Phase Equilibria of Alkali Nitrates ($NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$) in Glycerol + H_2O System at Various Temperatures

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By using a homemade research device for phase equilibrium, the equilibrium solubility of the alkali nitrates ($NaNO_3$/KNO_3/$RbNO_3$/$CsNO_3$) in the mixed solvent glycerol [$HOCH_2CH(OH)CH_2OH$] + H_2O in the mass fraction range of glycerol (0.0 to 1.0) at 35 and 45 °C was measured. Moreover, the density and refractive index of the saturated solutions of $NaNO_3$/KNO_3/$RbNO_3$/$CsNO_3$ + mixed solvent glycerol + H_2O were determined. The experimental results showed that, in all systems, with the increase of mass fraction of glycerol, the solubility of the salts and the density of the solution decreased, while the refractive index increased gradually. The solubility, refractive index, and density data were fitted by a four-parameter empirical equation.

Key words: *Alkali nitrate, glycerol, solubility, density, refractive index*

Introduction

Aqueous solutions containing salts are of increasing importance in separation and purification processes in chemical engineering. For example, the addition of an organic solvent to the aqueous solution of a salt normally decreases the solubility of the salt, which is called "salting out effect". Therefore, 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. For instance, much research has been done on the physicochemical properties of NaCl/KCl + alcohol + H_2O systems. *Gomis et al*. investigated the ternary 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 at 298.15 K.[1–4] *Galleguillos et al*.[5] reported the solubilities, densities, and refractive indices of systems NaCl/KCl + ethanol + H_2O at different temperatures. Some researchers focused on the study of systems that include alkali nitrates. For example, reported were the solubility, refractive index, density, electrical conductivity and viscosity 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]

In previous work, our research groups have focused on the physical-chemical properties of rare alkali metal (Rb and Cs) salts + alcohol/PEG (polyethylene glycol) + water systems.[9–12] As a continuation of our work in this field, this paper presents the systematic study we carried out on the properties, including solubility, density and refractive index of the ternary systems of $NaNO_3$/KNO_3/$RbNO_3$/$CsNO_3$ + glycerol [$CH_3CH(OH)CH_2OH$] + H_2O at 35 and 45 °C. The data for the saturated systems were measured and correlated with an empirical equation. We also present a simple method for analysing the composition of the ternary systems by combining the refractive index and density.

Experimental

Materials

The reagents used were glycerol (purity > 99.0 %, Shanghai), sodium nitrate and potassium nitrate (purity > 99.5 %, Shanghai), rubidium nitrate (purity > 99.5 %, Shanghai) and cesium nitrate (purity > 99.5 %, Sichuan). All of the chemicals used in this study were used without further purification. The above salts were preheated at 110 °C and dried to constant weight for 48 h. All the reagents were then stored over silica gel in desiccators. Double distilled water was used throughout this work.

Apparatus and procedure

The phase equilibrium study was carried out by mixing known masses of glycerol and water with excess salt. A detailed description of the equipment used in this paper has been presented in former work.[9] All the samples were prepared by mass using an analytical balance with precision of

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$\pm$ 1 $\times$ 10^{-4} g (Mettler Toledo, AL204). The samples were fixed on the carrier plate and stirred for 24 h. After standing for another 48 h ensuring that equilibrium was established, samples of the solution were taken for phase composition analysis.

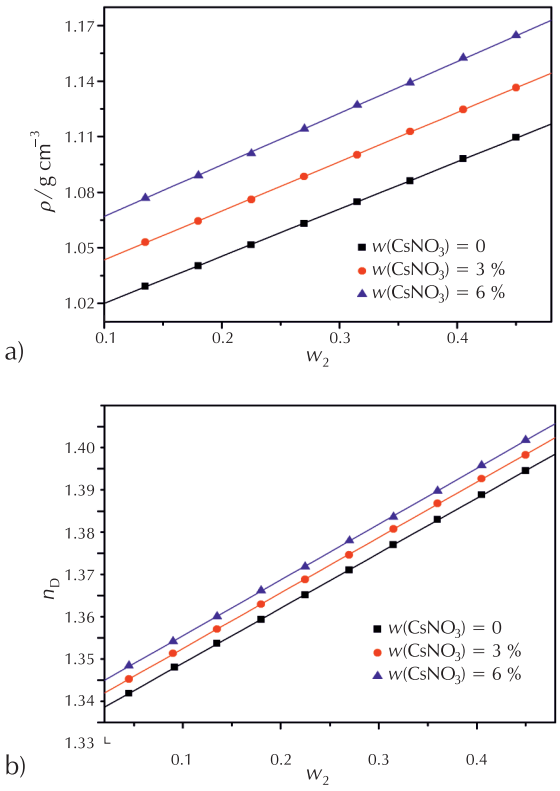
Refractive indices and densities of the solutions were determined using RXA 170 refractometer and DMA 4500 vibrating tube densimeter (Anton Paar) with precision of $\pm$ 4 $\times$ 10^{-5} and 1 $\times$ 10^{-5} g cm^{-3}, respectively. Both instruments were calibrated prior to initiation of each series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

