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OF SOLUTIONSSolubility Diagrams of the Potassium Iodide–Water–Ethanol
and Iodine–Water–Ethanol Ternary SystemsT. M. Varlamova, E. M. Rubtsova, and S. P. Mushtakova
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Abstract—The solubility of potassium iodide and iodine in water–methanol mixed solvents was studied by the method of sections at 25°C and atmospheric pressure. The solubility of potassium iodide was found to decrease as the content of ethanol in aqueous-alcoholic solutions increased. The solubility of crystalline iodine had a complex dependence on mixed solvent composition; it was maximum in mixtures containing 90 wt % alcohol. The compositions of the solid phases that crystallized in the KI–H₂O–C₂H₅OH and I₂–H₂O–C₂H₅OH systems were substantiated by X-ray measurements.

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INTRODUCTION

Pure solvents are largely used to extract iodine from various objects and develop fairly sensitive methods for its determination. In practice, the use of aqueous-organic mixtures is a more promising approach; it opens up fundamentally new possibilities for selecting optimum media with the required properties. Among aqueous-organic solvents, aqueous solutions of monohydric alcohols have been studied fairly thoroughly [1–3].

In [4–7], we studied the solubility of iodine in the presence of potassium iodide in pure solvents (water and propanol-2) and the solubility of potassium iodide (iodine) in water–propanol-2 mixtures and selected the mixed solvent with the highest iodine solution ability. This work continues studies of phase equilibria in potassium iodide (iodine)–water–alcohol systems. Our purpose was to measure the solubility of potassium iodide and iodine in water–ethanol mixed solvents by the method of sections [8] at 25°C and atmospheric pressure.

Handbooks contain data on the solubility of potassium iodide and iodine in water–ethanol mixtures. However, either these data were obtained at 25°C over a narrow concentration range [9], or information about the duration of and the methods for controlling the establishment of thermodynamic equilibria in systems was absent [10]. The reliability of the solubility values obtained is therefore questionable.

EXPERIMENTAL

Crystalline iodine that we used was of farm. (pharmacological) grade (the content of the major component 99.7%) and was not subjected to additional purification. Potassium iodide of kh. ch. (chemically pure)

grade was purified as described in [4]. The absence of water was controlled by thermogravimetry. Ethanol of kh. ch. grade was not additionally purified. The content of water in ethanol was determined by coulometric titration according to Fischer [11] and by chromatography with an Agilent 6974N mass spectrometric detector. It was 3.80 wt %, which was taken into account in the preparation of mixtures. We used doubly distilled water. The solvents were identified by measuring their boiling points and refractive indexes.

The solubility of the KI–H₂O–C₂H₅OH and I₂–H₂O–C₂H₅OH ternary system components at 25°C was determined from the isothermal diagrams composition–property of the liquid phase of the mixture of the components. For this purpose, the necessary amounts of ternary mixtures were gravimetrically prepared in ampules in both homogeneous and saturated states. The ampules were sealed and held in a thermostat with periodically shaking them until equilibrium was established. The property measured was refractive index in the KI–H₂O–C₂H₅OH system and optical density in the I₂–H₂O–C₂H₅OH system (these solutions intensely absorbed light in the visible range). The criterion of the establishment of equilibrium was reproducibility of the results of liquid phase (saturated solution) property measurements made in various time intervals. We found that equilibrium between the liquid and solid phases was established in a week in the KI–H₂O–C₂H₅OH system and in 2–4 months in the I₂–H₂O–C₂H₅OH system. The refractive index of solutions was measured on an IRF-22 refractometer. For optical density measurements, an aliquot of a solution was dissolved with either ethanol (sections VII–IX) or the corresponding aqueous–ethanolic mixture (sections I–VI). The optical density of the liquid

phase (I_2 – H_2O – C_2H_5OH mixture components) was measured on a KFK-3 photoelectrocolorimeter in cells 1 or 0.3 cm thick at $\lambda = 530$ nm. The relative error in solubility values was ± 0.5 – 1.0% .

