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BRIEF COMMUNICATIONS

Salting out of Butyric Acid from Aqueous Solutions with Potassium Chloride

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Abstract—Visual-polythermic method was used to study the solubility of the components and critical phenomena in the ternary system constituted by potassium chloride, water, and butyric acid in the temperature range 5–80°C. The temperature dependence of the solution compositions corresponding to the critical solubility points was determined. The isothermal solubility diagrams of the system were constructed. The distribution coefficients of butyric acid at 5, 25, 50, and 80°C were calculated.

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Butyric acid and its aqueous solutions are widely used in treatment of rare-earth elements to remove alkaline-earth metals (magnesium, calcium, strontium, and barium), in decalcification of leather, perfume manufacture, synthesis of aromatic principles in food industry, and in production of plasticizers for lacquers and emulsifiers [1].

The introduction of the third substance, for example, salting out agent, into the binary homogeneous system constituted by water and butyric acid considerably changes its phase behavior [2, 3]. To our knowledge, only one study concerning the effect of sodium chloride on the water-butyric acid binary system at 25°C is available [4]. The introduction of the salt caused system to separate onto two liquid phases. In [4], the solubility of the components in the ternary system was determined by the method of isothermal titration, the compositions of coexisting liquid phases in the stratification region were found by analytical method, the isothermal phase diagram of the system was constructed, and the coordinates of the critical point in the stratification region were found approximately. It was pointed out that a homogeneous mixture of water and butyric acid becomes stratified in the presence of even minor amounts of the salt.

Thus, data on the effect exerted by salts on the water-butyric acid binary system are lacking from the literature and the temperature dependence of phase behavior in the ternary system constituted by salt, water, and butyric acid is unknown.

In the present study, the phase equilibria and critical phenomena in the ternary system constituted by potassium chloride, water, and butyric acid in the temperature range 5–80°C were analyzed in order to reveal the dependence of its phase behavior on the salting out ability and temperature. The above system has not been studied previously.

EXPERIMENTAL

The solvents (water and butyric acid of chemical purity grade) used in the study were thoroughly purified [5]. A potassium chloride preparation of chemical purity grade was dried as described in [6]. Preparations of butyric acid and salt were placed in the exciccators protected from a direct exposure to light and kept over calcined potassium chloride.

The phase equilibria in the mixtures of the components of the $KCl–H_2O–C_4H_8O_2$ ternary system were studied in glass ampoules under vapor pressure using the visual-polythermic method [7].

The solution compositions corresponding to the critical solubility points were found by the method of phase volume ratio [8]. The necessary temperature was maintained constant to within ±0.1°C with a Lauda A-

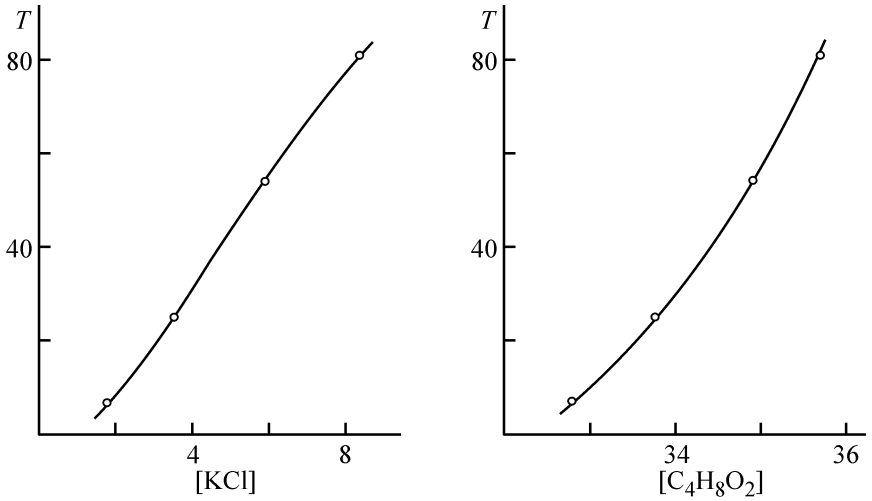

Fig. 1. Content (wt %) of KCl and $[C_4H_8O_2]$ in the potassium chloride-butyric acid system vs. temperature T(°C).

