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ФАЗОВЫЕ РАВНОВЕСИЯ, РАСТВОРИМОСТЬ И ЭКСТРАКТИВНАЯ КРИСТАЛЛИЗАЦИЯ СОЛИ В ТРОЙНОЙ СИСТЕМЕ СУЛЬФАТ ЛИТИЯ–ВОДА–ТРИЭТИЛАМИН В ИНТЕРВАЛЕ 15–90 °С

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Фазовые равновесия, растворимость, экстрактивная кристаллизация сульфата лития и эффект высаливания триэтиламина были изучены визуально-политермическим методом в смесях компонентов тройной системы сульфат лития – вода – триэтиамин в интервале 15–90 °С. Политермы фазовых состояний были построены по семи сечениям треугольника состава. В смесях компонентов были обнаружены следующие фазовые состояния: гомогенные и насыщенные растворы, монотектика и расслоение. Растворимость компонентов была определена при четырех температурах и изотермические фазовые диаграммы построены при 15,0, 25,0, 50,0 и 90,0 °С. Топологическая трансформация фазовой диаграммы изученной системы с изменением температуры характерна для тройных систем с высаливанием двойной жидкостной системы с образованием солью-высаливателем кристаллогидратов. Было установлено, что твердая фаза моногидрата сульфата лития находится в равновесии с двумя жидкими фазами. Составы равновесных органической и водной фаз монотектического состояния были установлены графически. Высаливающий эффект кристаллогидрата соли на водно-аминовые смеси усиливается с ростом температуры. Коэффициент распределения триэтиламина между жидкими фазами монотектического состояния, рассчитанный при пяти температурах, достигает своего максимального значения (997) при 90 °С. На основе анализа изотермических фазовых диаграмм был графически оценен выход кристаллов моногидрата сульфата лития в диапазоне от 15 до 50 °С. Обнаружено, что в этом диапазоне увеличение температуры и концентрации вводимого триэтиламина в водно-солевой раствор приводит к увеличению выхода кристаллов. Максимальный выход кристаллогидрата соли (56,8%) приходится на 90 мас.% введенного амина при 50 °С. Рентгенофлуоресцентный анализ показал, что в полученном после экстрактивной кристаллизации образце соли значительно снижено содержание соединений хлора, калия, фосфора, кальция и алюминия.

Ключевые слова: фазовые равновесия, растворимость, фазовая диаграмма, экстрактивная кристаллизация, высаливание, монотектика, триэтиламин, сульфат лития

PHASE EQUILIBRIA, SOLUBILITY, AND EXTRACTIVE CRYSTALLIZATION OF SALT IN THE TERNARY SYSTEM LITHIUM SULFATE – WATER – TRIETHYLAMINE IN THE RANGE OF 15–90 °C

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Phase equilibria, solubility, extractive crystallization of lithium sulfate, and the salting-out effect of triethylamine were studied by the visual-polythermal method in mixtures of the components of the ternary lithium sulfate – water – triethylamine system within the temperature range of 15–90°C. Phase state polytherms were constructed for seven sections of the composition triangle. The following phase states were identified in the component mixtures: homogeneous and saturated solutions, a monotectic, and liquid-liquid phase separation. The solubility of the components was determined at four temperatures, and isothermal phase diagrams were constructed at 15.0, 25.0, 50.0, and 90.0 °C. The topological transformation of the phase diagram of the studied system with temperature change is characteristic of ternary systems exhibiting salting-out of a binary liquid system without the formation of salt hydrates by the salting-out agent. It was established that the solid phase with lithium sulfate monohydrate is in equilibrium with two liquid phases. The compositions of the equilibrium organic and aqueous phases of the monotectic state were determined graphically. The salting-out effect of the salt crystal hydrate on water-amine mixtures intensifies with increasing temperature. The distribution coefficient of triethylamine between the liquid phases of the monotectic state, calculated at five temperatures, reaches its maximum value (997) at 90°C. Based on the analysis of the isothermal phase diagrams, the yield of lithium sulfate monohydrate crystals was graphically estimated in the range from 15 to 50°C. It was found that within this range, an increase in temperature and the concentration of introduced triethylamine in the aqueous salt solution leads to an increase in crystal yield. The maximum yield of the salt hydrate (56.8%) corresponds to 90 wt.% of introduced amine at 50°C. X-ray fluorescence analysis showed that the content of chlorine, potassium, phosphorus, calcium, and aluminum compounds is significantly reduced in the salt sample obtained after extractive crystallization.

