 298.15 K*

Tablica 3 – *Usporedba topljivosti (S), gustoće (ρ) i indeksa loma (n_D) soli u čistoj vodi pri 298.15 K*

Salt Sol	This work Ovo istraživanje			Literature Literatura		
	S (w/%)	ρ/g cm^{-3}	n_D	S (w/%)	ρ/g cm^{-3}	n_D
$NaNO_3$	47.97	1.39129	1.38855	47.7,[12] 47.90[13]	1. 39128[13]	1.3898[13]
KNO_3	27.51	1.18137	1.35923	27.7,[12] 27.65[14]	1.18924[15]	1.35915[15]

The effect of glycerol and temperature on the solubility, density and refractive index are depicted in Fig. 1. It can be observed that the solubility of the two salts decreased with the addition of glycerol. With higher temperature solubility is greater. However, the $NaNO_3$ system is not very sensitive to the change of temperature. The changing trend of the density of the solution varies for different salts. For $NaNO_3$ + glycerol + H_2O systems, the trend is similar to that of solubility. However, for KNO_3 + glycerol + H_2O systems, the density of the solution increased with the addition of glycerol in the mixed solvent. Moreover, the density curves at the two temperatures almost overlapped in the glycerol-rich area. However, a decreasing trend of the density curve is observed for KNO_3 + propan-2-ol + H_2O[15] systems when increasing the content of propan-2-ol. These phenomena can be attributed to three factors. Firstly, the density increased when the solubility of salts increased. Secondly, the density increased with increasing the content of glycerol, because the density of glycerol is greater than that of water. Thirdly, with higher temperature density will be lower. For the refractive index of the solutions, a monotonically increasing trend is observed with increasing the content of glycerol. Moreover, an interaction can be observed for KNO_3 + glycerol + H_2O systems as shown in Fig. 1c. However, for $NaNO_3$ + glycerol + H_2O systems, the refractive index curves at the two temperatures almost overlapped. This behaviour can be explained by

the fact that the refractive index of the saturated solution is mainly influenced by two factors: concentration of the salt and temperature. The refractive index increased with the increase in the mass fraction of the salt, and decreased with the enhancement of temperature. This phenomenon is different from that of KNO_3 + propan-2-ol + H_2O system.[15] For KNO_3 + propan-2-ol + H_2O system, the refractive index first decreases (until $w_{\text{propan-2-ol}} \approx 0.1$ at 298.15 K and $w_{\text{propan-2-ol}} \approx 0.2$ at 313.15 K) and then increases with the increase in propan-2-ol content. An interaction was also observed for the refractive index of KNO_3 + propan-2-ol + H_2O system at different temperatures. This is mainly due to the fact that the structure and properties of the organic solvent glycerol is very different from that of propan-2-ol.

For comparison, the solubility, refractive index, and density of the systems NaCl + glycerol + H_2O is plotted in Fig. 1.[10] It can be seen that the changing trends of solubility and refractive index of all the systems are similar. That is, the main effect on solubility and refractive index is the content of glycerol.

However, for the changing of density, different phenomenon can be observed from Fig. 1b. For NaCl + glycerol + H_2O system, the density of the solution increased with increasing the concentration of glycerol. However, the density of $NaNO_3$ + glycerol + H_2O system at the two temperatures are changed with a contrary tendency with increasing the glycerol content. This suggests that different salts play a dominant role in changing of density. These phenomena may further explain that the solubility, temperature, and the organic solvent all affect the properties of ternary systems.

Experimental data for the mass fraction of the salt, density, and refractive index of the saturated systems are correlated using the following equation:[16]

$$Y = A + Bw_2 + Cw_2^2 + Dw_2^3, \qquad (3)$$

where w_2 is the mass fraction of glycerol in the solution. Y represents the mass fraction of salts in the solution (w_1), numerical value of density (ρ / g cm^{-3}), or refractive index (n_D) of the solution. The obtained parameters *A, B, C, D* together with the relative standard deviation (δ) of the systems are listed in Table 4. From the obtained standard deviations, we conclude that equation (3) can be satisfactorily used to correlate solubility, density and refractive index data.

