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ФАЗОВЫЕ РАВНОВЕСИЯ, РАСТВОРИМОСТЬ И ЭФФЕКТ ВЫСАЛИВАНИЯ В ТРОЙНОЙ СИСТЕМЕ НИТРАТ КАЛИЯ–ВОДА–МАСЛЯНАЯ КИСЛОТА В ИНТЕРВАЛЕ 5–100 °С

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Фазовые равновесия, растворимость и эффект высаливания масляной кислоты были изучены визуально-политермическим методом в смесях компонентов тройной системы нитрат калия – вода – масляная кислота в интервале 5–100 °С. Политермы фазовых состояний были построены по двенадцати сечениям треугольника состава. В смесях компонентов были обнаружены следующие фазовые состояния: гомогенные и насыщенные растворы, монотектика и расслоение. Определена температура образования критической ноды монотектического состояния (18,0 °С). Это минимальная температура существования двух жидких фаз в трехкомпонентных смесях. Температурная зависимость составов, отвечающих критическим точкам растворимости, была найдена методом отношения объемов жидких фаз. Растворимость компонентов была определена при тринадцати температурах и изотермические фазовые диаграммы построены при 5,0, 18,0, 25,0, 50,0, 70,0 и 100,0 °С. Топологическая трансформация фазовой диаграммы тройной системы с изменением температуры характерна для тройных систем с высаливанием двойной гомогенной жидкостной системы. Составы жидких фаз монотектического состояния определены графически. Коэффициент распределения масляной кислоты между этими фазами рассчитан при пяти температурах как отношение концентраций кислоты в органической и водной фазах. Найдено, что эффект высаливания масляной кислоты значительно возрастает с увеличением температуры, что связано с изменением растворимости нитрата калия в растворах. Эффективность нитрата калия как высаливателя масляной кислоты из ее водных растворов сравнивается с ранее исследованными системами соль–вода–масляная кислота. Отмечается возможность успешного применения нитрата калия для концентрирования масляной кислоты при биохимическом способе производства из бродильных растворов.

Ключевые слова: фазовые равновесия, растворимость, фазовая диаграмма, высаливание, монотектика, масляная кислота, нитрат калия

PHASE EQUILIBRIA, SOLUBILITY AND SALTING-OUT EFFECT IN THE TERNARY SYSTEM POTASSIUM NITRATE – WATER – BUTYRIC ACID IN THE RANGE OF 5–100 °C

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Phase equilibria, solubility and the salting-out effect of butyric acid were studied by the visual-polythermal method in mixtures of the components of the ternary system potassium nitrate – water – butyric acid in the range of 5–100 °C. Polytherms of phase states in twelve sections of the triangle composition were plotted. The following phase states were found in mixtures of components: homogeneous and saturated solutions, monotectic and delamination. The formation temperature of the critical tie line of monotectic state (18.0 °C) is determined. It is the minimum temperature of existence of two liquid phases in three-component mixtures. The temperature dependence of the compositions of solutions corresponding to the critical solubility points were found by the phase-volume ratio method. The solubility of the components was determined at thirteen temperatures and isothermal phase diagrams were plotted at 5.0, 18.0, 25.0, 50.0, 70.0 and 100.0 °C. The topological transformation of the phase diagram of a ternary system with a temperature change is characteristic of these systems with the salting-out of a binary homogeneous liquid system. The compositions of the liquid phases of monotectic state were graphically determined. The butyric acid distribution coefficient between these phases was calculated at five temperatures as the ratio of acid concentrations in the organic and aqueous phases. It was found that the effect of salting-out butyric acid increases significantly with rising temperature, which is associated with a change in the solubility of potassium nitrate in solutions. The efficiency of potassium nitrate as a salting-out agent of butyric acid from its aqueous solution is compared with the previously studied salt – water – butyric acid systems. The possibility of the successful application of potassium nitrate for the concentration of butyric acid in the biochemical method of production from fermentation solutions is noted.

Key words: phase equilibria, solubility, phase diagram, salting-out, monotectic state, butyric acid, potassium nitrate

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INTRODUCTION

Recently, much attention has been paid to biochemical methods for obtaining organic substances from available natural raw materials. Butyric acid is one of the important products, whose production by butyric fermentation [1, 2] is very promising due to its greater environmental friendliness and almost unlimited raw material base compared to the traditional method of oxidation of butyric aldehyde or butanol [3]. Various types of lignocellulosic biomass have been proposed as raw materials for the biochemical method [1, 2], which are either obtained on purpose or formed as waste from other industries. The butyric acid produced by this method is often referred to as "biobutyric acid." The works [4-8] discuss improvements in microbial production of butyric acid, including modification of strains by genetic engineering and the development of new fermentation processes. The studies compare the yield of the product and its purity, the productivity of the use of raw materials, reducing the yield of by-products of biosynthesis. To expand the raw material base, it is proposed to use new sources as a substrate for the production of bio-butyric acid, for example, food waste [9] and hydrolysate of ground coffee rich in galactose [10].