For ternary systems containing organic compound (1) + salt (2) + water (3), the refractive index and density of the solution depends both on the content of the organic component and the salt.[13,14] For dilute aqueous solutions containing glycerol and a salt, the relation between the refractive index, n_D, or density, ρ, and the mass fractions of glycerol w_1, and a salt, w_2 is given by:

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

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

where ρ is the density, n_D is the refractive index, w_1 is the mass fraction of the alkali metal nitrates in the solution, w_2 is the mass fraction of the glycerol in the solution. a_1, b_1, c_1, a_2, b_2 and c_2 are parameters of the equation. The samples for calibration were prepared containing the salt with mass fraction of 0, 3 %, 6 % and glycerol with known and varying content. Then the density and refractive index of the samples were determined at 25 °C and plotted against the mass fraction of glycerol as shown in Fig. 1. The values of the six coefficients for the studied systems were obtained by the calibration plots 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. Then the combined equations 1 and 2 can be solved, and w_1 and w_2 in the ternary systems can be determined.



F i g . 1 – *Density (a) and refractive index (b) calibration curves for the $CsNO_3$ + $HOCH_2CH(OH)CH_2OH$ + H_2O system at 25 °C*

S l i k a 1 – *Kalibracijske krivulje gustoće (a) i indeksa loma (b) za sustav $CsNO_3$ + $HOCH_2CH(OH)CH_2OH$ + H_2O pri 25 °C*

Results and discussion

The solubility, density and refractive index data of the ternary saturated solution $NaNO_3$/ KNO_3/$RbNO_3$/$CsNO_3$ (w_1) + glycerol (w_2) + H_2O (w_3) at 35 °C and 45 °C are listed in Table 2. Table 3 presents the solubility and refractive index data of alkali metal nitrates at 45 °C in pure water. It can be seen that the obtained experimental data in this paper are in good agreement with the literature.[15–17]

T a b l e 1 – *Density and refractive index parameters of equations 1 and 2*

T a b l i c a 1 – *Parametri jednadžbi 1 i 2 za gustoću i indeks loma*

Salt Sol	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

Table 2 – *Solubility, density (ρ), and refractive index (n_D) for systems MNO_3 (1) + glycerol (2) + H_2O (3) (M = Na, K, Rb, Cs) at 35 and 45 °C*

Tablica 2 – *Topljivost, gustoća (ρ) i indeks loma (n_D) sustava MNO_3 (1) + glicerol (2) + H_2O (3) (M = Na, K, Rb, Cs) pri 35 i 45 °C*

w_2	w_1	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	0.1268	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				

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(nastavlja se na str. 158)

Table 2 – *Solubility, density (ρ), and refractive index (n_D) for systems MNO_3 (1) + glycerol (2) + H_2O (3) (M = Na, K, Rb, Cs) at 35 and 45 °C (continued)*

Tablica 2 – *Topljivost, gustoća (ρ) i indeks loma (n_D) sustava MNO_3 (1) + glicerol (2) + H_2O (3) (M = Na, K, Rb, Cs) pri 35 i 45 °C (nastavak)*

w_2	w_1	ρ / (g cm^{-3})	n_D	w_1	w_2	ρ / (g cm^{-3})	n_D
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 – *Comparison of solubility (S) and refractive index (n_D) of the alkali nitrates in pure water at 45 °C*

Tablica 3 – *Usporedba topljivosti (S) i indeksa loma (n_D) alkalijskih nitrata u čistoj vodi pri 45 °C*

Salt Sol	This work Ovo istraživanje		Literature Literatura	
	S (w / %)	n_D	S (w / %)	n_D
$NaNO_3$	52.23	1.39141	52.25[15]	1.3911[15]
KNO_3	42.02	1.37064	42.10*[16]	–
$RbNO_3$	57.94	1.38174	57.48[17]	1.3837[17]
$CsNO_3$	35.85	1.35598	35.28[18]	1.3582[18]

* The value is calculated by the fitting equation $S = A + bT + cT^2$ obtained from the data of reference 18.

* Vrijednost je izračunata jednadžbom $S = A + bT + cT^2$ prema podatcima iz lit. izvora 18.