100°C thermostat and measured with calibrated decimal mercury thermometers with the same accuracy. The equilibrium solid phase was identified by the thermal and X-ray phase analyses. At all temperatures, the solid phase of saturated solutions and monotectic corresponded to the composition KCl. The method used to process the results of the polythermic analysis and to construct isothermal phase diagrams of the ternary systems was described in [7]. The relative error in determining the mixture compositions corresponding to the phase transition points at the chosen temperature was ±0.5–1.0%.

The KCl–H_2O–$C_4H_8O_2$ ternary system under study is constituted by three binary systems. The binary system water-butyric acid is homogeneous over the entire temperature range of the liquid state and belongs to eutectic systems [2]. The eutectic point lies at 32.5 mol % water and –12.5° C. The phase diagram of the water-butyric acid system has a gently sloping curve of the ice crystallization extending over a wide range of compositions, to about 70 mol % water. According to [3], this system has a metastable stratification region with the upper critical dissolution temperature (–3°C) corresponding to 39 wt % of butyric acid. Over the stratification region, the ice crystallization curve has a large nearly horizontal plateau at –2°C. Above this temperature in the stable region (homogeneous solutions), Krupatkin et al. [3] considered the system to be in a close stratification, i.e., microheterogeneous, state.

In the water-potassium chloride ternary system, two three-phase invariant states, peritectic and eutectic, are realized [9]. A forming potassium chloride crystal hydrate of composition KCl · H_2O [10] melts incongruently at –6.6°C. The eutectic equilibrium of the system, whose solid phases are ice and KCl. H_2O, is at –10.8°C. Dissolution of anhydrous potassium chloride in the system is

Table 1. Solubility of the components in the ternary system constituted by potassium chloride, water, and butyric acid

T, °C	Composition of saturated solution, wt %					
	KCl	H_2O	$C_4H_8O_2$	KCl	H_2O	$C_4H_8O_2$
5.0	22.9	77.1	0.0	1.7	55.0	43.3
	11.0	80.1	8.9	1.7	43.3	55.0
	2.6	77.9	19.5	1.6	30.5	67.9
	1.7	66.8	31.5	1.6	22.6	75.8
	1.7[a]	65.6[a]	32.7[a]			
25.0	26.4	73.6	0.0	3.2	54.2	42.6
	10.9	80.2	8.9	2.6	42.9	54.5
	4.6	76.2	19.2	2.4	30.2	67.4
	3.5	65.6	30.9	2.3	21.5	76.2
	3.5[a]	62.7[a]	33.8[a]			
50.0	30.0	70.0	0.0	4.8	53.3	41.9
	12.6	78.7	8.7	3.5	42.5	54.0
	7.2	74.2	18.6	3.1	30.1	66.8
	5.8	64.2	30.0	3.0	21.3	75.7
	5.5[a]	59.7[a]	34.8[a]			
80.0	33.9	66.1	0.0	7.0	52.1	40.9
	16.7	75.0	8.3	5.4	41.6	53.0
	11.2	71.0	17.8	4.1	29.7	66.2
	9.1	61.8	29.1	3.9	21.2	74.9
	8.3[a]	56.0[a]	35.7[a]			

