

STUDY OF THE MUTUAL INFLUENCE OF COMPONENTS IN THE LITHIUM NITRATE–AMMONIUM CHLORIDE–WATER SYSTEM

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Abstract. The visual-polythermal approach was used to investigate the solubility of the $\text{LiNO}_3\text{--NH}_4\text{Cl--H}_2\text{O}$ nitrate system's constituents over a wide range of temperatures and concentrations. Internal incisions were used to study the system, and as a result, the system's polythermal solubility diagram was produced. The phase diagram delimits the crystallization fields of ice, $\text{LiNO}_3\cdot 2\text{H}_2\text{O}$, LiNO_3 , NH_4Cl and the new phase $\text{LiCl}\cdot 3\text{H}_2\text{O}$, NH_4NO_3 . The formation of a new compound was confirmed by the methods of chemical and physicochemical analysis. This system's features and composition are shown. It can provide a scientific foundation for the extraction of lithium compounds from water sources based on the knowledge learned about the solubility of the components in the system under study.

Keywords: solubility, system, concentration, crystallization, temperature.

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1. Introduction

Lithium is a lithophilic element that exists only in the form of compounds in nature. It is found in a variety of rocks, but it is most concentrated in acidic igneous (0.007 wt.%) and sedimentary (0.006 wt.%) rocks. Lithium is also contained in soils, where its concentration varies between $1\cdot 10^{-3}$ - $6.9\cdot 10^{-3}$ mass. %, coal, mineral springs (some sources rich in lithium - Vichy in France, Durkheim in Germany contain up to 0.4 wt.% LiCl), lakes and lake silts, groundwater, in seawater ($1.5\cdot 10^{-5}$ wt. %). Lithium is also found in living organisms and in many plants-seeds of cereals, tobacco leaves (the ashes of some tobaccos contain up to 0.44 wt. % lithium) (Bakhodir *et al.*, 2022; Yu *et al.*, 2023; Wang *et al.*, 2022). The largest deposits of lithium are known in granitic pegmatites of the natrolithium type; lithium in nature is closely associated with sodium (due to the similarity of the energy characteristics of lithium and sodium ions), especially in deposits of residual crystallization. Lithium is also concentrated in hydrothermal formations, which are characterized by a close association of lithium with fluorine to form several lithium fluorine-containing minerals. All endogenous lithium minerals, except micas, easily change under hypergenesis conditions, while lithium is washed out of the minerals

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by water, dispersed, and then adsorbed. These processes determine the third type of lithium deposits - sedimentary. In them, lithium is concentrated mainly in the brine of salt lakes (Weng *et al.*, 2020; Rafael 2021; Abdullah *et al.*, 2022; Yuecheng *et al.*, 2022).

In terms of ionic radius (0.074 nm), lithium is closer not to sodium (0.102 nm), but to magnesium (0.072 nm), iron (0.080 nm) and aluminium (0.054 nm) and plays the role of alkaline earth metals in minerals. The isomorphism of lithium with Mg, Fe (II), less often with Al (the coordination number of lithium in natural compounds is always 6) is a characteristic geochemical feature of lithium. This explains the inclusion of lithium in the composition of many magnesian-ferruginous minerals (biotites, tourmalines, amphiboles), cases of direct replacement of magnesium by lithium are known, and in muscovites, lithium can also replace aluminium without significant changes in their structure (Samadiy & Deng, 2021; Bakhodir *et al.*, 2023).