Fig. 2 depicts the variation trend of solubility, density and refractive index versus the mass fraction of glycerol for the systems $RbNO_3$/$CsNO_3$ (w_1) + glycerol (w_2) + H_2O (w_3) at 25 and 35 °C. As shown in Fig. 2a for the systems at fixed temperature, with increasing mass fraction of glycerol, the solubility of the salt in the mixed solvent decreased. Furthermore, the higher the temperature, the higher is the solubility. However, the variation tendency of density for the systems is slightly different from that of solubility as presented in Fig. 2b. For $RbNO_3$ + glycerol + H_2O systems, the density tendency is similar to that of solubility, which suggests that the density is mainly affected by the solubility. But for $CsNO_3$ + glycerol + H_2O, in the entire concentration range of glycerol, the density changed slightly. This phenomenon may be caused by both the density and the content of glycerol. The higher the glycerol content in the mixed solvent, the lower is the solubility of $CsNO_3$. But at the same time, because of the higher density of glycerol itself, the higher the content of glycerol in the mixed solvent, the higher is the density of solution. The effect of the glycerol content was more obvious in the systems KNO_3 + glycerol + H_2O. That is, the density first decreases and then increases with increasing of the glycerol content.

The refractive indices of the systems are given in Fig. 2c. First, the refractive index of the solution rises with the increase of the glycerol content, showing the contrary variation trend to solubility and density. This is, however, completely different from the systems of NaCl/KCl + ethanol + H_2O[5] and KNO_3 + propan-2-ol + H_2O.[7] Moreover, the refractive indices of the systems almost overlapped, except for $RbNO_3$ + glycerol + H_2O at low concentrations of glycerol. This can be explained by the two contrary factors that affect the refractive index of the systems. It is known that the refractive index increases with the increase in salt concentration and decreases with the rise in temperature. Thus, the increase by higher solubility induced by higher temperature and the decrease in temperature itself balanced themselves out.

For the studied systems, the empirical equation (3)[5] can be used for the fitting of solubility, density and refractive data. The resulting parameter values and relative standard deviation δ are listed in Table 4.

$$Y = A_0 + A_1 w_2 + A_2 w_2^2 + A_3 w_2^3, \qquad (3)$$

wherein Y represents the solubility, density, or refractive index in the studied systems, A_i denote fitting parameters and w_2 represents the mass fraction of glycerol. The standard deviations ranged from 0.0002 to 0.0032. It can be concluded that the equation can be satisfactorily used to correlate the experimental data.

