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Abstract

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THERMOCHEMICAL STUDY OF THE EXTRACTION OF NITRIC ACID BY TRIBUTYL PHOSPHATE

Knowledge of the behavior of nitric acid during extraction by tributyl phosphate (TBP) is of great importance in studies of the extraction of actinides and lanthanides. At present it is usually considered that nitric acid forms the solvate $HNO_3 \cdot TBP$, and at high concentrations also a solvate of composition $(HNO_3)_2 \cdot TBP$; on the other hand, in the region of high nitric acid concentrations one may suppose its dissolution in the solvate $HNO_3 \cdot TBP$ (^{1}). The thermal effects observed in the extraction of nitric acid with TBP have scarcely been studied. Only in work (^{2}) is it indi-

Table 1

Heats of mixing of nitric acid with TBP

Amount of HNO_3 after mixing	Amount of HNO_3 after mixing	Q_1, cal/mol of solution	Q_2, cal/mol HNO_3	Q_3, cal/mol TBP	$A = \frac{Q_1}{N(1-N)}$
moles	N, mole fraction				
0.00437	0.029	−306	−10 400	−314	−10 900
0.00874	0.057	−582	−10 300	−618	−10 800
0.0131	0.083	−885	−10 700	−964	−11 600
0.0175	0.108	−1168	−10 800	−1300	−12 200
0.0218	0.130	−1412	−10 800	−1640	−12 500
0.0262	0.153	−1716	−11 200	−2020	−13 300
0.047	0.204	−2170	−10 600	−2720	−13 400
0.164	0.473	−4210	−8880	−8000	−16 900
0.284	0.606	−4000	−6600	−10 200	−16 800
0.399	0.686	−3770	−5500	−12 000	−17 500
0.517	0.739	−3440	−4650	−13 200	−17 900
0.715	0.796	−2890	−3630	−14 200	−17 900

Figure 1: Heats of mixing of nitric acid with TBP and refractive indices of their mixtures.

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cated that the heat of solution of nitric acid in TBP is equal to −3800 cal/mol. However, the authors of (^{2}) give neither the concentrations of the components nor the experimental procedure.

We used an ordinary calorimeter with an isothermal jacket; the temperature was measured with a Beckmann thermometer; the correction for heat exchange was calculated by the Regnault-Pfaundler formula; the heat value of the calorimeter with solution after each experiment was determined by heating with an electric current (^{3}). A flow calorimeter was also used, the description of which will be the subject of a special publication. The accuracy of the calorimetric measurements was 1-2%.

Refractive indices were measured with an IRF-22 refractometer at 25°. TBP was twice distilled in vacuum; 100% nitric acid was obtained by the usual method (^{4}).

We measured the heats of mixing of nitric acid with TBP over a wide concentration range (Table 1 and Fig. 1). The heat of mixing, calculated in calories per 1 mole of solution, is maximal at $N = \sim 0.47$,

and in calories per 1 mole of nitric acid changes little, up to $N = \sim 0.2$. The large values of the heats of mixing can be explained by the considerable polarity of both liquids and, possibly, also by the formation of a hydrogen bond between molecules of nitric acid and TBP. Since the curve of the dependence of the heat of mixing on the mole fraction of some component in the solution is not completely symmetric, the values of A given in Table 1 change greatly with changes in the composition of the solution, and a solution of nitric acid in TBP cannot be regarded as regular.

Fig. 1. Heats of mixing of nitric acid with TBP and refractive indices of their mixtures. Heats of mixing are expressed: **I** —in calories per 1 mole of solution, **II** —in calories per 1 mole of HNO_3, **III** —in calories per 1 mole of TBP.

To resolve the question of the individuality of the properties of the solvate $HNO_3 \cdot TBP$, we determined the heats of dilution of a solution of this composition with pure TBP, and it was established that these heats vary according to a law corresponding to the mixing of a two-component mixture with an excess of one of them, and are calculated quite accurately from the data of Table 1 and Fig. 1. We have previously shown that solvates formed by TBP with nitrates of uranium and cerium (IV), when mixed with an excess of TBP, behave as individual liquid substances, and the heats of mixing for these cases are described by a curve similar to curve **I** in Fig. 1 (^{5,6}).

The picture of the thermal effects in the nitric acid—TBP system indicates that the process of formation of $HNO_3 \cdot TBP$, evidently, cannot prevail over the formation of solvates of another composition, since when the reaction proceeds under conditions of an excess of one of the components, the heat of the process, referred to a mole of the component taken in the smaller amount, should be constant, which in fact is not observed.

The refractive indices of mixtures of nitric acid with TBP testify to the same thing. As is seen from Fig. 1, here there is a positive deviation from additivity, and there are no extrema characteristic of systems in which chemical compounds are formed ([7]).

Thus, in our opinion, in the nitric acid—TBP system, solvates of variable composition are formed, similar to hydrates in the sulfuric acid—water system.

The thermochemical data obtained by us make it possible to calculate the heats of extraction of nitric acid by TBP at any concentrations of the aqueous and organic phases. Obviously, during extraction the following processes occur:

$$a\mathrm{HNO_3}(x\mathrm{H_2O}) \to a\mathrm{HNO_3}\,(\mathrm{l}), \tag{1}$$

$$a\mathrm{HNO_3}\,(\mathrm{l}) \to a\mathrm{HNO_3}(y\mathrm{TBP}), \tag{2}$$

$$b\mathrm{HNO_3}(x\mathrm{H_2O}) \to b\mathrm{HNO_3}(z\mathrm{H_2O}). \tag{3}$$

Summing (1)–(3), we obtain

$$(a+b)\mathrm{HNO_3}(x\mathrm{H_2O}) \to a\mathrm{HNO_3}(y\mathrm{TBP}) + b\mathrm{HNO_3}(z\mathrm{H_2O}),$$

$$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3. \tag{4}$$

Equation (4) describes the distribution of nitric acid between the aqueous and organic phases. The values of ΔH_1 and ΔH_3 can be taken from

of the handbook (8), and ΔH_2 from Table 1 and Fig. 1. Thus, the calculation of the heat of extraction of nitric acid by TBP (ΔH_4) presents no difficulty. The results of such calculations, together with the experimental data, are given in Table 2. As is evident from the data in Table 2, the calculated values agree well with the experimental ones. The observed differences are probably a consequence of the insufficient accuracy of the calculation of ΔH_1 and ΔH_3, obtained by graphical interpolation from the data of (8).

Table 2

Heats of extraction of nitric acid by TBP

Initial aqueous phase	Initial aqueous phase	Weight of TBP, g	Equilibrium conc. of HNO_3 in org. phase, g/g soln.	Heat of extraction, cal/mol HNO_3	Heat of extraction, cal/mol HNO_3
weight, g	content of HNO_3, g/g soln.	Weight of TBP, g	Equilibrium conc. of HNO_3 in org. phase, g/g soln.	exper.	calc.
3.012	0.568	31.868	0.0199	−7700	−7050
1.496	0.328	32.391	0.0130	−3420	−3550
2.197	0.328	32.250	0.0171	−3810	−3730
2.285	2.328	33.541	0.0158	−3710	−3740
2.282	0.328	33.283	0.0181	−3790	−3700
2.194	0.234	33.694	0.00642	−2780	−2820

Thus, it may be considered that equations (1)–(4) describe the process of extraction of nitric acid by TBP quite satisfactorily, without assuming the formation of any solvate of constant composition.

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