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Abstract

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ON THE INTERACTION OF TRI-*n*-BUTYL PHOSPHATE WITH NITRIC ACID AND WATER

Tri-*n*-butyl phosphate $(C_4H_9O)_3PO$ has found wide application as an extractant for the recovery of uranium and a number of other elements (^{1}). Extraction is often carried out in a nitric-acid medium, and investigation of the interaction of tributyl phosphate (TBP) with nitric acid is of definite interest. According to data from a number of authors, after saturation of TBP with aqueous solutions of nitric acid, the compound $TBP \cdot HNO_3$ is present in the organic phase ($^{2-15}$), its formation being expressed by the equation

$$H^+_{aq} + NO^-_{3\,aq} + TBP_{org} \rightleftharpoons TBP \cdot HNO_{3\,org}.$$

The equilibrium constant is close to 0.2 ($^{2-4}$). The best agreement with the data on the formation of the 1 : 1 compound was obtained for an organic phase that is a dilute solution of TBP in inert organic solvents—benzene (^{2}), kerosene (^{3,8}), carbon tetrachloride (^{6}). It proved that the value of the constant depends on the nature of the diluent (^{12}). As the concentration of HNO_3 in the aqueous phase is increased, its absolute amount in the equilibrium organic phase increases. This is explained either by the formation of other compounds richer in nitric acid (^{2,3}), for example $TBP \cdot 2HNO_3$ (^{4,5}), $TBP \cdot 3HNO_3$ (^{13}), $TBP \cdot 4HNO_3$ (^{14}), or by dissolution in the organic phase of acid in excess of the composition of the 1 : 1 compound (^{2,3,8}). In a mixture of TBP and 100% nitric acid, the formation, by the IR-spectroscopy method, of only the 1 : 1 compound (^{15}), which also exists in solutions of TBP and HNO_3 in CCl_4 (^{6,13}), has been shown.

In equilibrium with aqueous solutions of nitric acid, the presence in the organic phase of $TBP \cdot HNO_3 \cdot H_2O$ compounds is also assumed for dilute solutions (^{3,7,15}) and, for solutions more concentrated in acid, of the compound $TBP \cdot 2HNO_3 \cdot H_2O$ (^{6}); there is also another opinion (^{16}). In these latter assumptions, the existence of the compound $TBP \cdot H_2O$ (^{3,7}), the formation of which in a mixture of TBP with H_2O (^{15}) and in the ternary system H_2O—TBP—C_6H_6 (^{17,18}) has been characterized in sufficient detail, is taken as a premise. The equilibrium constant of the reaction

Fig. 1. Properties of the liquid phase of the TBP—HNO_3 system.

Figure 1: Fig. 1. Properties of the liquid phase of the TBP—HNO_3 system.

$$H_2O + \mathrm{TBP} \rightleftharpoons \mathrm{TBP} \cdot H_2O$$

is equal to 14.4 ± 0.2 (^{17}).

We considered it advisable to study, by some properties of the liquid phases of the systems TBP—HNO_3, TBP—H_2O, and TBP—HNO_3—H_2O, the interaction of TBP with nitric acid and water from the standpoint of physicochemical analysis. The 100% nitric acid obtained by us for the work (^{19}) had a slight yellowish coloration. Anhydrous TBP was prepared from the commercial product by washing with soda solution and distillation under vacuum over NaOH (^{20}). The water was distilled twice. Mixtures were prepared from weighed amounts of each of the components. The nitric-acid content was checked by titration with $0.1\,N$ KOH solution; water was determined by the Fischer method. Before the measurements were begun, the mixtures were kept for 1.5-2 hours in a thermostat at a temperature of $25 \pm 0.1°$; the specific gravity and viscosity of the solutions were measured. The specific gravity was determined simultaneously in three different pycnometers of 2-3 ml capacity. The viscosity was measured in two Ostwald viscometers; the outflow time—

the mixtures proved to be 90-120 sec; each value represents the mean of 5-6 readings. For the TBP—HNO_3 system, measurements of specific gravity and viscosity were carried out at 0° (melting ice); for some compositions of the TBP with H_2O mixture, data were obtained on crystallization of the solid phase from solutions.

The specific-gravity curves of the TBP—HNO_3 system have no singular points (Fig. 1). The viscosity curve at 0° has a maximum, but already at 25° it is

Fig. 1. Properties of the liquid phase of the TBP—HNO_3 system. *a*, *b*—specific gravity of series I and II of the experiments; *c*, *d*—viscosity of series I and II of the experiments; *e*—viscosity according to data of (21); α—absolute temperature coefficient of viscosity

$$\alpha = \frac{\eta^0_{t_1} - \eta^0_{t_2}}{t^0_1 - t^0_2};$$

β—relative temperature coefficient of viscosity

$$\beta = \frac{\eta^0_{t_1} - \eta^0_{t_2}}{t^0_1 - t^0_2} \cdot \frac{1}{\eta_{\mathrm{av}}}.$$

Isomolar series for solutions of TEF + HNO_3 in CCl_4: I—intensity of light absorption according to data of (6); ϵ—dielectric permittivity according to data of (13)

hardly noticeable at all. This indicates the instability of the compound formed in solution. The reason for the discrepancy between the data of (21) on the viscosity of TBP with HNO_3 mixtures (dashed line in Fig. 1) and our data is explained below. The maximum of the temperature coefficient of viscosity corresponds to a content of 65 mole % HNO_3. This system belongs to the irrational type, and a further decrease in temperature will shift the maximum toward the ordinate of the composition of the 1:1 compound, whose existence in a mixture of pure TBP and HNO_3 has been shown by optical investigation (15). The distinct manifestation of the 1:1 compound in approximately 0.1 M solutions of TBP + HNO_3 in CCl_4 in spectrophotometric study (6) and from the change in dielectric permittivity (13) is explained

is explained by the possibility of the existence, in an inert solvent, of isolated particles of the molecular compound $TBP \cdot HNO_3$, which does not form hydrogen bonds with the solvent.

