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Solubility of Lithium Nitrate in Solutions of Lithium Halides

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Summary. Solubility isotherms in $LiNO_3$ – Li*X* – H_2O ($X = Cl$, Br, I) systems at 298.15 K were measured for the first time with special regard to the retrograde solubility of lithium nitrate trihydrate. The compositions of solutions used as media in absorption refrigerators and heat pumps were compared with the results and subsequently discussed.

Keywords. Crystallization; Lithium nitrate; Lithium halides; Solubility.

Introduction

Systems consisting of lithium nitrate, lithium halide, and water were proposed as working fluids in absorption refrigerators and heat pumps [1, 2] to improve their performance characteristics and to minimize the corrosion at the same time. However, all relevant studies have been performed by the visual polythermal method using phase complexes of empirically chosen $LiNO_3$ – Li*X* ($X = Cl$, Br, I) ratios. As far as the author is aware, solubility studies covering the whole compositional range are so far missing.

Otherwise, numerous solubility isotherms in systems containing lithium nitrate as one component were reported. Most of them were measured at 25°C. In these systems lithium nitrate displays a quite variable behaviour, as far as the shape of its crystallization field and the overall form of the solubility diagram are concerned.

At 25°C there is no evidence for the formation of solid solutions and/or solid ternary compounds in any of these systems. Most of the systems are of the eutonic type [3–7]. In several systems lithium nitrate trihydrate loses its water under the influence of the added component and anhydrous lithium nitrate appears as the equilibrium solid phase [8–13]. Finally, in some systems where both lithium nitrate and the other salt component are hydrates, the solubility curve [14–17] is terminated by an area of hydrated melt and in a certain concentration interval no solid–liquid phase equilibrium exists. If in such systems a complete solubility diagram should be measured, anhydrous lithium nitrate must be taken as the starting material.

In most systems studied, a strong hydration ability of the lithium cation has been observed and the comparison of shapes of the solubility isotherms led to a general discussion on the organization of saturated solutions of salt hydrates [18]. Therefore the experimental determination of solubility isotherms in the title systems might be of interest both generally and from the point of view of the practical application of concentrated solutions of these systems.

Results and Discussion

The solubility diagrams in the systems investigated are given in Tables 1–3 and Figs. 1–3. In the case of the iodide diagram, no figurative points were placed at the solubility branch of lithium iodide, as the respective solutions were coloured intensively by liberated iodine and therefore no real equilibrium in ternary system exists there. In all cases, dehydration of lithium nitrate trihydrate under the influence of added halide has occurred. This effect was also observed in systems containing lithium nitrate and nitrates of strongly water bonding cations such as H^+ [8], NH_4^+ [9], Be^{2+} [10], Ca^{2+} [11], and some transition metals [12, 13].

Besides, in the crystallization field of $LiNO_3 \cdot 3H_2O$ the solubility curve has a special shape, designated as retrograde solubility. This phenomenon is demonstrated at Fig. 2 in the case of the system $LiNO_3$ – LiBr – H_2O. Here, the phase mixture of anhydrous $LiNO_3$ and $LiBr \cdot 2H_2O$ at, *e.g.*, composition A dissolves by addition of water at composition A_1, but addition of further portions of water to the formed solution causes crystallization of $LiNO_3 \cdot 3H_2O$ at A_2, this mixture dissolves again at composition A_3.

Beside this retrograde solubility in the crystallization field of $LiNO_3 \cdot 3H_2O$, the solubility isotherm in the system $LiNO_3$ – LiCl – H_2O (Fig. 1) exhibits an inflexion