The cost of producing biobutyric acid is rather high, but despite this, the manufacturers of food supplements or pharmaceuticals [1] prefer it. Butyric acid and its derivatives play an important role in the work of the gastrointestinal tract [11, 12]. Violation of its synthesis in the body can provoke the development of irritable bowel syndrome. Drugs capable of enzymatically releasing butyric acid in the gastrointestinal tract have shown their effectiveness in metabolic diseases such as diabetes [13].

The production of butyric acid by the biochemical method remains unprofitable and uncompetitive due to the difficulty of extraction, since its concentration in fermentation solutions is rather low (usually no more than 8 wt%). Concentration by traditional methods, such as distillation, is not effective due to the high boiling point of the acid (163.5 °C; [3]). Therefore, researchers' attention is turned to the development of less expensive methods, including liquid extraction, extractive fermentation, electrodialysis, pervaporation, and salting-out [14, 15].

Selective extraction of butyric acid from the broth was carried out using a silicone membrane [16]. Ionic liquids [17], octyl acetate [18], as well as trioctylamine with natural sunflower and soybean oils as diluents have been proposed to be used as extractants of butyric acid [19]. The combination of extraction of isobutyric acid by polyethylene glycols with salting with sodium sulfate showed high efficiency [20, 21].

Salting-out is one of the most technically simple and least expensive methods. When certain salts are added to fermentation solutions, delamination into two liquid phases occurs, one of which (upper) concentrates biobutyric acid. The task of researchers is to select the optimal salt and conditions for its effective concentration from fermentation solutions. In few studies [14, 15], attempts were made to select salting-out salts for butyric acid from aqueous solution. Fu et al. [14] proposed to use such salts as NaH_2PO_4, $(NH_4)_2SO_4$, $CaCl_2$ to isolate butyric acid from model solutions containing additional acetic acid. It has been established that the process using NaH_2PO_4 as a salting-out agent in the presence of ethanol as an extractant is highly efficient. Dan et al. [15] studied the effect of a number of chlorides (NaCl, KCl, $MgCl_2 \cdot 6H_2O$, and $CaCl_2$) on dilute solutions of butyric acid in water. It was found that the value of the distribution coefficient of butyric acid in the studied mixtures decreased in the series $CaCl_2 > MgCl_2 \cdot 6H_2O > NaCl > KCl$. Its value in the ternary system calcium chloride – water – butyric acid decreased with increasing temperature, namely: at 15 °C it was 21.41, while at 45°C it was only 16.89. The combined effect of the salting-out agent K_2HPO_4 and an extractant (aliphatic alcohols) on aqueous solutions of a number of monocarboxylic acids was studied by Yan et al. [22]. Data on the reduced yield of butyric acid from its solution when increasing temperature or decreasing the solution acidity are given. High recovery rates of butyric acid (more than 90%) were achieved by performing a second step of salting-out extraction with NaH_2PO_4 as a salting-out agent and *n*-butyl acetate with ethanol as extractants [23].

Some works [14, 15, 22, 23] provide no phase diagrams for the studied systems containing butyric acid. The phase diagram is a tool to allow optimizing the isolation processes of various substances, including butyric acid, from their aqueous solutions with high efficiency. In [24] determined the position of the monotectic triangle and the binodal curve on the diagram of the sodium chloride – water – butyric acid system at 25 °C using isothermal titration. Four tie lines were built on the delamination field, diverging like a fan towards the binary water – salt system. The effect of salting-out of butyric acid with sodium chloride in this system was not evaluated.

In our laboratory, the influence of sodium chloride (in the range of 10.0-60.0 °C) [25], potassium chloride (in the range of 5.0-80.0 °C) [26] and cesium nitrate (in the range of 5.0-100.0 °C) [27] on the phase behavior of the binary water – butyric acid system was previously studied using the visual-polythermal method. For each ternary system, isothermal phase diagrams were plotted for several temperatures and the distribution coefficients of butyric acid between the equilibrium liquid phases of monotectic state were calculated. The possibility of using sodium and potassium chlorides to concentrate butyric acid from its dilute solution was discussed [25, 26]. For the ternary cesium nitrate – water – butyric acid system [27], the formation temperature of the critical tie line of monotectic state (96.2 °C) was found and the low efficiency of $CsNO_3$ for salting-out butyric acid was shown. Despite this, cesium salts can be effective salting agents of some organic substances from aqueous solutions [28].