To complete this study, unsaturated systems $NaNO_3/KNO_3$ (1) + glycerol (2) + H_2O (3) at fixed mass ratios of solvent ($w_2 : w_3$ = 1 : 9, 3 : 7, 5 : 5, 7 : 3, 9 : 1) and different temperatures (288.15 and 298.15 K) were also investigated. The density and refractive index of the unsaturated systems are listed in Tables 5–6. Both the density and refractive index increased with the increase of the glycerol-to-water ratio and with the increase of the salts content. However, the higher the temperature, the lower are the density and refractive index.

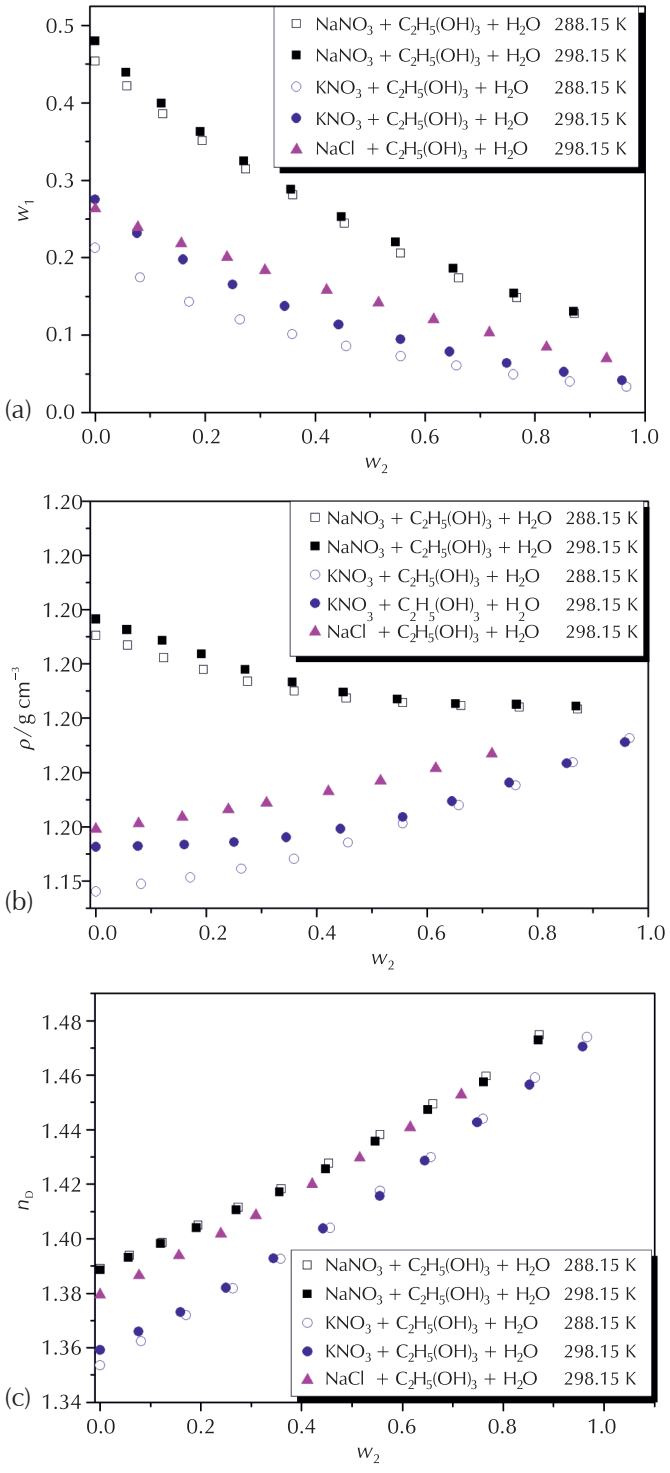

Fig. 1 – *Solubility (a), density (b), and refractive index (c) as a function of the content of glycerol for $NaNO_3/KNO_3$ (1) + glycerol (2) + H_2O (3) and NaCl (1) + glycerol (2) + H_2O (3)[10] systems at 288.15 K and 298.15 K*