Keywords: phase equilibria, solubility, phase diagram, extractive crystallization, salting, monotectic, triethylamine, lithium sulfate

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INTRODUCTION

As a typical lithophilic element, lithium predominantly concentrates in geochemical systems enriched with sodium, particularly in granite pegmatites, saline brines, and within rock-forming silicate minerals. The primary industrial deposit types are rare-metal granite pegmatites (containing minerals such as spodumene, lepidolite, etc., accounting for 25% of global reserves) and salt lake brines (75% of reserves). The largest of these are located in Australia, Chile, Argentina, Bolivia and China [1]. In Russia, promising sources of deep-seated chloride brines of various types are known. They are represented by deep-seated formation brines and mineralized waters, concentrated primarily in the North Caucasus and Siberian regions, as well as brines of the East Ciscaucasian artesian basin, within which oil and gas extraction enterprises operate, located in the Stavropol Krai and Dagestan [2].

Known methods for processing natural brines (lithium content 0.32-1.7 g/L) typically share a common initial stage – their concentration. The latter is achieved through solar evaporation. For instance, the lithium concentration in the underground brines of the Atacama Desert increases in evaporation ponds from 0.2 to 4.3 wt.%. The extraction of lithium from the concentrated brine can be accomplished by various methods [3-30].

Currently, a technology for the selective sorption extraction of lithium from chloride-calcium type brines has been developed. This technology employs a granular sorbent based on defective forms of $LiCl{\cdot}2Al(OH)_3{\cdot}mH_2O$ (DGAL-Cl), enabling the production of lithium chloride solutions (lithium-selective sorption eluates) as the primary product. These eluates contain approximately 10 g/L of lithium chloride and up to 1 g/L of impurity chlorides of magnesium and calcium [2, 3].

Numerous studies [4-10] have demonstrated that inorganic crystalline solids, including various aluminum hydroxide $Al(OH)_3$ compounds, aluminum oxides (AlO_x), manganese oxides (MnO_x), and titanium oxides (TiO_x), are selective lithium sorbents.

Study [10] investigated the possibility of selectively extracting lithium ions from aqueous solutions using composite porous membranes. The membranes were prepared by phase inversion based on polyvinylidene fluoride (PVDF) with a filler – partially protonated potassium polytitanate ($K_{1.3}H_{0.7}Ti_{4.1}O_9$). The membranes exhibited high selectivity towards Li^+ ions in the presence of competing cations Na^+ and K^+. The separation factor (α) for the Li^+/Na^+ pair was 16.4, and for Li^+/K^+ – 11.6. The selectivity is attributed to the structural features of the polytitanate, specifically its variable interlayer distance, which is more accessible to lithium ions due to their smaller ionic radius.

Lithium can also be extracted from brine via chemical precipitation reactions [11], using sodium aluminate as the precipitating agent, which proves more effective than aluminum chloride in an alkaline medium (pH 10-13). Maximum lithium recovery (~99%) is achieved at pH 11.5 using high-purity $NaAlO_2$ and after preliminary removal of calcium and silica from the solution. However, lithium recovered by precipitation requires thorough purification and subsequent processing to meet the standards for lithium battery production or other applications.

Solvent extraction is a well-established technology for the recovery of metals from aqueous solutions. It has been demonstrated that solvent extraction methods can be used for the quantitative and selective recovery of lithium from aqueous solutions. Extraction methods for lithium recovery from saline solutions employ the following as solvents:

1. crown ethers [12, 13];
2. multicomponent systems consisting of an extractant, a synergistic co-extractant, and a diluent [14-19];
3. ionic liquids [20-23].

Particular attention in the processes of recovering high-purity lithium salts from process solutions is deserved by extractive crystallization. The essence of the method lies in introducing an organic anti-solvent into the aqueous salt solution, which sharply reduces its solubility and causes precipitation. The most important advantages of this method include lower energy consumption compared to evaporation, effectiveness for salts with a negative temperature coefficient of solubility (e.g., lithium carbonate and sulfate), and the combination of the crystallization process with purification from impurities [24-30]. However, its implementation is rarely based on established physicochemical patterns, which leads to erroneous conclusions regarding the choice of process conditions.

The authors of study [30] investigated four ternary systems lithium sulfate (formate) – water – diisopropylamine (triethylamine) to assess the practicability of using these amines in the extractive crystallization process of the salts. A temperature of 20 °C was chosen for the regeneration of the amines. The salt crystallization process in the lithium sulfate – water – triethylamine system was conducted at a temperature of 2 °C, while a range from –5 to 1 °C was proposed for the system with diisopropylamine. For the two ternary systems lithium formate – water – triethylamine (diisopropylamine), a crystallization temperature of 1 °C was selected. It was concluded that both triethylamine and diisopropylamine are promising anti-solvents. However, for producing lithium sulfate and formate, the use of triethylamine is more advantageous, as its content in the organic phase is higher than that of diisopropylamine, while the content of both amines in the aqueous phase is practically the same.