The X-ray patterns of the solid phases at equilibrium with saturated solutions were obtained on a DRON-3 diffractometer, $CuK\alpha$ radiation. Interplanar distances were determined using the tabulated data [12].

RESULTS AND DISCUSSION

The $KI(I_2)$ – C_2H_5OH , $KI(I_2)$ – H_2O , and H_2O – C_2H_5OH binary systems constitute the potassium iodide (iodine)–water– C_2H_5OH ternary system. The solubilities of the salt and iodine in pure solvents were taken from [4, 10, 13]. The H_2O – C_2H_5OH binary system is a Timmermans system. This means that it is homogeneous over wide temperature and concentration ranges. We must, however, expect a decrease in the mutual solubility of water and alcohol when a third component is introduced [6]. Monohydric alcohols are known to dissolve in water in large amounts because of the formation of strong H-bonds with water molecules. According to [1], the concentration dependences of the properties of aqueous solutions of aliphatic alcohols can be used to identify three regions of structures: water, mixed aqueous-alcoholic, and alcohol structures. It was found in X-ray structure studies [2] that, in the region of low alcohol concentrations, the tetrahedral structure of water was retained. In the region of medium monohydric alcohol concentrations, we observe a continuous transition from the structure of water to the structure of the alcohol, and, at high alcohol concentrations, the structure of the alcohol with water molecules incorporated into it predominates.

The structure of aqueous-alcoholic solutions was studied quantum-chemically [3]. A possible structure of such solutions was suggested, and quantum-chemical calculations of a possible structure of water–alcohol associates were performed. It was shown that the addition of methanol to water decreased interlayer distances compared with pure water. Interlayer distances gradually increased as the size of the alkyl radical grew; that is, bulkier alcohol molecules caused destructuring accompanied by more substantial rearrangements of the spatial distribution of molecules in local water formations [3].

To study the influence of a third component on the mutual solubility in the water–ethanol system, we measured the solubility of the components of the KI – H_2O – C_2H_5OH and I_2 – H_2O – C_2H_5OH systems by the method of sections at $25^\circ C$. The solubility diagram of the KI – H_2O – C_2H_5OH system was constructed by studying component mixtures along three concentration triangle sections with variable salt contents and constant ratios between water and alcohol masses, namely, 75 : 25 (I), 50 : 50 (II), and 25 : 75 (III)

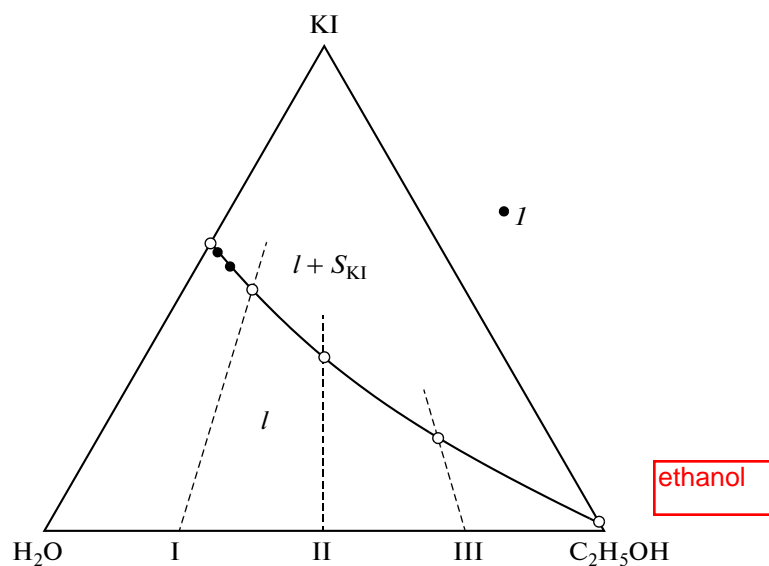


Fig. 1. Solubility diagram of the KI – H_2O – C_2H_5OH ternary system at $25^\circ C$; (I) solubility data from [9].