Slika 1 – *Topljivosti (a), gustoće (b) i indeksi loma (c) kao funkcije sadržaja glicerola za sustave $NaNO_3/KNO_3$ (1) + glicerol (2) + H_2O (3) i NaCl (1) + glicerol (2) + H_2O (3)[10] pri 288.15 K i 298.15 K*

Table 4 – *Parameters (A, B, C, and D) of equation (3) and the standard deviations (δ) of the correlation for the saturated systems $NaNO_3$/KNO_3 + glycerol + H_2O*

Tablica 4 – *Parametri (A, B, C i D) jednadžbe (3) i standardne devijacije (δ) korelacije zasićenih sustava $NaNO_3$/KNO_3 + glicerol + H_2O*

Physical quantity Fizička veličina	Salt Sol	T / K	A	B	C	D	δ
mass fraction of salt maseni udjel soli $Y = w_1$	$NaNO_3$	288.15	0.4625	−0.4403	−0.1279	0.1772	0.0038
		298.15	0.4804	−0.3998	−0.2524	0.2788	0.0031
	KNO_3	288.15	0.2197	−0.5051	0.5187	−0.2017	0.0013
		298.15	0.2963	−0.6864	0.7067	−0.2823	0.0012
density gustoća $Y = \rho/\mathrm{g\,cm^{-3}}$	$NaNO_3$	288.15	1.4084	−0.5863	0.5807	−0.2672	0.0011
		298.15	1.4221	−0.5633	0.4939	−0.1923	0.0011
	KNO_3	288.15	1.1405	−0.1629	0.3039	−0.1452	0.0009
		298.15	1.1811	−0.2690	0.3913	−0.1707	0.0009
refractive index indeks loma $Y = n_D$	$NaNO_3$	288.15	1.3866	0.0497	0.0122	−0.0069	0.0002
		298.15	1.3854	0.0334	0.0359	−0.0114	0.0002
	KNO_3	288.15	1.3533	0.0516	0.0716	−0.0405	0.0005
		298.15	1.3573	0.0511	0.0597	−0.0342	0.0006

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

Table 5 – *Density (ρ) and refractive index (n_D) for the unsaturated system of $NaNO_3$ (1) + glycerol (2) + H_2O (3) at 288.15 K and 298.15 K*

Tablica 5 – *Gustoća (ρ) i indeks loma (n_D) nezasićenog sustava $NaNO_3$ (1) + glicerol (2) + H_2O pri 288.15 K i 298.15 K*

	T = 288.15 K				T = 298.15 K			
$w_2 : w_3$	w_1	w_2	n_D	$\rho/\mathrm{g\,cm^{-3}}$	w_1	w_2	n_D	$\rho/\mathrm{g\,cm^{-3}}$
1 : 9	0.1086	0.0892	1.35798	1.09138	0.1154	0.0885	1.35645	1.09946
	0.1959	0.0804	1.36705	1.15926	0.2069	0.0793	1.36618	1.16721
	0.2676	0.0733	1.37519	1.22012	0.2812	0.0719	1.37437	1.22718
	0.3276	0.0672	1.38197	1.27108	0.1154	0.0885	1.35645	1.09946
	0.3785	0.0622	1.38792	1.31872	0.2069	0.0793	1.36618	1.16721
	0.4222	0.0578	1.39397	1.36727	0.2812	0.0719	1.37437	1.22718
3 : 7	0.0829	0.2751	1.37893	1.12188	0.0897	0.2731	1.37767	1.12928
	0.1531	0.2541	1.38521	1.17681	0.1647	0.2506	1.38438	1.18181
	0.2134	0.2360	1.39125	1.22129	0.2283	0.2315	1.39015	1.22928
	0.2656	0.2203	1.39607	1.26682	0.2829	0.2151	1.39517	1.27205
	0.3113	0.2066	1.40046	1.30512	0.3302	0.2010	1.39956	1.31102
	0.3517	0.1945	1.40496	1.34496	0.3628	0.1885	1.40393	1.35002