In our laboratory, the influence of triethylamine [29, 30] on the phase behavior of the binary water – lithium chloride system was previously studied using the visual-polythermal method in the range of 20.0-90.0 °C. Isothermal phase diagrams for several temperatures were constructed, and the distribution coefficients of the amine between the equilibrium liquid phases of the monotectic state were calculated. An assessment of the efficiency of using triethylamine in the extractive crystallization of lithium chloride monohydrate was performed. It was established that the maximum yield of the salt hydrate (39.6%) is observed at 70 wt.% triethylamine and 20 °C. The high amine content in the organic phase (93.2 wt.%) is favorable for its regeneration. X-ray fluorescence analysis was conducted to assess the degree of purification of the obtained salt. It showed a reduction in impurities of bromine, iodine, and a number of other element compounds after extractive crystallization.

Thus, there are few works in the literature that establish the conditions (concentration of the anti-solvent and salt in the solution, process temperature) and determine the purity degree of the precipitated crystals in the case of lithium salts via the extractive crystallization method. The present work is devoted to studying phase equilibria and determining the solubility of components in the ternary lithium sulfate – water – triethylamine system within the range of 15-90 °C in order is to find the optimal conditions (concentration of the in

troduced anti-solvent and process temperature) for the extractive crystallization of the salt from aqueous solutions under the influence of triethylamine and to establish the possibility of their purification from impurities. Additionally, it was intended to reveal the salting-out effect of lithium sulfate in the binary water – triethylamine system for the successful regeneration of the amine used.

EXPERIMENTAL

Materials

All the reagents used in this work were purified and dried. The deionized water of high purity (specific electrical resistance 18.0 MΩ × cm at 298.15 K) was gotten using a "Spectrum OSMOS" water treatment system [31]. A TEA sample (analytical grade, Vekton, Russian Federation) was dried over KOH within 72 h, and the filtrate was then distilled on a fir reflux device exchanger (a 50 cm height) and the fraction characterized by a boiling point from 89.9 to 90.3 °C [32] was isolated**.** The content of the main substance in the sample was determined by gas–liquid chromatography (a Finnigan chromato-mass spectrometer, a Trace DSQ model). The purified TEA was stored over 4 Å molecular sieves. Lithium sulfate monohydrate was prepared by recrystallization and drying of a commercial salt sample. The crystals were dried in an oven at 70 °C to constant weight over 5 days. The resulting salt sample contained no anhydrous crystals, as confirmed by X-ray diffraction analysis (Fig. 1). The obtained preparations of the salt and TEA were stored in a dry atmosphere. The chemical substances used in our research are described in Table 1.

Table 1

Information of the substances

***Таблица 1*. Информация о веществах**

Chemical name (CAS)	Source	Initial purity (mass fraction)	Method of purification	Final purity (mass fraction)	Method of analysis
lithium sulfate monohydrate (10102-25-7)	Novosibirsk Rare Metals Plant	>0.990[a]	recrystallization and drying	>0.995	XRD[b]
water high-purity deionized (7732-18-5)	Self-made		none		
triethylamine (121-44-8)	Vekton	0.990[a]	distillation	0.998	GC[c]

Notes: a The purity of all substances was provided by the suppliers;
b X-ray diffraction analysis (Fig. 1). c Gas–liquid chromatography
Примечания: a) Чистота всех веществ была обеспечена поставщиками; b) Рентгенофазовый анализ (рис. 1); c) Газожидкостная хроматография

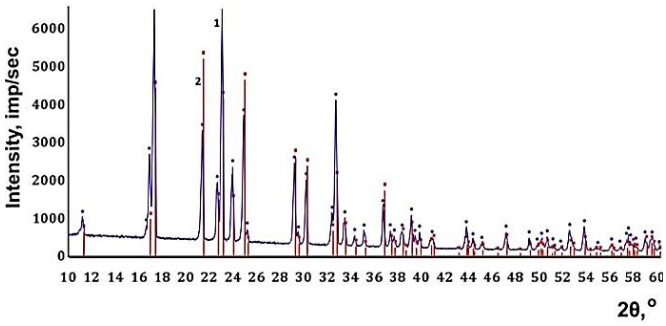

Fig. 1. Comparison of the diffraction pattern of the $Li_2SO_4 \cdot H_2O$ sample (blue curve, strokes and markers, designated 1) with the bar diffraction pattern of the $Li_2SO_4 \cdot H_2O$ phase (PDF Card # 01-078-0955, red strokes and markers, designated 2)

Рис. 1. Сравнение дифрактограммы образца $Li_2SO_4 \cdot H_2O$ (синяя кривая штрихи и маркеры, обозначена 1) со штрих-дифрактограммой фазы $Li_2SO_4 \cdot H_2O$ (PDF-карточка № 01-078-0955, красные штрихи и маркеры, обозначены 2)

