

DOI: 10.17725/rensit.2021.13.177

Salting-in–salting-out effect of potassium salts on the binary liquid water + n-butoxyethanol system with a closed delamination region

Maksim P. Smotrov, Dmitry G. Cherkasov, Konstantin K. Il'in

N.G. Chernyshevsky Saratov National Research State University, <https://sgu.ru/>
Saratov 410012, Russian Federation

E-mail: maxim-smotrov@yandex.ru, dgcherkasov@mail.ru, ilinke@sgu.ru

Received 11 May, 2021, peer-reviewed 14 May, 2021, accepted 18 May, 2021

Abstract: The work is devoted to the comparative characteristics of the salting-in –salting-out effect of potassium formate, nitrate and perchlorate on the binary liquid water + n-butoxyethanol system with a closed delamination region in a temperature range of 10–150°C. The introduction of potassium formate or potassium nitrate into the mixtures of the critical composition of the binary water + n-butoxyethanol system leads to a decrease in the LCST (lower critical solution temperature) and an increase in the UCST (upper critical solution temperature) of this system, while the addition of potassium perchlorate leads to an increase in the LCST and a decrease in the UCST. For three ternary systems potassium salt + water + n-butoxyethanol, the distribution coefficients of n-butoxyethanol between the aqueous and organic phases of the monotectic state were calculated for several temperatures. It has been found that the distribution coefficient increases with temperature in each system. It has been established that potassium formate and potassium nitrate have a salting-out effect, the former having a particularly strong one. Potassium perchlorate at low concentrations and relatively low temperatures is characterized by a salting-in effect, which turns into a weak salting-out effect at higher temperatures. The results obtained can be used to develop practical recommendations for carrying out selective extraction of organic solvents and extractive crystallization of salts.

Keywords: phase equilibria, critical phenomena, binary system, ternary system, salting-in, salting-out

UDC 544.344.016+536.44

For citation: Maksim P. Smotrov, Dmitry G. Cherkasov, Konstantin K. Il'in. Salting-in–salting-out effect of potassium salts on the binary liquid water–n-butoxyethanol system with a closed delamination region. *RENSIT*, 2021,13(2):177-186. DOI: 10.17725/rensit.2021.13.177.

CONTENTS

1. INTRODUCTION (177)
 2. CHARACTERISTICS OF THE BINARY LIQUID WATER–N-BUTOXYETHANOL SYSTEM (181)
 3. INFLUENCE OF POTASSIUM SALTS ON THE COORDINATES OF CRITICAL POINTS OF THE BINARY WATER–N-BUTOXYETHANOL SYSTEM AND THEIR SALTING-IN–SALTING-OUT EFFECT (181)
 4. DISTRIBUTION COEFFICIENTS OF N-BUTOXYETHANOL IN TERNARY SYSTEMS (183)
 5. CONCLUSION (184)
- REFERENCES (185)

1. INTRODUCTION

The phenomenon of salting-out and the opposite phenomenon of salting-in often occur in systems that differ in the number and nature of components and coexisting phases [1]. The behavior of salts in aqueous non-electrolyte solutions is a complex phenomenon, since various interactions take place in water–electrolyte–non-electrolyte systems, namely: water–electrolyte, water–non-electrolyte, and electrolyte–non-electrolyte. As a result, as noted by many researchers [2–4], no rigorous thermodynamic theory of

salting-in–salting-out of non-electrolytes has been developed.

A systematic study of the effect of salts on the solubility of non-electrolytes in water has revealed a number of general regularities, namely: 1) in the overwhelming majority of cases, electrolytes reduce the solubility of non-electrolytes in water; 2) as a rule, the smaller the size of the ion at a given charge, the stronger the salting-out effect it has; and 3) an increase in the radius of the ion (either cation or anion) leads to a decrease in salting-out and a switch to salting-in. These regularities were revealed when studying the properties of dilute aqueous solutions of electrolytes and non-electrolytes by various methods and served as the basis for the development of salting-in – salting-out theories, which are reviewed in Refs. [2–5].