Lithium has been found in more than 50 minerals, although 28 native lithium minerals are known. Many of them are extremely rare, and their findings are isolated. Most of the lithium minerals are silicates and phosphates (silicates predominate) and only one each is halides, oxides and borates. The most important lithium minerals - spodumene, lepidolite, petalite, zinnwaldite, amblygonite - are mostly found in rare-metal pegmatites containing minerals of other rare elements - pollucite, beryl, zircon, columbite-tantalite. In essence, their deposits are polymetallic (Afandiyeva *et al.*, 2018; Grosjean *et al.*, 2012; Toba *et al.*, 2021). From the end of the 19th century until 1940, the main sources of lithium compounds were lepidolite and amblygonite (50% of world production), zinnwaldite (30%) and spodumene (20%). In subsequent years, five minerals found practical use - spodumene, lepidolite, petalite, amblygonite, and zinnwaldite, especially the first three. The share of these minerals in the world production of lithium raw materials (%), spodumene - 60, lepidolite - 22, petalite - 13, amblygonite - 1.3, zinnwaldite - 0.7. The remaining 3% are deposits of a sedimentary type - lake brine (~0.02% LiCl). However, in recent years, deposits of sedimentary type and underground mineralized waters have become increasingly important. Thus, traditional ore raw materials are being replaced by brines, associated oil waters, and lithium-containing clays, since more than 70% of the explored lithium reserves are concentrated in these sources (Kesler *et al.*, 2012). The small size of the lithium atom and ion and the resulting high surface charge density leads to some noticeable differences in the chemical properties of lithium from other group elements. In many properties, the chemistry of lithium turns out to be closer to that of magnesium (diagonal rule). The polarizing ability of Li^+ , which is the highest among alkali ions, leads to unusually high solvation and the formation of a covalent bond Choubey *et al.*, 2016; Tadesse *et al.*, 2019). Li is the only one of the alkali metals that gives a stable nitride, Li_3N (like Mg). Lithium forms more stable complexes than other alkaline elements, being a complexing agent (for example, $[\text{Li}(\text{NH}_3)_4]^+$) (Ivanov *et al.*, 2022). Lithium nitrate LiNO_3 is an alkali metal salt of lithium and nitric acid. A white substance, highly hygroscopic, which melts without decomposition, decomposes upon further heating. Relative molecular weight 68.95 relative density in solid and liquid state 2.38 g/cm³, melting point 253 °C. Lithium nitrate decomposes at temperatures from 475 °C to 650 °C with the formation of lithium oxide, nitrogen oxide and water: $4\text{LiNO}_3 = 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$ (Wang *et al.*, 2023). Lithium chloride, LiCl, is a colourless substance that crystallizes in an fcc lattice of the NaCl type ($a = 5.1398 \text{ \AA}$), density 2.07 g/cm³, melting point 607 °C, enthalpy of formation 405 kJ/mol. Above 880 °C, LiCl evaporates noticeably. Lithium chloride, unlike NaCl and KCl, is hygroscopic, spreads more strongly in the air than CaCl_2 , and dissolves well in

water. The solubility of LiCl (20°C) is 80.6 g/100 g H₂O, with increasing temperature, the solubility increases. LiCl is isolated from aqueous solutions in the form of crystalline hydrates (Gu *et al.*, 2022; Prakash *et al.*, 2023).

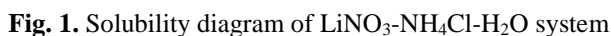
2. Experimental part

Double recrystallized ammonium chloride was used in the work. An identified sample using an X-ray diffractometer (XRD, Lab XRD-6100, Shimadzu Co. 1 td., Japan) indicates that the spectrogram matches the standard product. The purity of the doubly recrystallized lithium nitrate was determined by a chemical method combined with an analytical check on an inductively coupled plasma optical emission spectrometer (ICPOES, Prodigy, Leman Co., USA). The water was freshly ionized distilled water (DDW) using an ultrapure water system (ULUP-11-10T, Ulupur Technologies Co.1 td., China). The study of the LiNO₃-NH₄Cl-H₂O system investigated by a visual-polythermal method, which makes it possible to establish the composition of the formed solid phases in wide concentration and temperature ranges. In this study, the system consisting of LiNO₃-NH₄Cl-H₂O, the visual polythermal approach was used to investigate this.

3. Results and discussion

To develop a polythermal solubility diagram in the LiNO₃-NH₄Cl-H₂O system, binary systems NH₄Cl-H₂O and LiNO₃-H₂O were studied. The binary system NH₄Cl-H₂O was examined in the -19.0 °C to 70.0 °C temperature range, which is characterized by the presence of ice and ammonium chloride crystallization branches at a temperature of -19.0 °C, a concentration of 21.2% NH₄Cl and 78.8% H₂O. The binary system lithium nitrate water was the object of research by several authors. When studying this system, on the solubility diagram, the existence of two crystallization fields was confirmed. The information on the location of the eutectic and the areas where lithium nitrate crystal hydrates exist is in agreement with information from the literature.