Table 1. Solubility in the $LiNO_3$ – LiCl – H_2O system at 298.15 K

$LiNO_3$		LiCl		H_2O	Solid phase
100·*w*	mol·kg^{-1} water	100·*w*	mol·kg^{-1} water	100·*w*	
46.2	12.5	0	0	53.8	$LiNO_3 \cdot 3H_2O$
43.7	11.9	3.1	1.4	53.2	$LiNO_3 \cdot 3H_2O$
44.5	12.7	4.8	2.2	50.7	$LiNO_3 \cdot 3H_2O$
43.1	12.5	6.8	3.2	50.1	$LiNO_3 \cdot 3H_2O$
46.9	15.7	9.8	5.3	43.28	$LiNO_3 \cdot 3H_2O$
50.1	17.0	7.2	4.0	42.7	$LiNO_3 \cdot 3H_2O$
54.5	19.9	5.8	3.4	39.7	$LiNO_3 \cdot 3H_2O + LiNO_3$
48.5	17.3	10.8	6.26	40.68	$LiNO_3$
40.5	13.7	16.2	8.82	43.28	$LiNO_3$
35.9	12.1	20.9	11.5	43.12	$LiNO_3$
19.7	5.55	28.7	13.17	51.60	$LiNO_3$
19.0	5.54	31.3	14.8	49.72	$LiNO_3$
14.4	4.39	38.0	18.8	47.6	$LiNO_3 + LiCl \cdot H_2O$
5.75	1.62	2.64	19.5	51.61	$LiCl \cdot H_2O$
0	0	45.4	19.6	54.58	$LiCl \cdot H_2O$

Table 2. Solubility in the $LiNO_3$ – LiBr – H_2O system at 298.15 K

$LiNO_3$		LiBr		H_2O 100·*w*	Solid phase
100·*w*	mol·kg^{-1} water	100·*w*	mol·kg^{-1} water		
46.2	12.4	0	0	53.8	$LiNO_3 \cdot 3H_2O$
45.6	12.4	0.92	0.198	53.5	$LiNO_3 \cdot 3H_2O$
45.6	12.5	1.35	0.293	53.0	$LiNO_3 \cdot 3H_2O$
38.0	11.1	12.2	2.82	49.8	$LiNO_3 \cdot 3H_2O$
42.0	13.7	13.5	3.49	44.5	$LiNO_3 \cdot 3H_2O$
40.3	10.9	6.235	1.34	53.5	$LiNO_3 \cdot 3H_2O$
43.0	11.4	2.48	0.524	54.5	$LiNO_3 \cdot 3H_2O$
48.0	16.7	10.2	2.81	41.8	$LiNO_3 \cdot 3H_2O$
52.1	19.0	8.06	2.33	39.8	$LiNO_3 \cdot 3H_2O$
51.1	18.1	7.90	2.22	41.0	$LiNO_3 \cdot 3H_2O$
55.6	21.0	6.0	1.80	38.4	$LiNO_3 \cdot 3H_2O + LiNO_3$
57.1	21.9	5.1	1.55	37.8	$LiNO_3$[a]
45.6	16.7	14.7	4.27	39.7	$LiNO_3$
41.6	15.3	18.9	5.51	39.5	$LiNO_3$
30.7	11.5	30.6	9.10	38.7	$LiNO_3$
23.4	8.88	38.4	11.6	38.2	$LiNO_3$
16.9	6.52	45.5	13.9	37.6	$LiNO_3$
11.0	4.57	54.1	17.8	34.9	$LiNO_3 + LiBr \cdot 2H_2O$
9.0	3.82	56.8	19.1	34.2	$LiBr \cdot 2H_2O$
0	0	61.5	18.4	38.5	$LiBr \cdot 2H_2O$