Thus, in previous works based on the study of model three- and four-component systems, some salts were proposed to be suitable for concentrating butyric acid from its aqueous solution by salting-out. The range of salts studied is mainly limited to chlorides of some alkali and alkaline earth metals, as well as hydro- and dihydrophosphates of alkali metals. The effect of other salts, in particular, nitrates, on the phase behavior of the binary water – butyric acid system has not been sufficiently studied.

This work is devoted to the study of phase equilibria and determination of the solubility of the components in the ternary potassium nitrate–water–butyric acid system in the range of 5-100 °C in order to evaluate the efficiency of using potassium nitrate as a salting-out agent for concentrating butyric acid from its aqueous solution.

Binary systems involved in the studied ternary system

The ternary $KNO_3–H_2O–C_4H_8O_2$ system under study includes three binary systems. Let's briefly characterize them.

The binary water – butyric acid system is homogeneous throughout the entire temperature range of its liquid state and belongs to eutectic-type systems (32.5 mol.% water, –12.5 °C) [29]. The ice crystallization branch on the phase diagram has been established to be gentle. It was established [30] that there is a metastable delamination range with an upper critical solution temperature (UCST) at –3 °C (mixtures with 39 wt.% butyric acid) in this binary system. The ice crystallization curve has an extended horizontal section around –2 °C above the delamination range. Above this temperature, homogeneous mixtures of the two components are in a covertly delaminating state, i.e. are microheterogeneous [30]. Phase equilibria and the solubility of the components of the binary water – butyric acid system in the range of –10–0 °C were studied in most detail in [25]. It has been established that a eutectic phase reaction occurs in mixtures of the components at –9.5 °C. The content of butyric acid in the eutectic mixture is 94.2 wt.%, which differs from that given by [29]. A metastable delamination range was found in the ice crystallization field, bounded by a tie line curve with an upper critical point (UCST = –3.7 °C, 37.3 wt.% $C_4H_8O_2$).

Aqueous solutions of butyric acid have been studied in detail for a number of physicochemical and thermodynamic properties. Romero et al. [31] experimentally found the enthalpy of dissolution of butyric acid in water at 293.15, 298.15, 303.15, and 308.15 K. The results obtained were used to evaluate solute – solvent and solute – solute interactions and the hydrophobic behavior of butyric acid in water. The density and surface tension of dilute aqueous butyric acid solutions were measured at 293.15, 298.15, 303.15 and 308.15 K [32]. The apparent and excess molar volumes were calculated from experimental data depending on the composition at each temperature. The apparent molar volumes were calculated, based on the obtained data on the density in dilute aqueous solutions of butyric acid at 298.15 K [33].

The solubility diagram of the $KNO_3 – H_2O$ system is characterized by eutectic equilibrium at –3.0 °C, whose solid phases are ice and potassium nitrate. This salt is highly soluble in water and has a positive temperature solubility coefficient [3]. No data on the solubility of potassium nitrate in butyric acid have been found in the reference literature. We have found that the solubility of this salt in butyric acid does not exceed 0.05 wt.% within the temperature range studied.

EXPERIMENTAL

Materials

High-purity deionized water (electrical resistivity of 18.2 MΩ·cm at 25 °C) was obtained using water filtration and purification equipment Gamma SMART (Synergy UV); Butyric acid of pure grade (JSC "Ecos-1", TU 6-09-530-75) was dried over calcined magnesium sulfate for 5 days. Then the desiccant was filtered off and the filtrate was distilled in a plant with a 0.5 m high dephlegmator; the fraction with a boiling point of 163.3-163.5 °C to be collected. The refractive index of the purified butyric acid preparation matched the reference data ($n_{20}^{D} = 1.3977$) [3]. It was measured on an IRF-22 refractometer with an error of $\pm 1 \cdot 10^{-4}$.

Potassium nitrate of analytical grade (Vekton JSC, GOST 4217-77), which was additionally recrystallized and finely ground in an agate mortar, was used in the work. The salt was thoroughly dried first in air and then in vacuum over phosphorus (V) oxide at 100 °C to constant weight. Thermogravimetric analysis showed the absence of moisture in the prepared salt sample. The obtained preparations of the salt and butyric acid were stored in a dry atmosphere.