Apparatus and Procedure

Phase behavior in various mixtures of the three-component system Li_2SO_4 + H_2O + TEA were studied by the visual polythermal method [33] within a range of 15-90 °C. Several mixtures of the three components were made by weighing on an analytical balance AND HR-250AZG (an accuracy of $\pm 1 \cdot 10^{-4}$ g) in 6 mL thermostable glass ampoules for their compositions to be changed in few selected sections of the concentration triangle. Lithium sulfate monohydrate does not have high hygroscopicity, so work with it can be carried out in air. The ampoules were sealed and placed into a U-10 ultrathermostat. Heating and cooling of the mixtures were conducted at a low rate (about 0.5 °/min) near the temperatures of phase transitions. Distilled water was used as a hear carrier.

Each value of the phase transition temperature in the case of LLE, LSE, and LLSE was an average of several repeated measurements and characterized by an accuracy of ±0.1 °C. The phase transition temperatures in the case of LLE was determined by sequential heating and cooling of each mixture with constant stirring in the ampoule, visually noting the disappearance or formation of a second liquid phase. Phase transition temperatures for LSE and LLSE were determined by

slowly cooling the ampoules with constant stirring, visually noting the disappearance of the last crystal (the solid phase in the studied system was characterized by a negative temperature coefficient of solubility). The ampoules containing these mixtures were then heated to precipitate the crystals, and this experiment was repeated until the results agreed within ±0.1 °C. Reproducibility of the phase transition temperature results served as an indicator of equilibrium in heterogeneous mixtures. For LLE, the equilibrium time was 1 h, and for LSE and LLSE, 3 h. The experimental procedure was delineated in detail previously [31, 33, 34].

Based on the experimental results, polytherms of phase states as the dependences of the temperatures of phase transitions on the content of $Li_2SO_4 \cdot H_2O$ or TEA in the studied ternary mixtures were drawn for all sections of concentration triangle. Polythermal data of sections were used to determine the compositions of mixtures relating to the points of phase transitions at selected temperatures by graphical interpolation. The phase diagrams of studied three-component system were then drawn at several temperatures.

To assess the correctness of our results of analyzing the compositions of the equilibrium liquid phases of the monotectic state by the graphical method, the liquid phases of the component mixtures of the ternary system under study were analyzed at temperatures of 15.0 and 25.0 °C for the TEA content using gas chromatography with mass-selective detection (GC-MS) (Finnigan Trace GC-DSQ chromatograph mass spectrometer). Analysis conditions: mobile phase: helium (purity 99.995%, flow rate 1.0 ml/min); chromatographic column brand: Restek Stabilwax capillary column (polyethylene glycol was the highly polar phase), length 30 m, internal diameter 0.25 mm, phase thickness on the inner walls of the column 0.25 μm. The analysis time was 15.2 min; temperature program: thermostatting at 70 °C for 5 min, then heating at a rate of 15 °C/min down to 180 °C and thermostatting for 5 min. Injector temperature 250 °C, ion source temperature 200 °C. Scanning was performed in the range of 45-150 amu (Full Scan); electron energy was 70 eV; Splitless mode (without flow division), sample heating time in the injector was 1 min. MS Transfer Line 240 °C. Filament (cathode, electron source) switch-on time was 4.00 min after sample injection. Volume of chromatographed aliquot was 2.0 μl. Mass spectral libraries used: NIST library, 2011, Wiley. Recognition of the detected compounds was performed by comparing the mass spectra obtained with the corresponding mass spectra from the libraries.

The correctness of the results of determining the yield of salt crystallohydrate by the extractive crystallization method, obtained graphically, was checked by gravimetric analysis. To do this, few component mixtures with the presence of a solid phase and various TEA contents were prepared and kept in a thermostat with continuous stirring at a given temperature for two hours. The solid phase of each mixture was then filtered off at the same temperature. The precipitates of $Li_2SO_4 \cdot H_2O$ were dried and weighed. The difference between the calculated and experimental results did not exceed 2%. The chemical composition of the $Li_2SO_4 \cdot H_2O$ samples obtained was found by X-ray fluorescence analysis for fundamental parameters using an EDX-720 energy dispersive analyzer (manufacturer SHIMADZU, Japan). An X-ray tube with a Rh anode (voltage 50 kV, current 100 μA) was used to excite the spectrum.