[a] Metastable equilibrium

Table 3. Solubility in the $LiNO_3$ – LiI – H_2O system at 298.15 K

$LiNO_3$		LiBr		H_2O 100·*w*	Solid phase
100·*w*	mol·kg^{-1} water	100·*w*	mol·kg^{-1} water		
46.20	0.00	53.80	12.45	0.00	$LiNO_3 \cdot 3H_2O$
44.70	2.80	52.50	12.35	0.40	$LiNO_3 \cdot 3H_2O$
42.40	6.90	50.70	12.13	1.02	$LiNO_3 \cdot 3H_2O$
40.80	9.00	50.20	11.79	1.34	$LiNO_3 \cdot 3H_2O$
40.50	10.50	49.00	11.99	1.60	$LiNO_3 \cdot 3H_2O$
39.50	14.00	46.50	12.32	2.25	$LiNO_3 \cdot 3H_2O$
39.50	18.00	42.50	13.48	3.16	$LiNO_3 \cdot 3H_2O$
39.90	21.00	39.10	14.80	4.01	$LiNO_3 \cdot 3H_2O$
42.50	20.00	37.50	16.44	3.98	$LiNO_3 \cdot 3H_2O$
45.10	18.30	36.60	17.87	3.74	$LiNO_3 \cdot 3H_2O$
48.50	15.50	36.00	19.54	3.22	$LiNO_3 \cdot 3H_2O + LiNO_3$
45.50	20.00	34.50	19.13	4.33	$LiNO_3$
38.80	28.10	33.10	17.00	6.34	$LiNO_3$
33.30	35.00	31.70	15.24	8.25	$LiNO_3$
27.30	42.80	29.90	13.24	10.69	$LiNO_3$
0.00	62.80	37.20	0.00	12.61	$LiI \cdot 2H_2O$

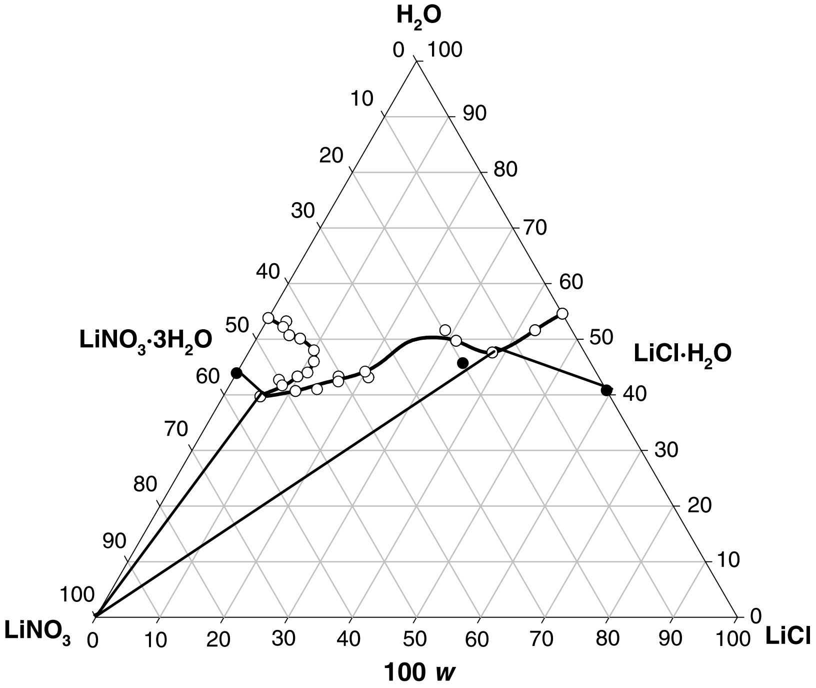

Fig. 1. Solubility isotherm in the $LiNO_3$ – LiCl – H_2O system at 298.15 K (● . . . the figurative point of the phase used in Ref. [1])