[a] Critical solubility point

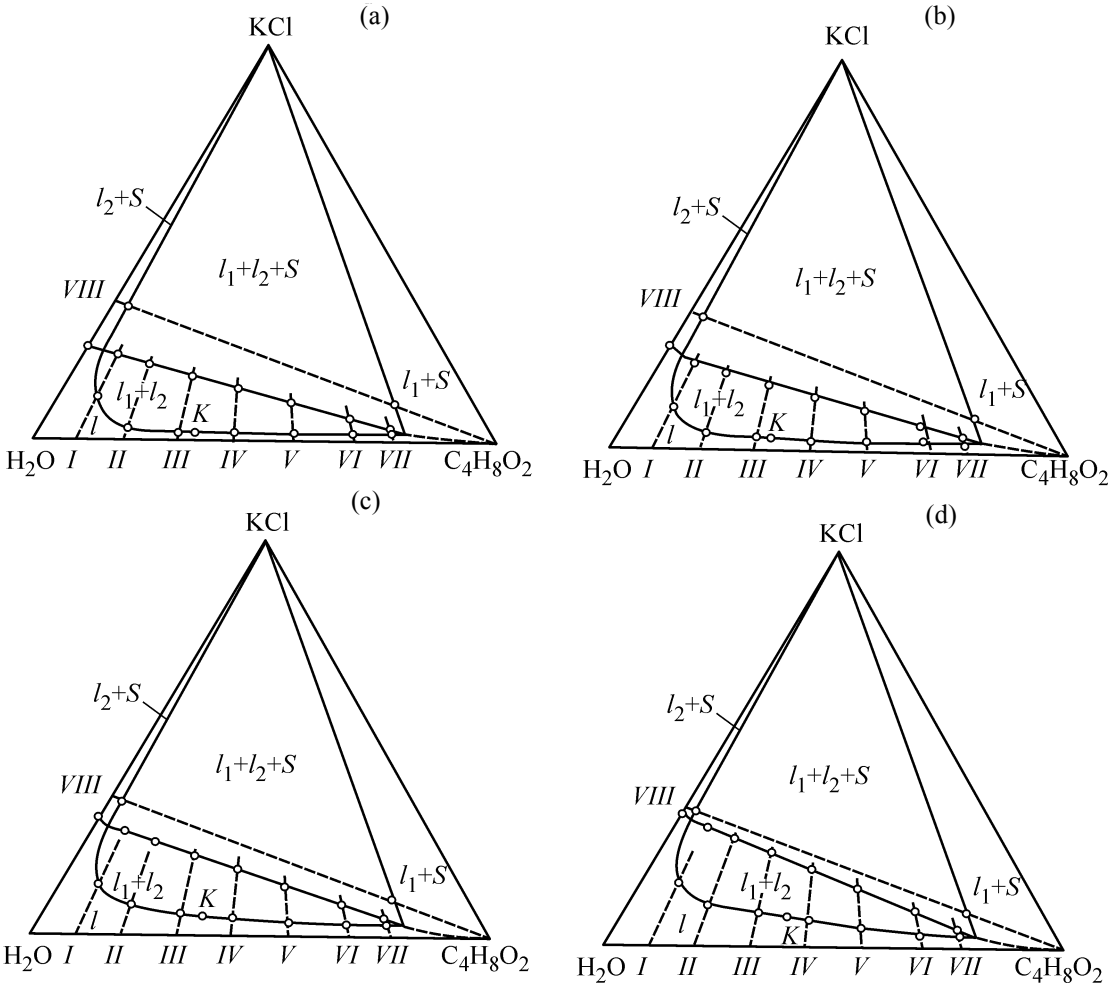

Fig. 2. Isotherms of the phase states (wt %) of the system constituted by potassium chloride, water, and butyric acid at (a) 5.0, (b) 25, (c) 50, and (d) 80°C.

observed above −6.6°C and increases with temperature. The boiling temperature of a saturated solution at the salt concentration 36.5 wt % is 108.5°C [11].

No quantitative data was found on the solubility of potassium chloride in butyric acid. The performed study showed that this salt is virtually insoluble in the above solvent.

The compositions of the three-component mixtures were varied along eight sections of the concentration triangle of the system under study. The component mixtures for sections *I*–*VII* had a variable content of potassium chloride and constant mass ratio between butyric acid and water: (*I*) 10 : 90, (*II*) 20 : 80, (*III*) 32 : 68, (*IV*) 44 : 56, (*V*) 56 : 44, (*VI*) 69 : 31, and (*VII*) 78 : 22 . The component mixtures for section *VIII* had a varied content of butyric acid and constant mass ratio between the salt and water (35 : 65). In the component mixtures, the following phase states were found: homogeneous-liquid, two liquid-phase, monotectic, and equilibrium between the liquid phase and salt crystals.