It follows from the Debye–Hückel theory that the smaller the cation radius, the more this electrolyte reduces the solubility of a non-electrolyte in water [2]. Indeed, many authors note that with an increase in the size of electrolyte ions, the salting-out effect decreases, and a switch to salting-in is observed. To explain this phenomenon, it is necessary to consider in more detail the processes occurring in aqueous electrolyte solutions with an increase in the size of ions and described by Samoilov in his monograph [6]. Ion hydration in solution can be divided into short-range and long-range. The former is the interaction of an ion with water molecules which make up the immediate environment of this ion in solution, and the latter is that with more distant water molecules. To explain the salting-in–salting-out phenomenon, one should first of all consider the short-range hydration, which characterizes the so-called kinetic properties of solutions. Short-range hydration is considered as the effect of

ions on the thermal, namely, translational movement of the nearest water molecules in the solution. Such hydration of ions can be quantitatively characterized by a change, under the action of ions, of the potential barrier (ΔE) separating the neighboring equilibrium positions of water molecules in the solution, in comparison with the value of the potential barrier for pure water. The values of ΔE depend on individual characteristics of the ions and can be either positive (meaning that the exchange of water molecules closest to the ions is difficult) or negative for different ions. In the latter case, water molecules become more mobile near ions than in pure water. This phenomenon is called negative hydration by Samoilov [6].

Krestov [7] has suggested using the total change in the entropy of water ΔS_{II} under the influence of a dissolved ion as a quantitative characteristic of the separation of ions into groups with positive ($\Delta S_{II} < 0$) and negative ($\Delta S_{II} > 0$) hydration. The author notes that the change in the thermodynamic properties of water upon the introduction of monatomic ions therein is associated with two contributions to the change in its structure. First, the interaction of an ion with water molecules leads to a violation of the mutual ordering of its molecules, which is characteristic of pure water. The disordering effect is observed, accompanied by an increase in entropy. Second, the stabilization of the structure of the solution is observed, which is accompanied by a decrease in its entropy (ordering effect). Accordingly, the resulting sign of the entropy change ΔS_{II} associated with structural changes in water depends on the predominant influence of one of these effects. The change in sign is determined by the size and charge of the ion, namely: the larger the radius and the smaller the charge of the ion, the larger the

value of ΔS_{II} becomes. Calculations show that the phenomenon of negative hydration is observed for K^+ , Rb^+ , Cs^+ , Fr^+ , Au^+ , Tl^+ , Br^- , I^- , At^- ions. For bivalent and more charged cations, the ordering effect always prevails over the disordering one. A number of large singly charged polyatomic ions also have negative hydration, namely: OCN^- , BH_4^- , $[Ag(CN)_2]^-$, NO_3^- , ClO_3^- , ClO_4^- , ReO_4^- , MnO_4^- , IO_4^- , BF_4^- , HSO_4^- , NH_4^+ [6–8].

Temperature is a powerful factor affecting the hydration of ions in aqueous and water–organic solutions [7]. Interesting results have been obtained for ions with negative hydration. With increasing temperature, the negative hydration of ions decreases, and above some limiting temperature T_{lim} , only positive hydration is observed, which increases with temperature. It is obvious that an increase in T_{lim} is facilitated by an increase in the radii of the ions and a decrease in the values of their charges. Such large ions as Cs^+ , I^- , ClO_4^- , IO_4^- become positively hydrated at temperatures above 60–95°C.

Krestov [7] has introduced a very important, in our opinion, concept of the critical temperature of solvation. This temperature is understood as the minimum temperature above which a positively solvated ion or a stoichiometric mixture of ions cannot be transferred to the region of negative solvation by changing the composition of the mixed solvent. Therefore, for any salt in an water–organic solution, there must be a well-defined temperature at which its ions, regardless of their size and charge, will always be positively solvated (hydrated). So, it can be assumed that any salt above a certain temperature will only have a salting-out effect. We have not found this hypothesis in the scientific literature.

It is known from the literature that the introduction of salts into binary liquid delaminating systems with an upper (UCST)

or lower (LCST) critical solution temperature leads not only to a change in the mutual solubility of the components, but also to a change in the parameters of the critical solution (composition and temperature). The Bancroft–Timmermans rule of thumb [9, 10] concerns the change in the UCST of binary systems upon the introduction of a third component and provides for two cases. According to the first case, the introduction of a third component into a binary liquid system, which is better soluble in one solvent than in another, increases the UCST of this binary system, i.e. reduces mutual solubility (salting-out). The greater the difference in the solubility of the third component in both solvents, the more the UCST increases. According to the second case, the introduction of a third component, which is approximately equally soluble in both solvents, lowers the UCST of the binary system, i.e. increases their mutual solubility (salting-in). Subsequently, this rule was thermodynamically substantiated [11].

No similar rule on the effect of the third component on critical parameters and mutual solubility has been formulated for binary systems with LCST. However, in Ref. [12] we find that the introduction of a third component into a binary liquid system with LCST, which is readily soluble in one solvent and almost insoluble in another, leads to a decrease in the critical solution temperature, i.e. decrease in the mutual solubility of components (salting-out). If the solubility of the third component in both solvents of the binary system with LCST does not differ too much, then the critical solution temperature increases, i.e. the mutual solubility of the components increases (salting-in).