Apparatus and Procedure

In component mixtures of the ternary potassium nitrate–water–butyric acid system, the solubility and phase equilibria were studied by the visual-polythermal method in sealed heat-resistant glass ampoules (6 ml in volume) under the pressure of solvent vapors and air in the temperature range 5-100 °C. Since the volume of the gas phase was always small (about 2-3 ml), the change in the composition of liquid mixtures due to evaporation of water and butyric acid with an increase in temperature did not significantly affect the temperatures of phase transitions in condensed phases. Changes in the boiling point of water in the presence of other components were not investigated. The research procedure is detailed in [34]. Sealed glass ampoules with mixtures were alternately placed into a Lauda A-100 ultrathermostat with transparent walls (working liquid being distilled water, the research range being 0-70 °C) or a Mechanic Medingen U-10 ultrathermostat (working liquid being glycerol, the research range being 70-110 °C). The temperature in the thermostats was maintained with an accuracy of 0.1 °C. It was measured with an LT-300-N electronic laboratory thermometer with an accuracy of 0.1 °C. The heating and cooling of the working liquids was carried out at a low rate (about 0.5 °C/min) near the phase transition temperature.

The procedures for the visual-polythermal study to determine the temperatures of phase transitions in the formation of a second liquid phase ($\ell+S \leftrightarrows \ell_1+\ell_2+S$ and $\ell \leftrightarrows \ell_1+\ell_2$) and the dissolution of crystals ($\ell_1+\ell_2+S \leftrightarrows \ell_1+\ell_2$ and $\ell+S \leftrightarrows \ell$) differed [34]. In both cases, the error in determining the transition temperature did not exceed ±0.1 °C. The criterion for establishing equilibrium in heterogeneous mixtures was the reproducibility of measurements of phase transition temperatures. According to the previously described procedure [34] with the phase-volume ratio method, the compositions of mixtures of three components were found where critical phenomena and equal volumes of two liquid phases (ℓ_1 and ℓ_2) were observed in equilibrium with the solid phase and without it at the phase transition temperature. Using thermal analysis (Paulik–Paulik–Erdey OD-102 derivatograph) and X-ray diffraction (DRON-8T diffractometer), it was established that the equilibrium solid phase was individual potassium nitrate over the entire temperature range of our study.

The obtained polythermal data were used to graphically determine the solubility of the components and to plot isothermal phase diagrams for a number of selected temperatures using the methodology developed earlier [34]. The solubility of the components was determined with a relative error of 0.5-1.0%.

RESULTS AND DISCUSSION

Polythermal studies

Ternary mixtures, whose compositions varied along twelve sections of the concentration triangle, were studied for the ternary potassium nitrate – water – butyric acid system.

Mixtures of the components in a number of sections were prepared with a constant mass ratio of butyric acid and water: 15.00:85.00 (section I, 14 mixtures), 28.00:72.00 (section II, 16 mixtures), 41.00:59.00 (section III, 13 mixtures), 56.00: 44.00 (section IV, 13 mixtures), 71.00:29.00 (section V, 13 mixtures), 80.00:20.00 (section VI, 12 mixtures), and 89.00:11.00 (section VII, 7 mixtures) and they contained a known variable amount of potassium nitrate. Mixtures of the components of other sections had a variable content of butyric acid and a fixed mass ratio between potassium nitrate and water: 35.00:65.00 (section VIII, 27 mixtures), 41.00:59.00 (section IX, 4 mixtures), 53.00:47.00 (section X, 3 mixtures), 68.00:32.00 (section XI, 8 mixtures), and 72.00:28.00 (section XII, 6 mixtures).

The types of the polytherm of phase states along sections I-VI are similar. Each polytherm has four fields of phase states corresponding to the following states: homogeneous solutions (ℓ), liquid – liquid equilibria (ℓ_1+ℓ_2, ℓ_1 is the organic phase, ℓ_2 the aqueous phase), liquid – solid (ℓ+S), and liquid – liquid – solid (monotectics ℓ_1+ℓ_2+S). All fields on the polytherms are separated from each other by smooth lines. Fig. 1(a) exemplifies the polytherm of section I. The polytherm of section VII (Fig. 1(b)) is the solubility line of potassium nitrate in mixtures of water and butyric acid of constant composition, which separates the field of a homogeneous liquid state ℓ from the field of saturated solutions ℓ+S (S is KNO_3).

Phase equilibria in mixtures of the components along sections IX and X were studied in a narrow temperature – concentration range in order to determine the phase transition temperature of $\ell_1+\ell_2 \leftrightarrows \ell$ and the delamination field boundary on isothermal phase diagrams. The polytherms of these sections are smooth lines separating the field of delamination ℓ_1+ℓ_2 and the field of the homogeneous-liquid state ℓ (no figures are shown).