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Table 5 – *(continued) Density (ρ) and refractive index (n_D) for the unsaturated system of $NaNO_3$ (1) + glycerol (2) + H_2O (3) at 288.15 K and 298.15 K*

Tablica 5 – *(nastavak) Gustoća (ρ) i indeks loma (n_D) nezasićenog sustava $NaNO_3$ (1) + glicerol (2) + H_2O pri 288.15 K i 298.15 K*

	T = 288.15 K				T = 298.15 K			
$w_2 : w_3$	w_1	w_2	n_D	ρ/g cm^{-3}	w_1	w_2	n_D	ρ/g cm^{-3}
5 : 5	0.0614	0.4693	1.40245	1.15964	0.0653	0.4674	1.40155	1.16356
	0.1157	0.4422	1.40634	1.19689	0.1225	0.4388	1.40543	1.20087
	0.1640	0.4180	1.40927	1.22967	0.1732	0.4134	1.40847	1.23467
	0.2074	0.3963	1.41235	1.26088	0.2182	0.3909	1.41153	1.26658
	0.2464	0.3768	1.41553	1.29195	0.2587	0.3707	1.41473	1.29735
	0.2818	0.3591	1.41826	1.32481	0.2883	0.3524	1.41708	1.32831
7 : 3	0.0416	0.6709	1.42951	1.20031	0.0443	0.6690	1.42896	1.20411
	0.0799	0.6441	1.43081	1.22717	0.0850	0.6405	1.43034	1.22859
	0.1152	0.6193	1.43229	1.25182	0.1222	0.6144	1.43199	1.25213
	0.1479	0.5965	1.43384	1.27327	0.1566	0.5904	1.43334	1.27426
	0.1783	0.5752	1.43543	1.29456	0.1883	0.5682	1.43461	1.29497
	0.2066	0.5554	1.43708	1.31419	0.2204	0.5476	1.43598	1.31441
9 : 1	0.0284	0.8745	1.45742	1.24503	0.0310	0.8722	1.45712	1.24780
	0.0552	0.8503	1.45805	1.26017	0.0602	0.8459	1.45781	1.26468
	0.0805	0.8275	1.45874	1.27682	0.0876	0.8211	1.45849	1.28077
	0.1046	0.8059	1.45931	1.29187	0.1135	0.7979	1.45918	1.29474
	0.1274	0.7853	1.45998	1.30456	0.1380	0.7758	1.45986	1.30850
	0.1491	0.7658	1.46064	1.31501	0.1540	0.7552	1.46033	1.31662

Table 6 – *Density (ρ) and refractive index (n_D) for the unsaturated system of KNO_3 (1) + glycerol (2) + H_2O (3) at 288.15 K and 298.15 K*

Tablica 6 – *Gustoća (ρ) i indeks loma (n_D) nezasićenog sustava KNO_3 (1) + glicerol (2) + H_2O pri 288.15 K i 298.15 K*

	T = 288.15 K				T = 298.15 K			
$w_2 : w_3$	w_1	w_2	n_D	ρ/g cm^{-3}	w_1	w_2	n_D	ρ/g cm^{-3}
1 : 9	0.0340	0.0966	1.34845	1.04325	0.0479	0.0952	1.34914	1.04696
	0.0658	0.0934	1.35130	1.06281	0.0915	0.0908	1.35248	1.07186
	0.0955	0.0905	1.35379	1.08104	0.1313	0.0869	1.35594	1.09873
	0.1234	0.0877	1.35634	1.10189	0.1677	0.0833	1.35917	1.12673
	0.1497	0.0851	1.35924	1.12485	0.2012	0.0799	1.36289	1.15534
	0.1744	0.0826	1.36207	1.14718	0.2319	0.0768	1.36594	1.18209

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Table 6 – *(continued) Density (ρ) and refractive index (n_D) for the unsaturated system of KNO_3 (1) + glycerol (2) + H_2O (3) at 288.15 K and 298.15 K*