EXPERIMENTAL

Polythermal Studies of Phase Equilibria

The compositions of the ternary mixtures changed in seven sections of the concentration triangle. The component mixtures in sections I – V had variable contents of Li_2SO_4 and constant TEA and H_2O mass ratios: 10:90 (I), 20:80 (II), 35:65 (III), 50:50 (IV), 65:35 (V). In sections VI and VII the mixtures of the components were characterized by variable TEA concentrations and constant mass ratios of Li_2SO_4 and H_2O: 13:87 (VI) and 28:72 (VII).

The polytherms of phase states in sections I–V are similar to each other. Each of them represents two smooth lines (for example, Fig. 2a, the polytherm in section II) separating the regions of delamination $\ell_1 + \ell_2$ (respectively, ℓ_1 and ℓ_2 denote the organic and aqueous phases) from the fields of the homogeneous state ℓ and monotectic $\ell_1 + \ell_2 + S_1$ (S_1 denotes the solid state $Li_2SO_4 \cdot H_2O$). On the polytherm of section VI (Fig. 2b) a smooth line separates the fields of homogeneous solutions ℓ and delamination $\ell_1+\ell_2$ from each other. Two smooth lines on the polytherm of section VII (Fig. 2c) separate the field of monotectic $\ell_1 + \ell_2 + S_1$ from two fields of saturated solutions $\ell_1 + S_1$ and $\ell_2 + S_1$. These polytherms, as well as the polytherms of sections I-V, were used to determine the position of the triangle of the monotectic state on the composition triangle at different temperatures.

Isothermal Phase Diagrams

The obtained polythermal data on sections I-VII were used to determine graphically the compositions of mixtures relative to points of all phase transitions at the temperatures selected by us and to plot phase diagrams. The results of the component solubility (in mass fractions) in three-component Li_2SO_4 + H_2O + TEA system are presented in Table 2.

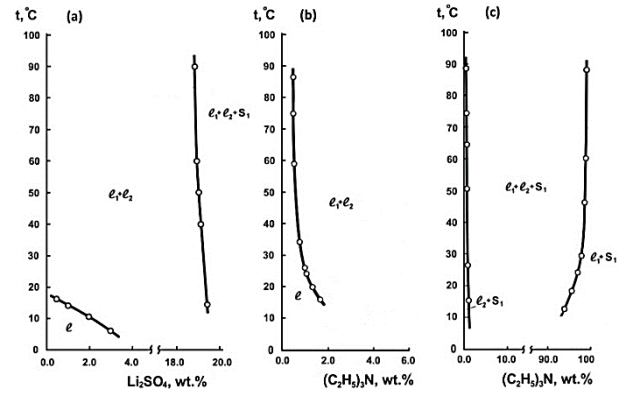

Fig. 2. Polytherms of phase states in sections II (a, 20.00 wt.% TEA), VI (b, 13.00 wt.% Li_2SO_4) and VII (c, 28.00 wt.% Li_2SO_4) of the composition triangle of the lithium sulfate – water – triethylamine system.

Рис.2. Политермы фазовых состояний по сечениях II (a, 20,00 мас.% ТЭА), VI (b, 13,00 мас.% Li_2SO_4) и VII (c, 28,00 мас.% Li_2SO_4) концентрационного треугольника тройной системы сульфат лития–вода–триэтиламин

Table 2

Solubility of the components of the ternary lithium sulfate – water – triethylamine system, wt.%

***Таблица 2*. Растворимость компонентов тройной системы сульфат лития – вода–триэтиламин, мас.%**

t, °C	Saturated solution composition		
	Li_2SO_4	H_2O	TEA
15.0	26.1	73.9	0
	12.8	85.6	1.6
	1.9	88.3	9.8
	0.8	79.4	19.8
	0.7 [a]	67.6 [a]	31.7 [a]
	0.6	64.6	34.8
	0.2	49.9	49.9
	0.1	64.9	35.0
25.0	25.8	74.2	0.0
	12.9	86.1	1.0
	0.0	93.1	6.9
	0.0	10.0	90.0
50.0	25.0	75.0	0.0
	12.9	86.5	0.6
	0.0	97.0	3.0
	0.0	3.5	96.5
90.0	23.7	76.3	0.0
	12.9	86.6	0.5
	0.0	99.6	0.4
	0.0	1.0	99.0

Notes: [a] Composition corresponding to the critical point of liquid–liquid equilibrium

Примечания: [a] Состав, соответствующий критической точке жидкостно-жидкостного равновесия

The solubility of the components of the ternary system changes insignificantly with temperature (Table 2). To follow the topological transformation of the phase diagram of the ternary system with increasing temperature, it was sufficient to plot three isothermal phase diagrams at 15.0, 25.0, 50.0, and 90.0 °C (Fig. 3). As we have determined no solubility of Li_2SO_4 in H_2O in the temperature range studied, the solubilities of this salt in water at the specified temperatures were extracted from Handbook [35].