Solubility in the LiNO₃-NH₄Cl-H₂O system was studied using five internal cuts. Sections 1 and 2 are drawn from the top of LiNO₃ to the side NH₄Cl-H₂O, and 3, 4 and 5 from the top of NH₄Cl to the side LiNO₃-H₂O. Based on the data of binary systems and In the temperature range of -30.0 °C to 35.0 °C, a full polythermal diagram of the LiNO₃-NH₄Cl-H₂O system was constructed and solubility isotherms were plotted at temperatures of -20, -10, 0, 10, 20, 30 °C (Fig. 1). The diagram of polythermal solubility, the crystallization fields of ice, LiNO₃·2H₂O, LiNO₃, NH₄Cl and new phases LiCl·3H₂O and NH₄NO₃ are demarcated. The initial components of lithium nitrate dehydrate, lithium nitrate and ammonium chloride obtained in the phase diagram and the isolated two new phases LiCl·3H₂O and NH₄NO₃ were identified by classical methods of chemical analysis, which are widely used for the analysis of salt compounds (Ouyang *et al.*, 2011, Luo *et al.*, 2013). These fields converge at four triple nodal points, wherein the equilibrium solution compositions and related crystallization temperatures are calculated (Table 1). The nodal point at -23.0 °C corresponds to the composition of 8.1% LiNO₃ and 23.4% NH₄Cl, the second at -27.0 °C contains 11.8% LiNO₃ and 14.8% NH₄Cl, the third corresponds to a temperature of -30 °C and 24.8% LiNO₃ and 7.9% NH₄Cl, the fourth at 23.0 °C corresponds to 33.2% LiNO₃ and 11.2% NH₄Cl.



New phases were isolated in crystalline form and identified by chemical methods of analysis.

Table 1. Double and triple nodal points of the $\text{LiNO}_3\text{-NH}_4\text{Cl-H}_2\text{O}$ system

Liquid phase, %			Crystallization temperature °C	Solid phase
LiNO ₃	NH ₄ Cl	H ₂ O		
26.0	-	74.0	-24.0	Ice+LiNO ₃ ·2H ₂ O
52.0	-	48.0	30.0	LiNO ₃ ·3H ₂ O
24.8	7.9	74.3	-30.0	Ice+LiNO ₃ ·2H ₂ O+LiCl·3H ₂ O
25.8	8.2	66.0	-22.2	LiNO ₃ ·2H ₂ O+LiCl·3H ₂ O
30.4	9.8	59.8	1.0	Same
32.6	10.8	56.6	12.0	-/-
33.2	11.2	55.6	23.0	LiNO ₃ ·2H ₂ O+LiCl·3H ₂ O+LiNO ₃
35.0	12.8	52.2	25.0	LiNO ₃ +LiCl·3H ₂ O
37.4	14.2	48.4	28.0	Same
38.0	14.8	47.2	29.0	-/-
40.2	16.4	43.4	35.0	-/-
46.8	3.5	49.7	28.5	LiNO ₃ +LiNO ₃ ·2H ₂ O
50.0	1.5	48.5	29.4	-/-
11.8	14.8	73.4	-27.0	Ice+LiCl·3H ₂ O+NH ₄ NO ₃
13.8	15.4	70.8	-23.5	LiCl·3H ₂ O+NH ₄ NO ₃

14.8	13.6	71.6	-22.0	Same
21.5	16.7	61.8	-19.0	-//-
24.0	18.0	58.0	-16.0	-//-
26.4	20.0	53.6	-11.0	-//-
27.8	21.4	50.8	-8.0	-//-
29.2	24.4	46.4	-3.2	-//-
30.8	29.0	40.2	3.0	-//-
10.8	16.4	72.8	-26.0	Ice+ NH_4NO_3
8.1	23.7	68.2	-23.0	Ice+ NH_4NO_3 + NH_4Cl
7.5	28.0	64.5	-18.0	NH_4NO_3 + NH_4Cl
5.5	36.5	58.0	8.0	Same

Where equilibrium solution compositions and crystallization temperatures are computed (Table 1) with the following results (wt %): Li-7.38; Cl-36.39 and NH_4NO_3 $N_{\text{am.}}$ - 17.32 and $N_{\text{nit.}}$ -17.32, which corresponds to their composition in LiCl and NH_4NO_3 compounds.

4. Conclusion

The solubility of components in the LiNO_3 - NH_4Cl - H_2O . The visual-polythermal method was used to investigate the system from the temperature of complete freezing -30 °C to 35 °C. The fields of crystallization of the starting components are depicted on the phase diagram such as lithium nitrate dehydrate, lithium nitrate, and ammonium chloride and two new phases $\text{LiCl}\cdot 3\text{H}_2\text{O}$ and NH_4NO_3 are distinguished whose uniqueness is proved by chemical analysis. The results obtained indicate the occurrence of an exchange reaction between the components and the formation of a sparingly soluble LiCl salt.

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