Tablica 6 – *(nastavak) Gustoća (ρ) i indeks loma (n_D) nezasićenog sustava KNO_3 (1) + glicerol (2) + H_2O pri 288.15 K i 298.15 K*

	T = 288.15 K				T = 298.15 K			
$w_2 : w_3$	w_1	w_2	n_D	ρ/g cm^{-3}	w_1	w_2	n_D	ρ/g cm^{-3}
3 : 7	0.0223	0.2933	1.37358	1.08902	0.0320	0.2904	1.37364	1.09154
	0.0436	0.2870	1.37498	1.10181	0.0619	0.2814	1.37546	1.10764
	0.0640	0.2808	1.37643	1.11347	0.0901	0.2730	1.37769	1.12746
	0.0835	0.2749	1.37804	1.12735	0.1166	0.2650	1.37943	1.14582
	0.1023	0.2693	1.37950	1.14286	0.1417	0.2575	1.38135	1.16482
	0.1201	0.2639	1.38102	1.15937	0.1654	0.2504	1.38319	1.18578
5 : 5	0.0154	0.4923	1.40034	1.13775	0.0209	0.4896	1.39969	1.13826
	0.0303	0.4849	1.40144	1.14736	0.0410	0.4795	1.40044	1.15039
	0.0448	0.4776	1.40267	1.15712	0.0603	0.4699	1.40125	1.16186
	0.0588	0.4706	1.40276	1.16543	0.0788	0.4606	1.40202	1.17568
	0.0724	0.4638	1.40389	1.17576	0.0966	0.4517	1.40285	1.18743
	0.0859	0.4572	1.40393	1.18544	0.1137	0.4431	1.40373	1.19817
7 : 3	0.0107	0.6925	1.42843	1.18759	0.0140	0.6901	1.42890	1.18819
	0.0211	0.6853	1.42864	1.19389	0.0277	0.6807	1.42905	1.19557
	0.0314	0.6781	1.42883	1.19997	0.0409	0.6714	1.42921	1.20356
	0.0414	0.6710	1.42913	1.20669	0.0538	0.6623	1.42941	1.21185
	0.0512	0.6642	1.42957	1.21332	0.0663	0.6536	1.42952	1.21958
	0.0607	0.6574	1.42998	1.21981	0.0787	0.6450	1.42966	1.22657
9 : 1	0.0069	0.8937	1.45874	1.24114	0.0109	0.8917	1.45698	1.24186
	0.0138	0.8876	1.45914	1.24414	0.0181	0.8837	1.45706	1.24447
	0.0205	0.8815	1.45925	1.24744	0.0269	0.8758	1.45719	1.24916
	0.0272	0.8755	1.45938	1.25112	0.0355	0.8680	1.45734	1.25385
	0.0338	0.8695	1.45943	1.25488	0.0440	0.8604	1.45750	1.25858
	0.0402	0.8637	1.45951	1.25946	0.0525	0.8529	1.45768	1.26241

The seven-parameter empirical equation was used to fit the unsaturated density and refractive index data:[16]

$$Y = (A_0 + A_1 w_1 + A_2 w_2 + A_3 w_1 w_2 + A_4 w_1 w_2^2) \cdot \cdot \exp[A_5(w_2/w_3) + A_6(w_2/w_3)^2] , \quad (4)$$

where Y represents numerical value of density (ρ / g cm^{-3}) or the refractive index (n_D) of the ternary system, where w_1, w_2, and w_3 are the mass fractions of salts, glycerol, and water in the solution, respectively. The coefficients of Eq. (4) (A_i, i = 0 to 6) along with the corresponding standard deviations for the investigated systems are given in Table 7. Based on the obtained standard deviations, it can be seen that Eq. (4) is satisfactory for the systems in this work.