(Fig. 1). Component mixtures along these sections were either homogeneous solutions (I) or solutions saturated with respect to potassium iodide ($I + S_{KI}$).

These data were used to construct functional curves describing the dependence of the refractive index of liquid component mixtures on the content of potassium iodide (figures are not given). The intersection points of functional curve branches were used to draw the solubility line on the composition triangle of the potassium iodide–water–ethanol system (Fig. 1). This line is continuous, which corresponds to the crystallization of only one solid phase (potassium iodide) in the system. Figure 1 shows that the solubilities of potassium iodide in water–ethanol mixtures reported in [9] closely agree with our experimental data. We revealed a monotonic decrease in the solubility of potassium iodide as the content of ethanol in mixed solvents increased. This conclusion coincides with the results obtained in studies of the solubility of potassium iodide in water–alcohol (methanol, isopropanol, and *tert*-butanol) mixtures [7, 14].

The iodine–water–ethanol phase diagram was obtained by studying component mixtures along nine sections (Fig. 2). Component mixtures of the first six sections had variable water–alcohol mixture and constant iodine contents. Component mixtures of sections VII–IX had variable iodine contents and constant water : ethanol mass ratios.

The functional curves of the dependence of the optical densities of liquid component mixtures on the concentrations of iodine (sections I–VI) and ethanol (sections VII–IX) are similar. By way of example, the functional curves of sections IV, VIII, and IX are shown in Fig. 3. They consist of two branches corresponding to

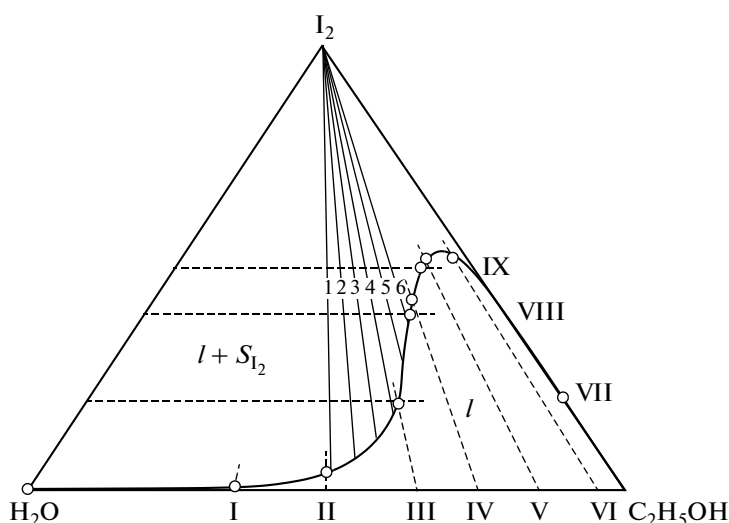


Fig. 2. Solubility diagram of the I_2 - H_2O - C_2H_5OH ternary system at 25°C.

component mixture states homogeneous (l) and saturated with respect to iodine ($l + S_{I_2}$). The functional curves of the first six sections contain horizontal regions characterized by constant values of optical density for each section (Fig. 3a). According to the method of sections [8], this can be explained by the coincidence of sections I–VI with saturated solution field nodes with pure iodine as the solid phase. The functional curve branches of sections VIII and IX corresponding to component mixture states monosaturated with respect to iodine ($l + S_{I_2}$) coalesced into one curve (Fig. 3b) with a monotonic decrease in the optical density of the liquid phase of component mix-

tures as the content of water in them increased. This is one more evidence that all the nodes of this saturated solution field coincide with secants from the concentration triangle vertex corresponding to iodine. The construction of nodes 1–6 fully substantiated this conclusion.