Mixtures of the components along sections VIII, XI and XII were studied to clarify the boundaries of the monotectic and delamination fields; therefore, the same phase states occur in them. For example, the polytherm along section VIII (figure 1(c)) consists of four curves separating the fields of states: liquid – solid (ℓ_1+S, ℓ_2+S), liquid – liquid – solid monotectics (ℓ_1+ℓ_2+S), liquid – liquid (ℓ_1+ℓ_2) and homogeneous solutions (ℓ). The curve separating the ℓ_1+S, ℓ_2+S and ℓ_1+ℓ_2+S fields consists of two branches joining at the critical point KS. This point corresponds to the mixture with equal volumes of two liquid phases in equilibrium with potassium nitrate crystals (S) at 18.0 °C. This temperature is the minimum one for the existence of two liquid phases in the ternary system under study, i.e. potassium nitrate delaminates mixtures of water and butyric acid above 18.0 °C only. The point KS belongs to the critical tie line of monotectic state.

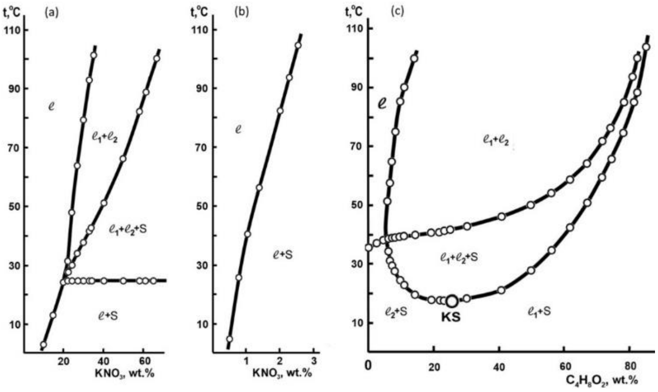

Fig. 1. Phase state polytherms in sections I (a), VII (b), and VIII (c) of the composition triangle of the ternary potassium nitrate–water–butyric acid system

Рис.1. Политермы фазовых состояний по сечениям I (a), VII (b) и VIII (c) концентрационного треугольника тройной системы нитрат калия–вода–масляная кислота

To plot the temperature dependence of the composition of the critical liquid–liquid equilibrium solution, mixtures of the components of six additional cross sections were prepared and examined. The mixtures of these sections were chosen so that they had a variable known content of potassium nitrate and a constant mass ratio of water and butyric acid for each section, namely: 65.00:35.00; 64.50:35.50; 64.00:36.00; 63.70:36.30; 63.30:36.70; and 62.70:37.30.

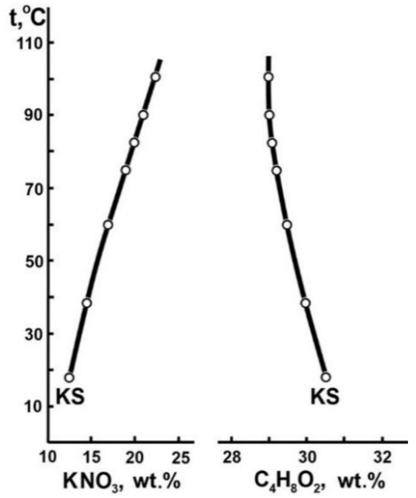

Fig. 2. Potassium nitrate and butyric acid contents in the critical solutions with liquid–liquid equilibrium as a function of temperature in the ternary potassium nitrate–water–butyric acid system

Рис.2. Содержание нитрата калия и масляной кислоты в критических растворах равновесия жидкость–жидкость в тройной системе нитрат калия–вода–масляная кислота в зависимости от температуры

In critical solutions, the content of potassium nitrate increases, while that of butyric acid decreases with increasing temperature (Fig. 2). The dependences obtained start at 18.0 °C at the point KS corresponding to the composition of the liquid phase (the critical end point) of the critical tie line of monotectic state.

Solubility and isothermal phase diagrams

The solubility values of the components at the chosen temperatures were found graphically from the polythermal data (Table 1). The solubility of potassium nitrate in water at these temperatures was not measured by us; they are reference data.