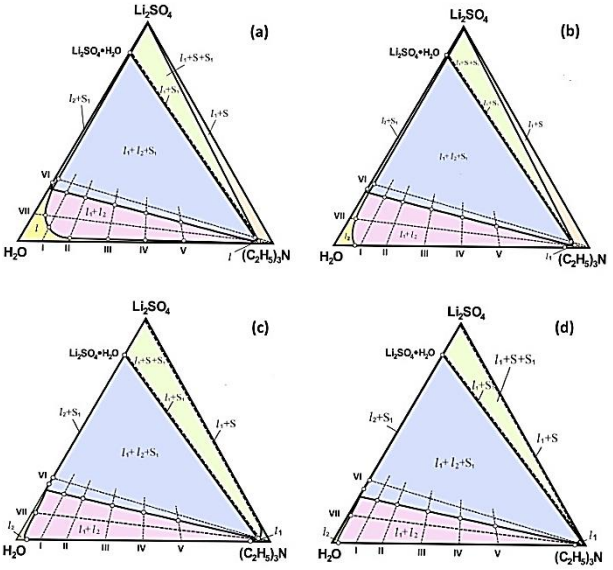

Fig. 3. Isothermal phase diagrams (wt.%) of the lithium sulfate – water – triethylamine system at 15.0 (a), 25.0 (b), 50.0 (c), and 90.0 °C (d). The thick solid and dotted lines separate fields of phase states; the thin dotted lines indicate the position of sections I–VII in the composition triangle; S – Li_2SO_4, S_1 – $Li_2SO_4·H_2O$

Рис. 3. Изотермические фазовые диаграммы (мас. %) системы сульфат лития – вода – триэтиламин при 15.0 (a), 25,0 (b), 50,0 (c) и 90,0 °C (d). Толстые сплошные и пунктирные линии разделяют области фазовых состояний; тонкие пунктирные линии указывают положение сечений I–VII в треугольнике состава; S – Li_2SO_4, S_1 – $Li_2SO_4·H_2O$

Li_2SO_4 is known to form a crystal hydrate $Li_2SO_4·H_2O$ over a wide temperature range from –22.9 to 233 °C [36]. Therefore, the solid phase of the monotectic state S_1 will correspond to this compound over the entire temperature range studied, and the phase diagram of the system is significantly complicated by additional crystallization fields of two solid phases compared to ternary systems with salting-out without the formation of crystal hydrates by the salt is the salting-out agent [30, 37].

At all temperatures in the phase diagram of the ternary system (Fig. 3), the sides of the monotectic triangle $\ell_1 + \ell_2 + S_1$ are adjacent to the crystal hydrate crystallization fields $\ell_1 + S_1$, $\ell_2 + S_1$ and the stratification field $\ell_1 + \ell_2$. The stratification field at temperatures below the LCST of the water – TEA binary system (18.3 °C [38]), as for example in the isotherm at 15.0 °C (Fig. 3a), does not touch the H_2O + TEA side of the composition triangle. The critical point K of the

delamination region is located on the binodal curve. At temperatures higher than the LCST of the binary liquid system, in the isothermal diagrams at 25.0, 50.0, and 90.0 °C (Fig. 3b-3d), the delamination field extends to the H_2O + TEA side of the composition triangle. With increasing temperature, the sizes of all fields change insignificantly due to a decrease in the solubility of the salt. However, with increasing temperature, the stratification field $\ell_1 + \ell_2$ increases slightly, while the dimensions of the monotectic triangle $\ell_1 + \ell_2 + S_1$ and the fields of homogeneous solutions ℓ_1 and ℓ_2 decrease due to the decreased solubility of the components in the binary liquid system.

The concentration triangle also contains a triangular field of a three-phase peritectic state of two solid phases S and S_1 with one liquid phase ℓ_1 (Fig. 3a-3d). Two crystallization regions adjoin the peritectic triangle $\ell_1 + S + S_1$ in the phase diagrams: the anhydrous salt $\ell_1 + S$ and its monohydrate $\ell_1 + S_1$. It was found that the crystallization regions $\ell_1 + S$ and $\ell_1 + S_1$ are very small. Their exact boundaries could not be determined quantitatively, so they are indicated by thick dotted lines in the diagrams at all temperatures.

Distribution coefficients of TEA

Using polythermal data, triangles of the monotectic state were plotted on the concentration triangle at five temperatures, and the liquid phase compositions of the monotectics were evaluated graphically (Table 3). The organic phase was significantly enriched in TEA, while its content in the aqueous phase was very low at all temperatures in the studied range.