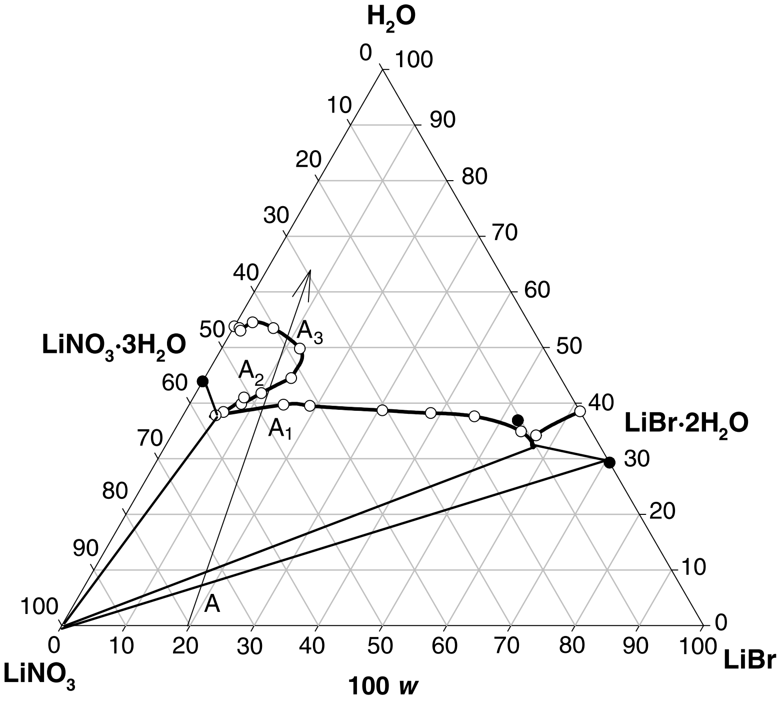

Fig. 2. Solubility isotherm in the $LiNO_3$ – LiBr – H_2O system at 298.15 K (● . . . the figurative point of the phase used in Ref. [2], description of the points see text)

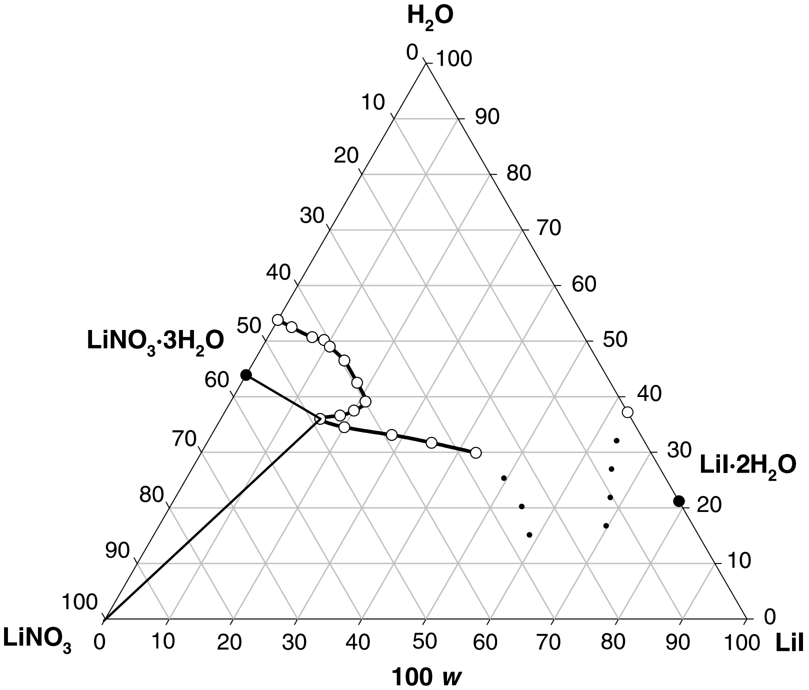

Fig. 3. Solubility isotherm in the $LiNO_3$ – LiI – H_2O system at 298.15 K

point at the solubility branch of anhydrous $LiNO_3$. By this shape of the solubility curve, the system resembles very strikingly the system $LiNO_3$ – $Be(NO_3)_2$ – H_2O at the same temperature [10].

In Figs. 1 and 2, also the phase complexes used in Refs. [1] and [2] are depicted. It is obvious, that in the case of the chloride systems the authors worked on the metastable solubility curve of $LiCl{\cdot}H_2O$, in the bromide system their phase complex was situated close to the transition point belonging to the equilibrium $LiBr{\cdot}2H_2O + LiNO_3$. The former result is in full agreement with our experience, where metastable equilibria were observed frequently especially in the vicinity of transition points and the conditions of equilibration had to be checked carefully to find the real equilibrium. On the other side, a break has been observed in Ref. [1] on the solubility of the system with the $LiCl/LiNO_3 = 4$ ratio when the temperature is elevated. This break was understood as an evidence of a change of solid phase. According to our opinion, the specification of this neighbouring solid phase in Ref. [1] is dubious, anhydrous $LiNO_3$ being the probable equilibrium solid phase appearing at elevated temperature in the respective phase complex.