Isothermal phase diagrams of the ternary system potassium nitrate – water – butyric acid were plotted at six temperatures (5.0, 18.0, 25.0, 50.0, 70.0 and 100.0 °C, Fig. 3(a-f)). Their analysis will reveal the topological transformation of its phase diagram with a change in temperature. In the range of 5.0-18.0 °C, the diagram is characterized by the presence of a solubility line separating the field of homogeneous liquid state ℓ and that of saturated solutions ℓ + S (for example, on the isotherm at 5.0 °C, Fig. 3(a)). An increase in temperature leads to the point K (critical end point) appearing on the solubility line at 18.0 °C, and the critical tie line KS of monotectic state appears on the field of saturated solutions (Fig. 3(b)). The point K corresponds to the mixture with equal volumes of the identical organic (ℓ_1) and aqueous (ℓ_2) phases. The composition of this critical solution (12.5 wt.% KNO_3, 57.0 wt.% H_2O, and 30.5 wt. % $C_4H_8O_2$) was determined graphically on the concentration triangle from the point where the critical tie line KS intersects the solubility line at 18.0 °C.

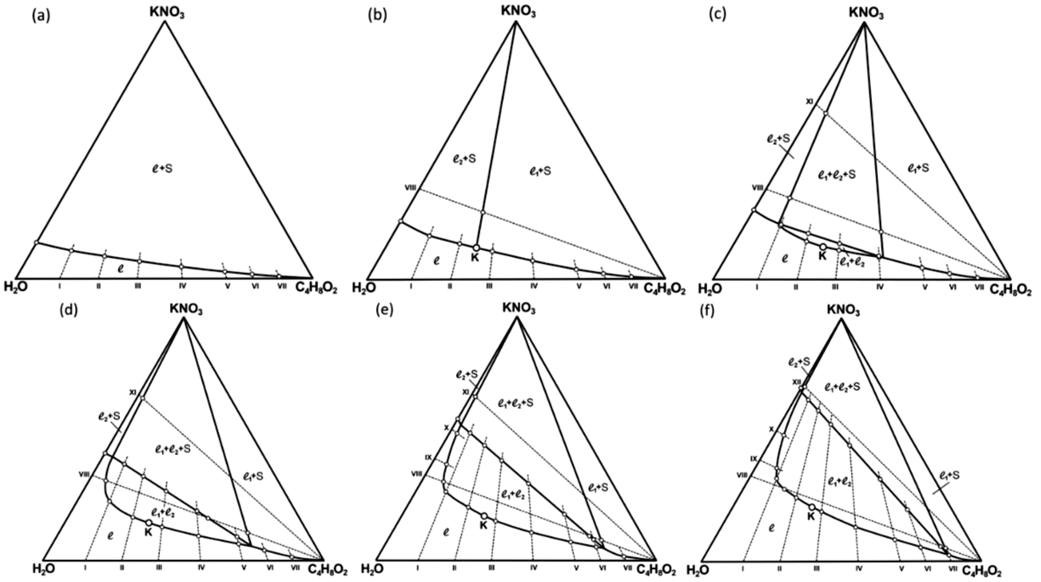

Fig. 3. Isothermal phase diagrams (wt.%) of the ternary potassium nitrate–water–butyric acid system at 5.0 (a), 18.0 (b), 25.0 (c), 50.0 (d), 70.0 (e) and 100.0 °C (f). The solid lines separate fields of phase states. The dotted lines indicate the position of sections I-XII in the concentration triangle

Рис.3. Изотермические фазовые диаграммы (мас.%) тройной системы нитрат калия–вода–масляная кислота при 5,0 (a), 18,0 (b), 25,0 (c), 50,0 (d), 70,0 (e) и 100,0 °С (f). Сплошные линии разделяют поля фазовых состояний. Пунктирные линии указывают положение сечений I-XII на концентрационном треугольнике

An increase in temperature (the isotherm at 25.0 °C, Fig. 3(c)) leads to the critical tie line KS transforming into the triangle $\ell_1+\ell_2+S$ of monotectic state. Two of its sides are adjacent to the fields of saturated solutions ℓ_1+S, ℓ_2+S, and the third side is adjacent to the small delamination field $\ell_1+\ell_2$ with the critical point K. A further increase in temperature leads to no qualitative changes in the phase state isotherms of the system (the isotherms at 50.0, 70.0 and 100.0 °C, Fig. 3(d-f)). Quantitative changes are observed due to an increase in the salting-out effect of salt and an increase in temperature: the delamination field expands, while the fields of saturated solutions shrink.