Table 7 – *Parameters A_i (i = 0 – 6) of equation (4) and the standard deviation (δ) of the correlation for the unsaturated systems $NaNO_3/KNO_3$ + glycerol + H_2O*

Tablica 7 – *Parametri A_i (i = 0 – 6) jednadžbe (4) i standardna devijacija (δ) korelacije za nezasićene sustave $NaNO_3/KNO_3$ + glicerol + H_2O*

Y	T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	δ
					$NaNO_3$				
ρ / cm^{-3}	288.15	0.9624	0.8999	0.2872	0.0227	−0.1419	0.0051	−0.0005	0.0033
	298.15	0.9656	0.8735	0.2940	0.0248	−0.1449	0.0017	−0.0002	0.0039
n_D	288.15	1.3321	0.1245	0.1218	0.0464	−0.0537	0.0035	−0.0003	0.0004
	298.15	1.3299	0.1233	0.1236	0.0464	−0.0523	0.0036	−0.0003	0.0005
					KNO_3				
ρ / cm^{-3}	288.15	0.9853	0.7595	0.2906	0.1443	−0.0446	−0.0035	0.0003	0.0018
	298.15	0.9756	0.7653	0.3068	0.1324	−0.0774	−0.0048	0.0004	0.0021
n_D	288.15	1.3314	0.1042	0.1321	0.0586	−0.0403	0.0014	−0.0001	0.0003
	298.15	1.3316	0.0986	0.1245	0.0590	−0.0625	0.0035	−0.0003	0.0003

Conclusion

The equilibrium solubility, density, and refractive index of the ternary systems of $NaNO_3/KNO_3$ + glycerol + H_2O were determined at temperatures 288.15 and 298.15 K in this work. For the saturated systems, the phase is a single solid–liquid equilibrium with the solid being $NaNO_3$ or KNO_3. The solubility for the saturated solutions was found to decrease with the increase in glycerol concentration, and increased with the increase in temperature. That is, the salting out effect is observed when adding organic solvent glycerol into water. The refractive index of all the systems increased with the addition of glycerol in the mixed solvent, because of the greater refractive index of glycerol itself. However, the temperature effect on the refractive index is complicated, because the temperature affects both the concentration of salts in the solution and the refractive index of the solution. The changing trend of density curves is completely different from that of solubility and refractive index. These phenomena imply that density of the solution is controlled by the solubility of different salts and temperature. The investigation of the unsaturated systems show that both density and refractive index increased with the increase in the glycerol-to-water ratio, and with the increase in salts content.

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List of symbols
Popis simbola

A, B, C, D, A_i, a_i, b_i, c_i – parameters – parametri

n_D – refractive index – indeks loma

S – solubility – topljivost

T – temperature, K – temperatura, K

w_1 – glycerol mass fraction – maseni udjel glicerola

w_2 – salt mass fraction – maseni udjel soli

w_3 – water mass fraction – maseni udjel vode

Y – physical quantity (solubility, density, refractive index) – fizička veličina (topljivost, gustoća, indeks loma)

ρ – density, g cm^{-3} – gustoća, g cm^{-3}

δ – standard deviation – standardna devijacija

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SAŽETAK

Fazna ravnoteža u sustavu $NaNO_3/KNO_3$ + glicerol + voda pri 288.15 K i 298.15 K

H.-Y. Zhang, W.-W. Zhu, G.-L. Qin* i *Z. Wei*

U ternarnom sustav $NaNO_3/KNO_3$ + glicerol + voda određeni su topljivost, gustoća i indeks loma pri 288,15 K i 298,15 K. Topljivost je izračunata na temelju gustoće i indeksa loma. U svim se slučajevima topljivost smanjuje s povećanjem udjela glicerola. Za indeks loma uočen je suprotan trend. Dodatkom glicerola smanjuje se gustoća otopine $NaNO_3$, a povećava gustoća otopine KNO_3.

Eksperimentalni podatci za zasićene i podzasićene otopine korelirani su empirijskom jednadžbom s četiri i sedam parametara. Istraživanje ovakvih sustava ima moguću primjenu u pročišćivanju i termodinamici.

School of Chemical and Biological Engineering
Hechi University
546 300 Yizhou, Guangxi
Kina

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