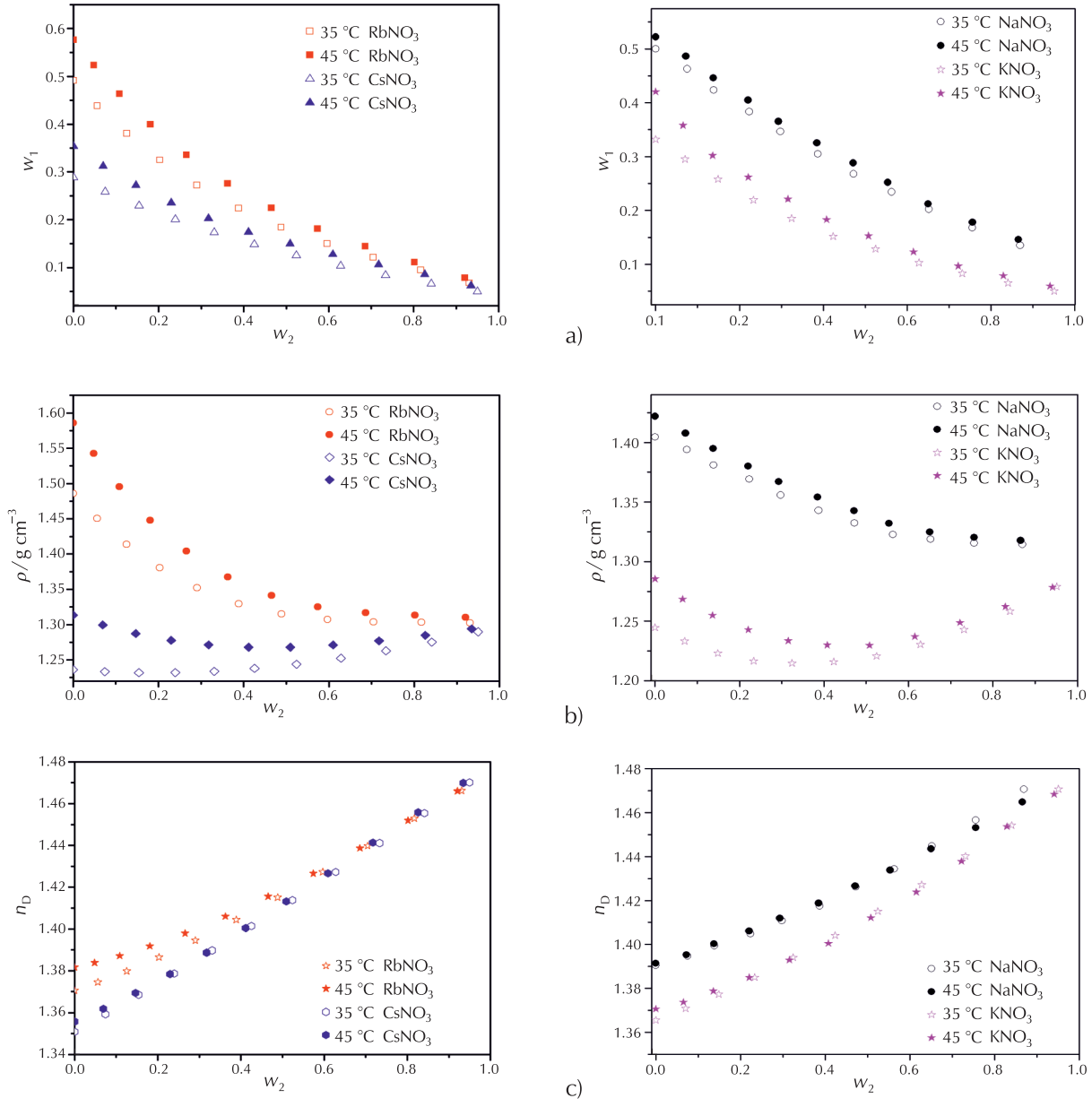

Fig. 2 – *Solubility (a), density (b), and refractive index (c) for the ternary systems $RbNO_3$/$CsNO_3$ (1) + $HOCH_2CH(OH)CH_2OH$ (2) + H_2O (3) at 35 °C and 45 °C*

Slika 2 – *Topljivosti (a), gustoće (b) i indeksi loma (c) za trokomponentne sustave $RbNO_3$/$CsNO_3$ (1) + $HOCH_2CH(OH)CH_2OH$ (2) + H_2O (3) pri 35 °C i 45 °C*

Table 4 – *Values of Eq. (3) parameters*
Tablica 4 – *Vrijednosti parametara jedn. (3)*

Systems Sustavi	A_0	A_1	A_2	A_3	δ
mass fraction / maseni udjel					
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 / gustoća					
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	0.0464	−0.0787	0.0005
45 °C KNO_3 (1) + $HOCH_2CH(OH)CH_2OH$ (2) + H_2O (3)	1.2855	−0.2788	0.3059	−0.1135	0.0006
35 °C $RbNO_3$ (1) + $HOCH_2CH(OH)CH_2OH$ (2) + H_2O (3)	1.4859	−0.6721	0.3958	−0.3407	0.0018
45 °C $RbNO_3$ (1) + $HOCH_2CH(OH)CH_2OH$ (2) + H_2O (3)	1.5857	−0.9506	0.8273	−0.4561	0.0021
35 °C $CsNO_3$ (1) + $HOCH_2CH(OH)CH_2OH$ (2) + H_2O (3)	1.2361	−0.0474	1.1274	−0.0225	0.0005
45 °C $CsNO_3$ (1) + $HOCH_2CH(OH)CH_2OH$ (2) + H_2O (3)	1.3134	−0.2214	0.1308	−0.1067	0.0009
refractive index / indeks loma					
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

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

Conclusions

In this paper, the solubility, density and refractive index of the ternary system $NaNO_3/KNO_3/RbNO_3/CsNO_3$ + glycerol + H_2O were investigated. The solubility of the salts decreased with the addition of glycerol, and increased with temperature. The density of the saturated solution is affected both by the solubility and the content of glycerol. For refractive index, two contrary factors of temperature and solubility led to the similar data at the two temperatures. The data of solubility, refractive index and density in the studied systems were fitted by the four-parameter empirical correlation equation.

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List of symbols
Popis simbola

A_i, a_i, b_i, c_i – parameters – parametri

n_D – refractive index – indeks loma

S – solubility – topljivost

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 alkalijskih nitrata ($NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$) u sustavu glicerol + H_2O pri različitim temperaturama

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Uređajem vlastite izrade mjerena je topljivost alkalijskih nitrata ($NaNO_3$/KNO_3/$RbNO_3$/$CsNO_3$) u smjesi otapala glicerol [$HOCH_2CH(OH)CH_2OH$] + H_2O u ovisnosti o masenom udjelu glicerola (0,0 – 1,0) pri 35 i 45 °C. Određene su gustoće i indeksi loma zasićenih otopina $NaNO_3$/KNO_3/$RbNO_3$/$CsNO_3$ + smjesa otapala glicerol + H_2O. Eksperimentalni rezultati su pokazali da se s povećanjem masenog udjela glicerola u svim sustavima smanjuju topljivost soli i gustoća otopine, dok se indeks loma postupno povećava. Topljivost, indeks loma i gustoća bili su postavljeni po četveroparametarskoj empirijskoj jednadžbi.

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