The intersection points of functional curve I–IX branches were used to construct the solubility line on the composition triangle. This line separates the field of homogeneously-liquid solutions from the iodine crystallization field (Fig. 2). The figure shows that the solubility of iodine has a complex dependence on the content of ethanol in mixed solvents. The solubility of iodine monotonically increases in mixtures containing 35–65 wt % ethanol and sharply increases from 20 to 52.5 wt % in mixtures containing more than 65 wt % ethanol. This can be explained by structural reasons. According to [1–3], mixed solvents have the structure of the alcohol with incorporated water molecules in this region of concentrations. In addition, Mikhailov et al. [10], who studied the solubility of iodine in aqueous-alcoholic solutions, showed that iodine had a destructuring action on the framework of water, and the strength of this action increased as the content of ethanol in water–ethanol mixtures grew (this was substantiated in calculations of the enthalpy and entropy of transfer of iodine from water into mixed solvents).

The compositions of the solid phases that crystallized in the KI - H_2O - C_2H_5OH and I_2 - H_2O - C_2H_5OH systems were substantiated by the X-ray data.

The experimental data on the solubility of the I_2 - H_2O - C_2H_5OH system components listed in the table differ substantially from those obtained in [10]. In addition, note that we did not observe stratification in the I_2 - H_2O - C_2H_5OH system, as distinct from the I_2 - H_2O - $2-C_3H_7OH$ system. It is known that the

Solubility of I_2 - H_2O - C_2H_5OH system components at 25°C

Saturated solution composition, wt %		
I_2	H_2O	C_2H_5OH
0.03	99.97	—
0.63	64.59	34.78
4.30	47.85	47.85
19.60	28.14	52.26
20.00	27.36	52.64
40.00	15.42	44.58
41.20	14.70	44.10
50.00	8.15	41.85
52.20	7.17	40.63
52.50	2.37	45.13
21.00	—	79.00

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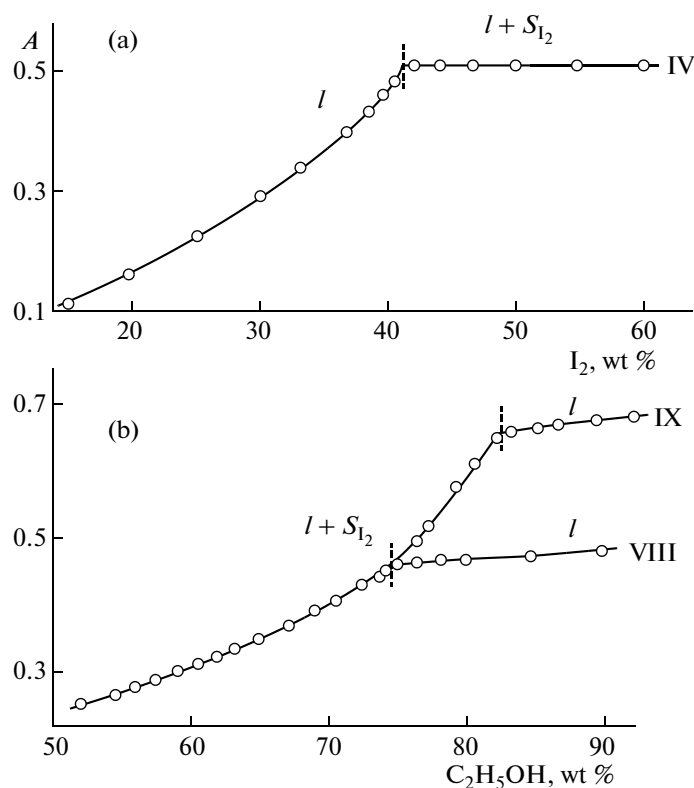


Fig. 3. Dependences of the optical density (A) of the liquid phase on the contents of (a) iodine and (b) ethanol in component mixtures along sections IV, VIII, and IX.

polarity of solvents decreases in the series of monohydric alcohols [15], and the salting out phenomenon observed in the system with isopropanol is likely caused by a decrease in the strength of intermolecular H-bonds between mixed solvent components.

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