To assess the accuracy of our graphical determination of the equilibrium liquid phase compositions of the monotectic state, they were analyzed for TEA content. Phases were collected at temperatures of 15.0 and 25.0 °C and analyzed by gas chromatography with mass-selective detection (GC-MS). It was found that the data obtained by the graphical method (Table 3) coincide with the GC-MS results within the error limits: the amine content at the indicated temperatures in the aqueous phase was 0.9 wt.%, and in the organic phase it was 95.3 wt.% (15.0 °C) and 95.6 wt.% (25.0 °C).

The salting-out effect of triethylamine from its aqueous solutions can be quantified by analyzing the compositions of the equilibrium liquid phases of monotectic state. For this, the distribution coefficient of triethylamine over these phases is calculated using the formula:

$$K_d = \frac{C_{TEA}(\ell_1)}{C_{TEA}(\ell_2)}, \quad (1)$$

where $C_{TEA}(\ell_1)$ is the content of triethylamine in the organic phase (wt.%), $C_{TEA}(\ell_2)$ the content of triethylamine in the aqueous phase (wt.%).

The coefficients of triethylamine distribution between liquid phases of monotectic state (Table 3) were calculated by Eq. (1).

Table 3

Compositions of the liquid phases of the monotectic state and the trimethylamine distribution coefficients K_d in the ternary lithium sulfate (1) – water (2) – trimethylamine (3) system

***Таблица 3.* Составы жидких фаз монотектического состояния и коэффициенты распределения триэтиламина K_p в тройной системе сульфат лития (1) – вода (2) – триэтиламин (3)**

t, °C	Compositions of the liquid phases in equilibrium with solid $Li_2SO_4 \cdot H_2O$, wt.%						Distribution coefficient, K_d
	Aqueous phase			Organic phase			
	(1)	(2)	(3)	(1)	(2)	(3)	
15.0	23.0	76.0	1.0	0.3	4.0	95.2	95
25.0	23.0	76.2	0.8	0.3	4.5	95.7	120
50.0	22.4	76.9	0.7	0.1	0.7	99.2	142
70.0	21.4	78.2	0.4	0.1	0.3	99.6	249
90.0	20.5	79.4	0.1	0.1	0.2	99.7	997

The enhanced salting-out effect of lithium sulfate on a mixture of water and triethylamine with increasing temperature is reflected in a significant increase in the triethylamine content in the organic phase of the monotectic state and an increase in the distribution coefficient. The increase in K_d with temperature can be explained by the weakening of intermolecular interactions between the components in the water-triethylamine binary system due to the breakdown of hydrogen bonds in triethylamine hydrates, which is compensated for by a decrease in the salt concentration in the aqueous phase of the monotectic state due to the negative temperature coefficient of lithium sulfate solubility in water. The maximum K_d value is achieved at the highest temperature in the studied range (90.0 °C).

Extractive crystallization of lithium sulfate monohydrate and assessment of the possibility of its purification from impurities

To assess the efficiency of lithium sulfate monohydrate extractive crystallization under the action of TEA at four temperatures in the range from 15.0 to 50.0 °C in the studied three-component system, we estimated the mass of the solid phase $Li_2SO_4 \cdot H_2O$ in equilibrium with two liquid phases of the monotectics, using the triangle gravity center rule. The calculation was carried out using a prepared working document of the MathCAD software for a saturated aqueous solution with a given Li_2SO_4 concentration (25.00 wt.%). The yield of $Li_2SO_4 \cdot H_2O$ crystals was calculated as the ratio of the mass of crystals precipitated during extrac-

tive crystallization to the mass of salt present in the initial solution (Table 4).

It was found that at any temperature in the specified range, increasing the concentration of TEA added to the aqueous salt solution resulted in an increased yield of $Li_2SO_4 \cdot H_2O$ crystals. The maximum yield of lithium sulfate monohydrate was achieved at a TEA concentration of 90 wt.%. At the same time, increasing the temperature at the same amine concentrations resulted in an increased crystal yield, which can be explained by the negative temperature coefficient of salt solubility in water and aqueous amine solutions.

The obtained data were visualized using Wolfram Mathematica 14.1 software (Fig. 4). A three-dimensional surface was constructed to describe the dependence of the $Li_2SO_4 \cdot H_2O$ yield on the TEA content and temperature. Based on an analysis of the obtained results, it was concluded that the best yield of lithium sulfate monohydrate crystals (55.9-56.8%) was observed in the range of 30-50 °C with the addition of 90 wt.% TEA (Table 4). The high TEA content in the monotectic organic phase (95-99 wt.%, Table 3) under these conditions facilitates its better regeneration. Increasing the temperature to 50 °C leads to an increase in the crystal yield of only about 1%, therefore, a temperature of 30 °C can be considered technologically more advantageous.