In a number of works [13–15], the change in solubility, as well as the values of

UCST and LCST in water–organic solvent systems under the action of salts is discussed from the standpoint of the concept of homoselective and heteroselective solvation of their ions. If both salt ions (cation and anion) are solvated by the same component of the mixed solvent, then homoselective solvation takes place. If the cation is solvated predominantly by one of the components of the binary solvent, and the anion is by another, then heteroselective solvation occurs. Homoselective solvation leads to the salting-out effect of a salt, while heteroselective one leads to the salting-in effect.

The effect of additives of a number of 1.1-, 2.1-, 3.1-electrolytes in small concentrations (less than 0.02 molar fractions) on the UCST and LCST of binary systems with a closed binodal curve water–*n*-butoxyethanol and water–tetrahydrofuran was revealed [15]. The authors have found that an increase in the charge of the cation in the $\text{Me}^+ - \text{Me}^{2+} - \text{Me}^{3+}$ series leads to an increase in the salting-out effect, i.e. increasing the UCST and lowering the LCST of these systems. It was found that, in the $\text{Cl}^- - \text{Br}^- - \text{I}^- - \text{NO}_3^- - \text{ClO}_4^-$ series of singly charged anions, the salting-out effect decreases with increasing radius. The results obtained are discussed from the standpoint of the concept of homoselective and heteroselective solvation of ions. The authors identified three cases of the effect of dissolved electrolytes on the mutual solubility of the components of binary systems with a closed binodal curve. The introduction of a salt can: 1) increase the UCST and lower the LCST simultaneously; 2) increase the UCST and LCST; or 3) lower the UCST and increase the LCTR. In the first case, expansion of the delamination region is observed in the water – organic solvent systems; such salts have a salting-out effect. The introduction of iodides

and perchlorates leads to a shrinkage of the delamination field (third case), i.e. these salts are salting-in agents. When some salts are introduced, the delamination field shifts along the T vs x diagram to the region of higher temperatures (second case), i.e. such salts have a salting-in effect at low temperatures and a salting-out one at high temperatures.

Studies of the phase diagrams of ternary systems salt–two solvents, in which the salt can only have a salting-in or salting-out – salting-out effect, are few. In the literature, it was possible to find only few papers by Krupatkin et al. [16–20], devoted to studying of the effect of salts (salting-in–salting-out agents) on binary delaminating systems and the construction of phase diagrams of the resulting ternary systems.

There are many studies on the salting-out of aliphatic alcohols, pyridine, acetone, acetonitrile, and aliphatic amines from aqueous solutions. However, there are few ternary systems salt–two solvents, for which complete phase diagrams would have been plotted, their topological transformation with a change in temperature would have been studied, the temperature of the onset of delamination would have been determined, and the change in the UCST and LCST of the constituent binary liquid systems under the influence of salting-in and salting-out salts in a wide range of their concentrations and temperatures would be investigated. In the overwhelming majority, these are the works of scientists from the Saratov school of physicochemical analysis of multicomponent condensed systems, whose review is given in the monograph [5]. Using the method of topological transformation, we have developed twelve variants of the general scheme of the topological transformation of the phase diagrams of ternary systems salt–two solvents with a change in temperature

for cases when the constituent binary liquid system is characterized by UCST, LCST, a closed binodal curve or does not delaminate in the entire temperature range of its liquid state, and the salt has both salting-in and salting-out effects [5].

This work is devoted to the comparative characteristics of the salting-in–salting-out action of potassium formate, potassium nitrate and potassium perchlorate on the binary liquid system water–n-butoxyethanol in a wide temperature range.

2. CHARACTERISTICS OF THE BINARY LIQUID WATER–N-BUTOXYETHANOL SYSTEM

The solubility diagram of the binary water–n-butoxyethanol system is characterized by the presence of a closed binodal curve with lower (LCST = 47.7°C) and upper (UCST = 130.3°C) critical solution temperatures [21]. The phase diagram of this system is shown in **Fig. 1**. The diagram of the system is typical for binary ones with a closed delamination region: the separation field $\ell_1 + \ell_2$ (ℓ_1 is the organic phase, ℓ_2 the aqueous phase) is displaced towards the component capable