Furthermore, dihydrate $LiI{\cdot}2H_2O$ (21.2% H_2O calcd, 21.1% H_2O found) was, in contact with its saturated solution, found to be the stable hydrate at 25°C. This is in contrast to the literature which reported the trihydrate as the stable phase in aqueous solution [19].

Experimental

Reagent grade $LiNO_3$ from Lachema Brno was used. Pure $LiCl{\cdot}H_2O$ (Lachema Brno) and $LiI{\cdot}H_2O$ (International Enzyme Limited, Windsor–Berkshire–England) were recrystallized before use, $LiBr{\cdot}2H_2O$ was synthesized of $LiCO_3$ (pure, Lachema Brno) and 50% solution of HBr.

Solubility diagrams were studied using the visually supported method of sections.

15–20 phase complexes were prepared by weighing of $LiNO_3$ and the respective halide hydrate. After that, an exactly weighed amount of water was added (when necessary) so that mixtures of solid and liquid phase appeared and the phase complexes were let to equilibrate. Equilibrium was checked by repeated measurements of the refractive index of the liquid phase. After equilibration which lasted 4–6 days in the case of chloride and bromide systems and 8–11 days in the case of the iodide system, the refractive index of the equilibrium liquid phase was measured: The phase complexes were weighed and another portion of water added. The data obtained by repeating this procedure were treated in an analogous way as described in Ref. [20] using the SPSS Sigma Plot Program (Version 4.1). From the dependences of the refractive indices on the composition of the phase complexes the shape of the phase diagram could be derived as demonstrated earlier [21].

References

[1] Iyoki S, Iwasaki S, Kuriyama Y, Uemura T (1993) J Chem Eng Data **38**: 396
[2] Iyoki S, Yamanaka R, Uemura T (1993) Int J Refrig **16**: 191
[3] Zbranek V, Eysseltova J (2001) Monatsh Chem **132**: 1465
[4] Kurtova LV, Bol'shakova LP, Plyushchev VE (1963) Zh Neorg Khim **8**: 14
[5] Ganina GI, Karnaukhov AS, Lepeshkov IN (1970) Zh Neorg Khim **15**: 2825
[6] Berthet J, Counioux JJ, Floreancing A, Cohen-Adad R (1990) Bull Soc Chim 616
[7] Ganina GI (1983) Mezvuzhnyi Sb Nauchn Trudov, Yarosl Gos Ped Univ **202**: 13
[8] Yakimov MA, Ti C, Filippov VK (1968) Zh Neorg Khim **13**: 1981
[9] Andronova NP (1972) Sbornik Nauchnykh Trudov, Yarosl Gos Ped Univ **103**: 50
[10] Balashova EF, Protsenko PI (1970) Izv Vyssh Ucheb Zaved, Khim Khim Tekhnol **13**: 1109
[11] Khripun MK, Chervonenko KYu, Efimov AYu, Khripun VD, Kiselev AA (2000) Zh Obshch Khim **70**: 217
[12] Pozharskaya SS, Golovanova TG (1972) Zh Neorg Khim **17**: 522
[13] Savenko AS, Andreeva TA (1975) Zh Neorg Khim **20**: 2514
[14] Zbranek V, Eysseltova J (2001) Monatsh Chem **132**: 1465
[15] Karnaukhov AS, Onishchenko MK, Shevchuk VG, Fedorenko TP (1978) Sb Nauch Trudov, Yarosl Gos Ped Univ **169**: 58
[16] Omelyan VI, Storozhenko DA, Shevchuk VG (1988) Zh Neorg Khim **33**: 1882
[17] Shevchuk VG, Dryuchko AG, Bunyakina NV, Kisel' NN (1985) Zh Neorg Khim **30**: 2170
[18] Eysseltova J, Ebert M, Zbranek V (2001) Z Naturforsch **56a**: 865
[19] Hüttig GF, Pohle F(1924) Z anorg allg Chem **138**: 14
[20] Ebert M, Eysseltova J (1971) Chemicke Zvesti **25**: 161
[21] Zhuravlev EF, Sheveleva AD (1960) Zh Neorg Khim **5**: 2630