Table 4

Yields of lithium sulfate monohydrate crystals as dependent on the amount of triethylamine added to water–salt solution (25.00 wt.% Li_2SO_4) at various temperatures

Таблица 4. **Выход кристаллов моногидрата сульфата лития в зависимости от количества триэтиламина, добавленного к водно-солевому раствору (25,00 мас.% Li_2SO_4) при различных температурах**

t, °C	$Li_2SO_4 \cdot H_2O$ crystals yield (%) at triethylamine concentration (wt.%)								
	10	20	30	40	50	60	70	80	90
15.0	7.2	8.0	9.5	10.1	10.7	13.1	16.8	24.1	44.8
25.0	9.6	11.2	11.4	12.5	13.4	16.4	21.0	25.2	50.0
30.0	10.9	11.3	13.2	14.5	15.9	18.0	25.2	25.8	55.9
50.0	13.6	14.4	15.1	15.7	16.0	19.6	25.3	30.1	56.8

Samples of the initial lithium sulfate monohydrate crystals, as well as samples obtained after extractive crystallization, were subjected to qualitative X-ray fluorescence analysis for impurities. The results of this analysis for both samples are presented in Table 5. It was found that the salt sample obtained after extractive crystallization exhibited significantly reduced levels of chlorine and potassium compounds and, to a lesser extent, phosphorus, calcium, and aluminum compounds. The sulfur content increased due to the increase in the content of the main substance in the sample after extractive crystallization.

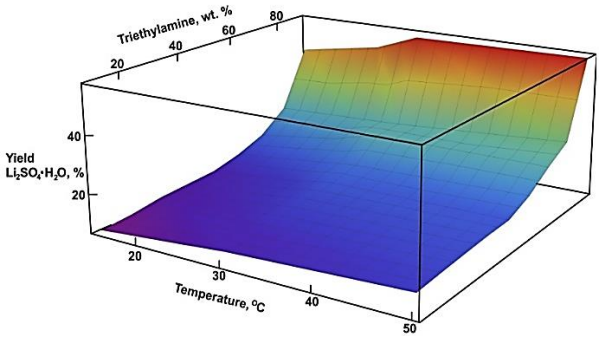

Fig. 4. Yield of lithium sulfate monohydrate crystals from an aqueous solution containing 25.00 wt.% salt vs. introduced triethylamine amount and temperature

Рис. 4. Выход кристаллов моногидрата сульфата лития из водного раствора, содержащего 25,00 мас.% соли, в зависимости от количества введенного триэтиламина и температуры

Table 5

Elemental composition (X-ray fluorescence analysis) of lithium sulfate monohydrate samples

Таблица 5. **Элементный состав (рентгенофлуоресцентный анализ) образцов моногидрата сульфата лития**

Element	Line	Relative content, %	
		Initial $Li_2SO_4 \cdot H_2O$ crystals	$Li_2SO_4 \cdot H_2O$ crystals after the extractive crystallization process
S	SKa	94.822	96.377
P	PKa	2.982	2.680
Cl	ClKa	1.815	0.723
Ca	CaKa	0.161	0.116
K	KKa	0.131	0.023
Cu	CuKa	0.061	0.061
Al	AlKa	0.028	0.020

CONCLUSIONS

New standard reference data on the solubility and phase equilibrium of the ternary Li_2SO_4 + H_2O + TEA system were obtained in the temperature range of 15-90 °C. These data can be used to model a number of chemical and technological processes. It was found that the resulting lithium sulfate monohydrate significantly salts out TEA from its aqueous solutions at all temperatures within the study range, which is reflected in the high TEA content (95-99 wt.%) in the organic phase of the monotectic state. The salting-out effect increases with increasing temperature, despite the salt's negative temperature coefficient of solubility in water and aqueous amine solutions.

Lithium sulfate is one of the most important intermediates in lithium production from ore. Evaporation of aqueous solutions for its production is energy-

intensive and ineffective, as this salt has a very small negative temperature coefficient of solubility. Furthermore, lithium salt solutions corrode equipment materials, leading to contamination of the target product with impurities. Based on an analysis of the phase diagrams of the studied ternary system at several temperatures, without chemical analysis, we identified the optimal conditions for the extractive crystallization of $Li_2SO_4 \cdot H_2O$. Our proposed approach allows us to obtain purer $Li_2SO_4 \cdot H_2O$ from its aqueous solutions with the addition of triethylamine, with a yield of over 55% at temperatures close to normal conditions. A clear advantage of our approach to obtaining $Li_2SO_4 \cdot H_2O$ crystals is its low energy consumption and the ability to separate the organic phase for subsequent regeneration of the TEA for reuse.

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CONFLICT OF INTERESTS

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

The authors declare the absence of a conflict of interest warranting disclosure in this article.

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