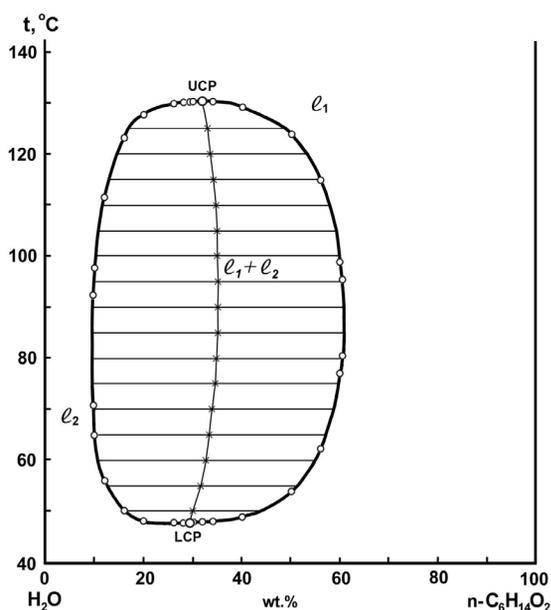


Fig. 1. Phase diagram of the binary water–n-butoxyethanol system in the range 40–140°C.

of strong association, i.e. water. The values of density and ultrasound velocity measured at 25, 40, and 55°C in the entire range of mixture compositions indicate the formation of clathrate-type structures between water and n-butoxyethanol molecules [22].

3. INFLUENCE OF POTASSIUM SALTS ON THE COORDINATES OF CRITICAL POINTS OF THE BINARY WATER–N-BUTOXYETHANOL SYSTEM AND THEIR SALTING-IN–SALTING-OUT EFFECT

For our study, we selected three potassium salts with a positive temperature coefficient of solubility in water, which form no crystal solvates in the studied temperature range, and are characterized by an increasing size of the anion. These are potassium formate, potassium nitrate, and potassium perchlorate with the following anion radii: 1.58 (HCOO⁻), 1.89 (NO₃⁻), 2.36 Å (ClO₄⁻) [7,23].

The results of studying the critical phenomena and topological transformation of the phase diagrams of the ternary systems potassium formate (nitrate, perchlorate) – water–n-butoxyethanol in a temperature range 10–150°C are presented in Refs. [24–26]. The dependences of the compositions of solutions corresponding to the critical liquid–liquid solubility points on temperature in two temperature ranges were established for each ternary system (**Figs. 2–4**). In the system with potassium formate, it was not possible to measure the formation temperature of the critical monotectic node, since the delamination did not disappear down to –30°C. The critical curves (**Fig. 2a**) begin at 24.7°C and end at the LCST (47.7°C) of the binary water–n-butoxyethanol system at the LCP (Lower Critical Point), which corresponds to the composition of its critical solution. In **Fig. 2b**, the critical curves begin at the UCST (130.3°C) at the UCP (Upper Critical Point),

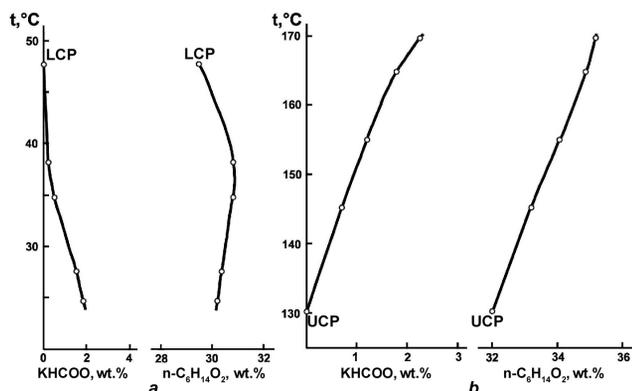


Fig. 2. Temperature dependences of the content of potassium formate and *n*-butoxyethanol in the critical solutions of the ternary potassium formate – water–*n*-butoxyethanol system in the ranges 24.7–47.7°C (a) and 130.3–169.8°C (b).

which corresponds to the composition of another critical solution of the binary water – *n*-butoxyethanol system.

In the ternary system with potassium nitrate, the critical curves (**Fig. 3a**) begin at the formation temperature of the critical node of monotectic equilibrium (18.3°C) at the critical end point corresponding to the composition of the liquid phase of the critical node KS (S being KNO_3), and ends at LCST at the LCP point corresponding to the composition of the critical solution of the binary liquid system. In **Fig. 3b**, the critical curves begin at the UCST at the UCP point, which corresponds to the composition of another critical solution of the binary liquid system.