Table 1

Solubility of the components of the ternary potassium nitrate – water – butyric acid system, wt.%

***Таблица 1.* Растворимость компонентов тройной системы нитрат калия–вода–масляная кислота, мас.%**

t, °C	Saturated solution composition		
	1	2	3
	KNO_3	H_2O	$C_4H_8O_2$
5.0	14.2	85.8	0.00
	10.9	75.7	13.4
	8.9	65.6	25.5
	7.0	54.9	38.1
	4.7	41.9	53.4
	2.9	28.2	68.9
	1.6	19.7	78.7
	0.5	10.9	88.6
10.0	17.3	82.7	0.00
	13.1	73.9	13.0
	10.8	64.2	25.0
	8.5	54.0	37.5
	5.7	41.5	52.8
	3.3	28.0	68.7
	1.8	19.6	78.6
	0.5	10.9	88.6
18.0	22.5	77.5	0.00
	16.8	70.7	12.5
	14.1	61.8	24.1
	12.5[a]	57.0[a]	30.5[a]
	11.3	52.3	36.4
	7.4	40.7	51.9
	4.0	27.8	68.2
	2.1	19.6	78.3
	0.6	10.9	88.5
20.0	24.0	76.0	0.00
	17.7	70.0	12.3
	14.5	60.6	24.9
	11.8[b]	57.6[b]	30.6[b]
	11.7	52.1	36.2
	7.9	40.5	51.6
	4.2	27.8	68.0
	2.2	19.6	78.2
	0.7	10.9	88.4
	1	2	3
25.0	27.2	72.8	0.00
	20.3	67.7	12.0
	15.0	61.2	23.8
	12.5[b]	57.0[b]	30.5[b]
	11.9	52.0	36.1
	8.8	40.1	51.1
	5.0	27.5	67.5
	2.5	19.5	78.0
	0.7	10.9	88.4
30.0	31.4	68.6	0.00
	21.6	66.6	11.8
	15.5	60.8	23.7
	13.1[b]	56.6[b]	30.3[b]
	12.1	51.9	36.0
	9.1	40.0	50.9
	5.4	27.4	67.2
	2.8	19.4	77.8
	0.8	10.9	88.3
40.0	39.0	61.0	0.00
	32.9	61.1	6.0
	23.2	65.3	11.5
	16.6	60.0	23.4
	14.4[b]	55.6[b]	30.0[b]
	12.9	51.4	35.7
	9.6	39.8	50.6
	6.8	27.0	66.2
	3.5	19.3	77.2
	1.0	10.9	88.1
50.0	44.0	56.0	0.00
	32.9	61.1	6.0
	24.3	64.3	11.4
	18.0	59.0	23.0
	15.7[b]	54.6[b]	29.7[b]
	13.9	50.8	35.3
	10.1	39.6	50.3
	7.3	26.9	65.8
	4.4	19.1	76.5
	1.2	10.9	87.9
60.0	52.0	48.0	0.00
	32.6	60.5	6.9
	26.1	62.8	11.1
	19.4	58.0	22.6
	17.0[b]	53.5[b]	29.5[b]
	15.1	50.1	34.8
	10.8	39.2	50.0
	7.6	26.8	65.6
	5.3	18.9	76.8
	1.5	10.8	87.7
70.0	58.0	42.0	0.00
	51.6	45.7	2.7
	38.8	55.8	5.4
	32.3	60.1	7.6
	28.1	61.1	10.8
	22.0	56.2	21.8
	18.3[b]	52.5[b]	29.2[b]

	1	2	3
70.0	16.4	49.3	34.3
	11.6	38.9	49.5
	7.9	26.7	65.4
	5.6	18.9	75.5
	1.7	10.8	87.5
80.0	62.8	37.2	0.00
	51.4	45.6	3.0
	38.6	55.6	5.8
	31.5	58.6	9.9
	30.1	59.4	10.5
	22.8	55.6	21.6
	19.6 [b]	51.3 [b]	29.1 [b]
	17.8	48.5	33.7
	12.3	38.6	49.1
	8.4	26.6	65.0
	5.7	18.9	75.4
	2.0	10.8	87.2
90.0	66.9	33.1	0.00
	51.3	45.4	3.3
	38.2	55.0	6.8
	32.4	57.5	10.1
	31.2	57.9	11.0
	24.8	54.1	21.1
	21.0 [b]	50.0 [b]	29.0 [b]
	19.2	47.7	33.1
	13.2	38.2	48.6
	8.7	26.5	64.8
	6.0	18.8	75.2
	2.2	10.8	87.0
100.0	71.1	28.9	0.00
	51.1	45.4	3.5
	37.7	54.3	8.0
	34.5	55.7	9.8
	29.9	55.5	14.6
	26.4	53.0	20.6
	22.3 [b]	48.8 [b]	28.9 [b]
	20.8	46.7	32.5
	14.3	37.7	48.0
	9.4	26.3	64.3
	6.4	18.7	74.9
	2.4	10.7	86.9