The specific-gravity curve in the TBP—H_2O system (Fig. 2) has no special points. The molar volumes of the solutions calculated from the values of specific gravity found by us for the homogeneous region of the system, within the limits of experimental error, agree with those calculated under the condition of additivity. This is evidence against the formation in the system of a 1 : 1 compound or others. In TBP, according to our data, 50.8 mole % H_2O dissolves, which corresponds to the composition of the compound $TBP \cdot H_2O$ ([3],[7],[16]) within the accuracy of analytical determination. In water at 24.4° there dissolves $2.7 \cdot 10^{-3}$ mole % TBP. Crystallization of ice in the region of liquid stratification in the binary TBP—H_2O system indicates that the compound $TBP \cdot H_2O$ cannot melt congruently, since this would contradict the phase rule. Incongruent melting of a 1 : 1 compound, if such a compound actually exists, must occur below 0°; therefore it is impossible to speak of the existence of the compound $TBP \cdot H_2O$ in the binary system at a temperature of +25°. The increase in the viscosity of TBP as the water content in it increases (our results, Fig. 2, agree well with the data of ([21])) indicates an interaction occurring in the system, but does not make it possible to assert the formation of a 1 : 1 compound. Data on the infrared absorption spectra of mixtures of TBP and H_2O confirm the interaction taking place ([15]): the maximum of the absorption band of the P=O bond in TBP is displaced, and the absorption band of the stretching vibration of the OH group in water is shifted, which is evidence of the appearance of a hydrogen bond in the solution. These results, like the viscosity measurements, however, do not allow one to speak of the existence of a definite compound in the mixture of water and TBP.

Fig. 2. Properties of the liquid phase of the TBP—H_2O system. **1** —specific gravity; **2** —viscosity; **3** —viscosity according to data of ([21]).

Fig. 2. Properties of the liquid phase of the TBP—H_2O system. 1 —specific gravity; 2 —viscosity; 3 —viscosity according to data of (21)

Figure 2: Fig. 2. Properties of the liquid phase of the TBP—H_2O system. 1 —specific gravity; 2 —viscosity; 3 —viscosity according to data of (21)

Fig. 3. Diagram of mutual solubility and projection of the viscosity isotherm for the homogeneous liquid phase of the ternary system TBP—H2O—HNO3 at +25°. K—critical solubility point

Figure 3: Fig. 3. Diagram of mutual solubility and projection of the viscosity isotherm for the homogeneous liquid phase of the ternary system TBP—H2O—HNO3 at +25°. K—critical solubility point

Figure 3 presents the results of the study of the ternary system. The saturation curve of the organic phase agrees well with that obtained after recalculation of literature data ([3], [7]), somewhat less well with the data of ([15]). The amount of TBP in the aqueous phase increases when it contains more than 20 mole % HNO_3. For such solutions the conjugate organic phases lie beyond the tie line H_2O—$TBP \cdot HNO_3$, and the TBP content in the organic phase decreases at a practically constant concentration of water. The least miscibility of the organic phase with water corresponds approximately to the composition of the compound $TBP \cdot HNO_3$, the maximum of stratification being shifted slightly toward the maximum on the viscosity curve of the binary TBP—HNO_3 system from the tie line H_2O—$TBP \cdot HNO_3$. Formation of a third phase in the system was not observed. The composition of the critical point of solubility was calculated graphically ([22]): 3.8% TBP, 65.7% HNO_3, 30.5% H_2O.

In the ternary system the solutions on the solubility curve of the organic phase, containing approximately 23% HNO_3 and 35% H_2O, have the greatest viscosity. The viscosity maximum for the organic phase was also observed by other investigators ([21],[23]). A very gentle second maximum in the ternary system belongs to solutions of TBP in HNO_3. The viscosity curve constructed by us for the isoconcentrate of the ternary system with a content of 10 mole % H_2O reproduces the data shown in Fig. 1 by the dashed line ([21]), which testi-

indicates the presence of about 3 wt. % H_2O in the acid used in the indicated study.

The first of the maxima determines the type of viscosity isotherm of the system. Its occurrence can be associated with the interaction of the three components of the system, since the numerical value of the viscosity at the maximum in the ternary system (5.7 centipoise) exceeds any of those observed in the binary systems at this temperature.

Fig. 3. Diagram of mutual solubility and projection of the viscosity isotherm for the homogeneous liquid phase of the ternary system TBP—H_2O—HNO_3 at +25°. K—critical solubility point

Institute of Inorganic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

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