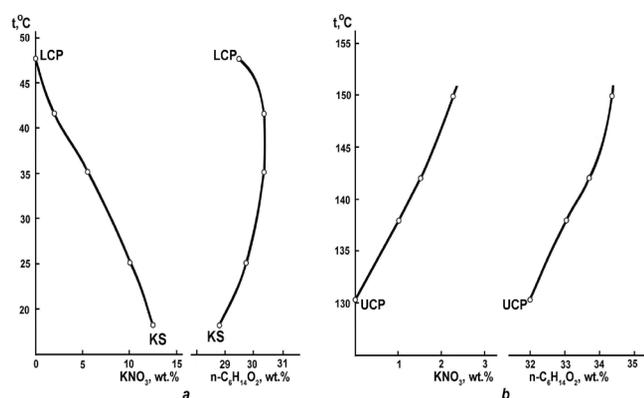


Fig. 3. Temperature dependences of the content of potassium nitrate and *n*-butoxyethanol in the critical solutions of the ternary potassium nitrate – water–*n*-butoxyethanol system in the ranges 18.3–47.7°C (a) and 130.3–150.0°C (b).

In general, the critical curves for the considered ternary systems are similar (**Fig. 2** and **3**). It can be seen that the introduction of potassium formate or potassium nitrate into the mixture of the critical composition of the water–*n*-butoxyethanol binary system leads to a decrease in the LCST and an increase in the UCST of this system. Therefore, potassium formate and potassium nitrate have a salting-out effect on mixtures of water and *n*-butoxyethanol at any temperature. It is known that alkali metal nitrates undergo homoselective solvation, i.e. both salt cation and anion are predominantly hydrated [13]. Such salts, as indicated in the Introduction, have a salting-out effect, they lower the LCST and increase the UCST of binary liquid systems [13–15]. It can be assumed that potassium formate in water–*n*-butoxyethanol solutions undergo homoselective solvation as well.

For the ternary system with potassium perchlorate, the shape of the critical curves is different (**Fig. 4**). In **Fig. 4a**, the critical curves begin at the LCST and end at the UCST of the binary water–*n*-butoxyethanol system at the LCP and UCP points corresponding to the compositions of the critical solutions of this system. In **Fig. 4b**, the curves of the critical

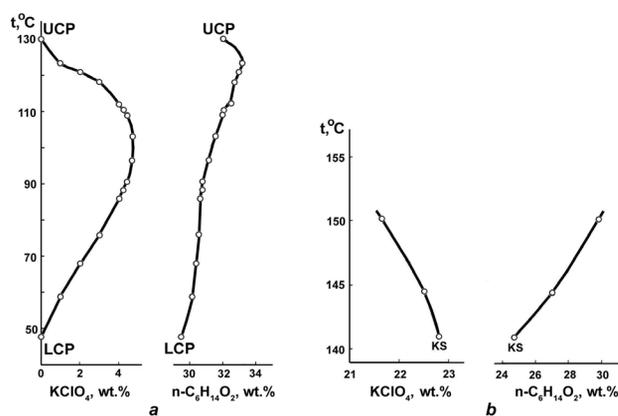


Fig. 4. Temperature dependences of the content of potassium perchlorate and *n*-butoxyethanol in the critical solutions of the ternary potassium perchlorate – water–*n*-butoxyethanol system in the ranges of 47.7–130.3°C (a) and 141.0–150.2°C (b).

points begin at the formation temperature of the critical node of monotectic state (141.0°C) at the end point corresponding to the composition of the liquid phase of the critical node KS (S being KClO_4). It can be seen from Fig. 4a that the introduction of potassium perchlorate into water–butoxyethanol solutions increases the LCST and lowers the UCST, i.e. promotes the mutual solubility of the components of the binary liquid system. Salting-in occurs under the action of the salt: when the salt content is above 5.8 wt%, delamination of mixtures of the components will not be observed at any mass water–n-butoxyethanol ratio in the temperature range from 40.0 to 141.0°C. It should be noted that, in the isothermal phase diagrams of the ternary system [26], in the temperature range 47.7–130.3°C, there is a delamination region adjacent to the concentration triangle side corresponding to the delaminating water–n-butoxyethanol system. As temperature rises, the salt solubility increases and at 141.0°C a critical monotectic node is formed and a small delamination region appears adjacent to a side of the monotectic triangle [26]. Thus, potassium perchlorate has a salting-out effect at high temperatures. The data obtained are consistent with the conclusions of Ref. [15], whose authors have found an increase in the LCST and a decrease in the UCST of this binary system with the addition of small amounts of sodium perchlorate.

The salting-in effect of potassium perchlorate is apparently associated with the large size of the perchlorate ion and, as a consequence, its negative hydration in aqueous and water–organic solutions. With increasing temperature, the negative hydratability of the perchlorate ion decreases and becomes positive above the critical solvation temperature, which is about 65°C for the perchlorate ion [7]. This leads to the appearance of weak salting-out

properties of potassium perchlorate at high temperatures.