Notes: [a] Composition corresponding to the critical end point of the critical tie line of monotectic state
[b] Composition corresponding to the critical point of liquid–liquid equilibrium
Примечания: [a] состав, соответствующий критической конечной точке критической линии моноэвтектического состояния
[b] состав, соответствующий критической точке равновесия жидкость-жидкость

Salting-out effect of butyric acid

The salting-out effect of butyric acid 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 butyric acid over these phases is calculated using the formula:

$$K_d = \frac{C_{C_4H_8O_2}(\ell_1)}{C_{C_4H_8O_2}(\ell_2)}, \qquad (1)$$

where $C_{C_4H_8O_2}(\ell_1)$ is the content of butyric acid in the organic phase (wt.%), $C_{C_4H_8O_2}(\ell_2)$ the content of butyric acid in the aqueous phase (wt.%).

The compositions of the liquid phases in equilibrium with the solid phase were found graphically at five temperatures (Table 2). The coefficients of butyric acid distribution between these phases were calculated by Eq. (1). The growing of the salting-out effect of potassium nitrate on a mixture of water and butyric acid with increasing temperature is reflected as a significant increase in the content of butyric acid in the organic phase of the monotectic state and the value of the distribution coefficient. The increase in K_d with temperature can be explained by the weakening of the intermolecular interactions of the components in the binary water – butyric acid system due to the destruction of hydrogen bonds and an increase in the salt concentration in the aqueous phase of monotectic state. The combined action of these two factors leads to promotion of the salting-out effect, which reaches its maximum at the highest temperature of the study range (100.0 °C).

Table 2

Compositions of the liquid phases of the monotectic state and the butyric acid distribution coefficients K_d in the ternary potassium nitrate (1) – water (2) – butyric acid (3) system

***Таблица 2.* Составы жидких фаз монотектического состояния и коэффициенты распределения масляной кислоты K_d в тройной системе нитрат калия – вода – масляная кислота**

t, °C	Compositions of the liquid phases in equilibrium with solid KNO_3, wt.%						Distribution coefficient, K_d
	Aqueous phase			Organic phase			
	(1)	(2)	(3)	(1)	(2)	(3)	
18.0	12.5	57.0	30.5	12.5	57.0	30.5	1.0
25.0	21.4	67.4	11.2	8.5	38.9	52.6	4.7
50.0	42.3	54.2	3.5	6.1	22.5	71.4	20.4
70.0	55.5	42.1	2.4	5.3	16.5	78.2	32.6
100.0	69.3	29.5	1.2	3.5	10.5	86.0	71.7

In the studied ternary system with potassium nitrate, the distribution coefficient of butyric acid (Table 2) at 25.0 °C is lower than in the systems with previously studied chlorides of sodium (61.2; [25]), potassium (22.1; [26]) and calcium (~20; [15]). With an increase in temperature, the salting-out effect of potassium nitrate, due to the higher temperature coefficient of salt solubility, increases faster than in the system with potassium chloride. Therefore, at temperatures above 70 °C, the distribution coefficient is higher in the system with potassium nitrate than with potassium chloride [26]. The decrease in the distribution coefficient with temperature in the ternary systems with sodium [25] and calcium [15] chlorides leads to potassium nitrate being the best salting-out agent of butyric acid above 60 °C. In the ternary system with cesium nitrate [27] the distribution coefficient is only 3.9 at 100 °C due to the weak salting-out effect of this salt.

CONCLUSIONS

The studied ternary potassium nitrate – water – butyric acid system is a second example of systems with salting-out of butyric acid, in which it was possible to establish the formation temperature of the critical tie line of monotectic state. However, in the system with cesium nitrate [27] the formation temperature of the critical tie line is significantly higher (96.2 °C) than in the system under study (18.0 °C). This can be explained by the larger crystallographic radius of the cesium ion and the lower degree of its hydration in comparison with the potassium ion. Our analysis of the isothermal phase diagrams of these ternary systems with potassium and cesium nitrates with temperature changes shows an analogy in their topological transformations. The plotted isotherms confirm a fragment of the general scheme of the topological transformation of the phase diagrams of ternary salt – binary solvent systems [34] for the case of salting-out of binary liquid homogeneous systems with a temperature change.

It has been established that potassium nitrate is a good salting-out agent of butyric acid from its aqueous solution at temperatures above 70 °C. The results obtained in our study can replenish databases on phase equilibria and solubility in ternary salt – two solvents systems and find practical application in the processes of concentration and isolation of biobutyric acid from its aqueous fermentation solutions.

CONFLICT OF INTERESTS

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

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

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