The temperature dependence of the solution composition corresponding to the critical solubility points in the stratification region was determined. To do this, we studied the component mixtures along four additional sections having a variable content of the salt and constant mass ratio between the acid and water. Temperature dependences of the content of potassium chloride and butyric acid in critical solutions are shown in Fig. 1. As temperature raises, the content of the salt and acid in critical solution increases.

The method of graphical interpolation was used to determine, from the polytherms of the phase states, critical curves (Fig. 1), and data on the solubility of potassium chloride in water [12], the mixture compositions

Table 2. Liquid-phase compositions of the monotectic equilibrium and the distribution coefficients K_d of butyric acid in the ternary system constituted by potassium chloride, water, and butyric acid

T, °C	Composition of liquid phases at equilibrium with solid KCl, wt %,						K_d
	Aqueous phase			Organic phase			
	KCl	H_2O	$C_4H_8O_2$	KCl	H_2O	$C_4H_8O_2$	
5.0	22.8	73.1	4.1	1.6	18.9	79.5	19.4
25.0	23.8	72.6	3.6	2.3	18.1	79.6	22.1
50.0	27.7	69.4	2.9	2.9	17.4	79.7	27.4
80.0	32.3	65.5	2.2	3.0	17.1	79.9	36.3

corresponding to the phase transition points at 5.0, 25.0, 50.0, and 80.0°C. The results of determination of the component solubility of the system are listed in Table 1.

The isotherms of the phase states in the ternary system at 5.0, 25.0, 50.0, and 80.0°C are shown in Fig. 2. A monotectic triangle $l_1 + l_2 + S$, to which fields of the saturated solutions, $l_1 + S$ and $l_2 + S$, and the stratification field $l_1 + l_2$ with the critical point K are adjacent, and a field of the homogeneous liquid state l adjacent to the triangle side H_2O–$C_4H_8O_2$ are present on the concentration triangle at all temperatures. The change in temperature does not affect the qualitative character of the isotherms of phase states of the system: the sizes of all fields vary only slightly. As temperature is decreased, the stratification field with the critical point K approaches the triangle side corresponding to the water-butyric acid binary system. Evidently, the above binary system behaves as a system with the upper critical solubility point lying in a low temperature region [13]. This result is consistent with a conclusion that the given binary system has a metastable region of stratification with the upper critical dissolution temperature [3, 4].

The salting out of butyric acid from its aqueous solutions with potassium chloride was estimated at quantitative level from the temperature dependence of the distribution coefficient K_p of butyric acid between equilibrium liquid phases of the monotectic composition.

The distribution coefficients K_d of butyric acid were calculated as the relative acid concentration in the organic and aqueous phase of the monotectic equilibrium. The results of the calculation at various temperatures are listed in Table 2. Increase in the distribution coefficient with temperature shows that the effect of salting out of the acid from aqueous solutions with potassium chloride becomes stronger. Evidently, this results from the decomposition of butyric acid hydrates and the increase in the salt concentration in the aqueous phase. The results obtained indirectly confirm conclusions of [3, 4] that the water-butyric acid binary system above –2°C is in the closed stratification state: its mixtures are microheterogeneous and easily decompose onto two liquid phases in the presence of a minor amount of salting out agent.

CONCLUSIONS

(1) The phase equilibria for the component mixtures along eight sections of the composition triangles of the ternary system constituted by potassium chloride, water, and butyric acid were studied. The following phase states were found: homogeneous-liquid, liquid-liquid, monotectic, and equilibrium between the liquid phase and the salt crystals. The solution composition corresponding to the critical solubility point in the stratification region was determined as function of temperature.

(2) The isotherms of phase equilibria in the ternary system at 5.0, 25.0, 50.0, and 80.0°C were constructed. The distribution coefficients of butyric acid between equilibrium liquid phases of the monotectic at the above temperatures were calculated. As temperature is elevated, the distribution coefficient increases, i.e., the ability of potassium chloride to salt out butyric acid from aqueous solution increases.

(3) A polythermic study of the solubility diagram of the ternary system constituted by potassium chloride, water, and butyric acid yielded results that can be used in extractive practice and as reference data.

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