4. DISTRIBUTION COEFFICIENTS OF N-BUTOXYETHANOL IN TERNARY SYSTEMS

The distribution coefficient K_D is a quantitative characteristic of the salting-out effect of a salt on water–organic mixtures. In each studied ternary system, the K_D of n-butoxyethanol was calculated as the ratio of its concentrations in the organic and aqueous phases of the monotectic state at a given temperature. The compositions of the liquid phases of monotectic state were found graphically from isothermal phase diagrams [24–26]. Fig. 5 shows the temperature dependence of the distribution coefficient of n-butoxyethanol in the systems “potassium formate (nitrate, perchlorate) – water–n-butoxyethanol”.

In the ternary systems with potassium formate in the range 25.0–150.0°C (curve 1, Fig. 5), with potassium nitrate in the range 18.3–150.0°C (curve 2), and with potassium

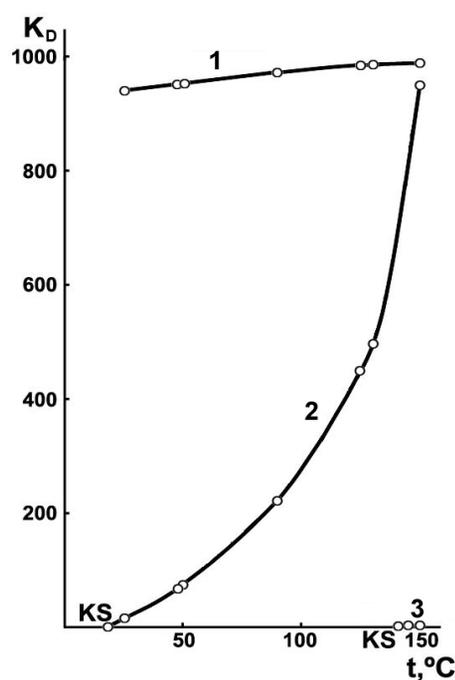


Fig. 5. Temperature dependence of the distribution coefficient of n-butoxyethanol in the ternary systems potassium formate (1), potassium nitrate (2), potassium perchlorate (3) –water–n-butoxyethanol.

perchlorate in the range 141.0–150.0°C (curve 3), the distribution coefficient increases with temperature. This is obviously due to the destruction of hydrogen bonds between water and *n*-butoxyethanol molecules and a significant increase in the salt concentration in the aqueous phase of the monotectic state [24–26]. It is seen from Fig. 5 that the K_D value in the system with potassium nitrate (curve 2) significantly increases with temperature ($K_D = 15.2$ at 25°C, $K_D = 949$ at 150°C). At the same time, the value of the distribution coefficient in the system with potassium formate changes little with temperature ($K_D = 941$ at 25°C, $K_D = 989$ at 150°C). This is explained by the higher temperature solubility coefficient of potassium nitrate than potassium formate. However, the distribution coefficient of *n*-butoxyethanol in the system with potassium formate already at 25°C is high, which indicates a strong salting-out effect of potassium formate in comparison with potassium nitrate. Fig. 6 shows the phase diagrams of the ternary systems with potassium formate and potassium nitrate at 25°C. It is clearly seen that the area of the delamination field $l_1 + l_2$ in the first diagram (Fig. 6a) is much larger than that in the second one (Fig. 6b), and the amount of potassium formate required for

the delamination of homogeneous water–*n*-butoxyethanol mixtures is significantly less than that of potassium nitrate. Potassium perchlorate causes no delamination in these mixtures at 25°C; even at 150°C, it has a very weak salting-out effect ($K_D = 3.0$).

Due to its high concentration in the aqueous phase of monotectic equilibrium at each temperature, potassium formate has a greater salting-out effect on water–*n*-butoxyethanol mixtures in comparison with potassium nitrate and, moreover, potassium perchlorate (Fig. 5). In addition, the salting-out effect in the $\text{KHCOO–KNO}_3\text{–KClO}_4$ row naturally decreases with an increase in the anion's radius. The organic phase in the system with potassium formate is significantly enriched in *n*-butoxyethanol, which allows it to be isolated from dilute aqueous solutions by adding this salt under normal conditions without using distillation.

5. CONCLUSION

The study of the effect of the salt nature and temperature on the liquid–liquid equilibrium in ternary salt–water–organic solvent systems is of great importance for the further development of the salting-in–salting-out theory and the

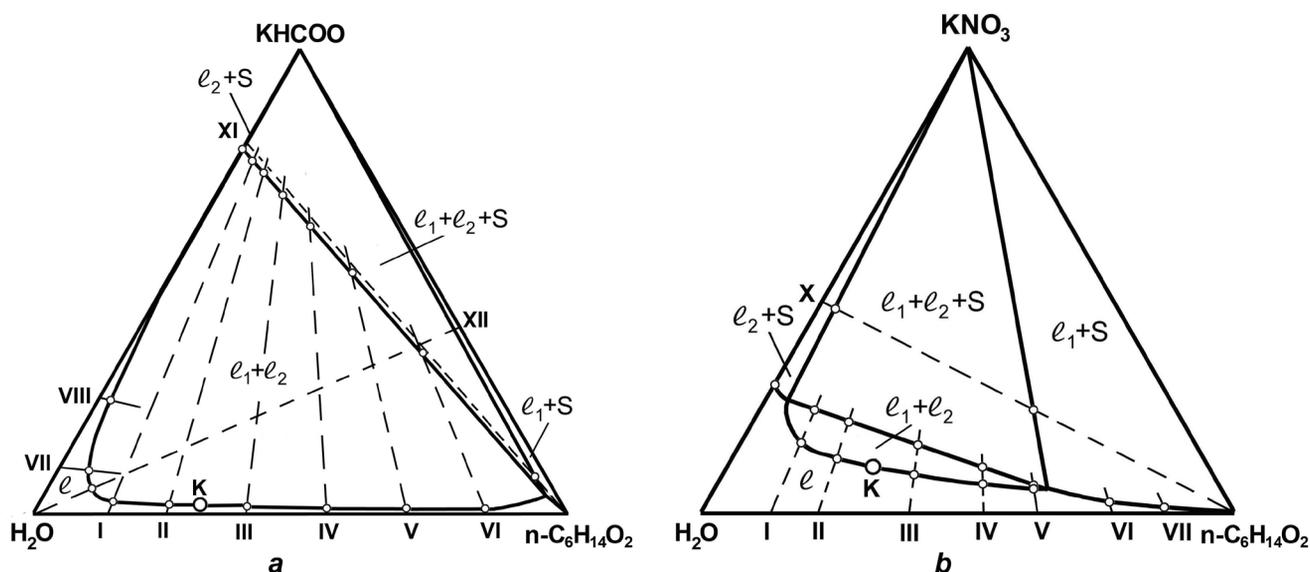


Fig. 6. Phase diagrams (wt%) of the ternary systems potassium formate – water – *n*-butoxyethanol (a) and potassium nitrate – water – *n*-butoxyethanol (b) at 25.0°C.

development of practical recommendations on the choice of salts for carrying out effective processes of selective extraction of organic solvents from aqueous solutions, and also the choice of solvents for extractive crystallization of salts in an optimal temperature range. Such studies make it possible to reveal the pattern of the topological transformation of the phase diagram of the system with a change in temperature, to establish the delamination onset temperature of and the dependence of the salting-in or salting-out effect on the nature of salt and temperature.

The concept of negative hydration of ions, which we have used, as a whole, successfully describes the salting-in effect of salts in heterogeneous liquid mixtures. An important result of our study was the conclusion that any salt at any temperature cannot have a salting-in effect only. The salting-in properties of a salt turn into its salting-out properties as temperature rises. The use of the concept of negative ion hydration is a necessary, but still insufficient condition for predicting the salting-in properties of a particular salt in a particular water–organic mixture. There is a need for a detailed polythermal study of the phase diagrams of systems with various salting-in salts. In addition, the use of the concept of negative and positive hydration of ions to explain the phase behavior of ternary systems “salt – two solvents”, in turn, requires a detailed study of the solvation of ions in water–organic solutions in wide ranges of concentrations and temperatures.

REFERENCES

1. Kuznetsov NT, Danilov VP, Zlomanov VP, Fedorov PP, Garkushin IK, Il'in KK, Drobot DV, Mazunin SA. *Terminology of physical and chemical analysis*. Moscow, LENAND Publ., 2017, 48 p.
2. Sergeyeva VF. Salting-out and salting-in of non-electrolytes. *Advances in Chemistry*, 1965, 34(4): 717–733.
3. Konnik EI. Salting-out – salting-in of gaseous non-electrolytes in aqueous solutions of electrolytes. *Advances in Chemistry*, 1977, 46(6):1097–1121.
4. Long FA, McDevit WF. Activity coefficients of nonelectrolyte solutes in aqueous salt solutions. *Chem. Rev.*, 1952, 51(1):119–169.
5. Il'in KK, Cherkasov DG. *Topology of phase diagrams of the ternary systems salt – two solvents with salting-in – salting-out*. Saratov, Sarat. University Publ., 2020, 212 p.
6. Samoilov OYa. *Structure of aqueous solutions of electrolytes and hydration of ions*. Moscow, AN SSSR Publ., 1957, 182 p.
7. Krestov GA. *Thermodynamics of ionic processes in solutions*. Leningrad, Khimiya Publ., 1984, 272 p.
8. Solovkin AS. Influence of the nature of anions on the structure of water. *Russ. J. Struct. Chemistry*, 1968, 9(2):305–306.
9. Bancroft WD. On ternary mixtures. *Phys. Rev.*, 1895, 3(1):21–33.
10. Timmermans J. Die kritische loesungstemperatur von ternaerengemengen. *Z. Phys. Chem.*, 1907, 58:129–213.
11. Prigogine I, Defay R. *Chemical thermodynamics*. Longmans Green & Co, London, New York, Toronto, 1954, 543 p.
12. Anosov VYa, Pogodin SA. *Basic principles of physicochemical analysis*. Moscow-Leningrad, AN SSSR Publ., 1947, 876 p.
13. Moollel M, Schneider H. Phase separation phenomena in ternary systems and selective solvation. *Z. Phys. Chem. (Frankfurt/Main)*, 1971, 74(3–6):237–247.
14. Gordon JE. *The Organic Chemistry of Electrolyte Solutions*. John Wiley and Sons, New York, London, Sydney, Toronto, 1975.

15. Erol M, Kocak M, Richter P, Steiger A, Becker F. The influence of dissolved electrolytes on the miscibility of binary liquid systems with closed miscibility gaps. *Ber. Bunsenges. Phys. Chem.*, 1987, 91(7):731-737.
16. Vorobieva LD, Krupatkin IL. Study of the action of sodium, potassium and ammonium thiocyanates on the water–triethylamine system. In: *Phase equilibria*. Kalinin, Kalinin University Publ., 1974, pp. 18–24.
17. Vorobieva LD, Krupatkin IL. Investigation of the equilibrium of liquid and solid phases in the systems water–aniline–sodium, potassium and ammonium thiocyanate. In: *Phase equilibria*. Kalinin, Kalinin University Publ., 1974, pp. 26–31.
18. Vorobieva LD, Krupatkin IL. Study of the effect of sodium and potassium thiocyanates on the water–phenol system at 45°C. In: *Phase equilibria*. Kalinin, Kalinin University Publ., 1974, pp. 32–36.
19. Maskhulia VP, Krupatkin IL. Investigation of salting-out – salting-in of aqueous solutions of furfural with sulfates and nitrates. In: *Phase equilibria*. Kalinin, Kalinin University Publ., 1975, 2:29–34.
20. Maskhulia VP, Krupatkin IL. Investigation of salting-out – salting-in of furfural solutions with iodides and bromides. In: *Phase equilibria*. Kalinin, Kalinin University Publ., 1975, 2:35–40.
21. Cherkasov DG, Smotrov MP. Mutual solubility of the components of the binary water–n-butoxyethanol system. *Chemical Sciences-2006, Coll. scientific. proc.* Saratov, Nauchnaya knuga Publ., 2006, 3:135–138.
22. Rao NP, Verrall RE. Ultrasonic velocity, excess adiabatic compressibility, apparent molar compressibility properties of binary liquid mixtures containing 2-butoxyethanol. *Can. J. Chem.*, 1987, 65(4):810–816.
23. Yatsimirsky KB. *Thermochemistry of complex compounds*. Moscow, AN SSSR Publ., 1951, 251 p.
24. Smotrov MP, Cherkasov DG, Il'in KK. Topological transformation of the phase diagram of the ternary potassium formate–water–n-butoxyethanol system. *Izvestiya of Saratov University. New Series. Series: Chemistry. Biology. Ecology*, 2010, 10(2):14–19.
25. Cherkasov DG, Smotrov MP, Il'in KK. Topological transformation of the phase diagram of the ternary potassium nitrate–water –n-butoxyethanol system. *Zhurn. fizich. khimii.*, 2010, 84(6):1030-1035 (in Russ.).
26. Cherkasov DG, Smotrov MP, Il'in KK. Phase equilibria and critical phenomena in the ternary potassium perchlorate–water–n-butoxyethanol system. *Zhurn. fizich. khimii.*, 2011, 85(4):667-674 (in Russ.).