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Abstract

Full Text

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THERMOCHEMICAL STUDY OF THE SYSTEM

$UO_2(NO_3)_2$–H_2O–TBP

At present it is generally accepted that, in the extraction of uranyl nitrate with tributyl phosphate (TBP), the following chemical reaction takes place:

$$UO_2^{2+} + 2NO_3^- + 2TBP \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP. \qquad (1)$$

This process is accompanied by the evolution of heat. However, in the literature known to us there are no data on the magnitude of this thermal effect obtained by direct calorimetric measurements (^{1}).

We determined the thermal effects in a calorimeter similar to that described in (^{2}). A Beckmann thermometer was used for temperature measurement; the correction for heat exchange was calculated by the Regnault-Pfaundler formula; the thermal value of the calorimeter with solution was determined by heating with an electric current (^{3}). The accuracy of the calorimetric determinations was 1-2%. The uranium content was determined by trilonometrically (^{4}).

In studying the thermochemistry of the extraction of uranyl nitrate by TBP, we proceeded from the assumption that the thermal effect of extraction (H_e) is composed of the heat of dilution of the aqueous phase (H_dil), the heat of formation of the solvate $UO_2(NO_3)_2 \cdot 2TBP$ at the phase boundary (H_c), and the heat of dissolution of this solvate in excess TBP (H_diss):

$$H_\mathrm{e} = H_\mathrm{dil} + H_\mathrm{c} + H_\mathrm{diss}. \qquad (2)$$

On this basis, we determined in separate series of experiments H_e, H_dil, and H_diss, and from them calculated H_c, which is essentially the thermal effect of reaction (1).

Table 1 gives the heats of dissolution of the solvate of uranyl nitrate in TBP. In carrying out the experiments, portions of solvate were introduced successively into one weighed portion of TBP; according to analysis, the solvate had the composition $UO_2(NO_3)_2 \cdot 1.87TBP$. In calculating H_diss (cal/mol), it was assumed that the solution consists of solvate and free TBP. The sign convention for the thermal effects here and below is thermochemical. From the data of Table 1 it is seen that dissolution of the uranyl nitrate solvate in TBP is accompanied by the evolution of heat, the amount of which increases with increasing mole fraction of uranyl nitrate in the solution.

Table 2 gives the heats of dilution of an aqueous solution of uranyl nitrate (close to saturated). As is evident from the data presented, this process is also accompanied by the evolution of heat, and the heat of dilution rapidly approaches its maximum value.

Table 3 presents the results of three experiments on determining the thermal effect of extraction (H_e) and calculating the heat of formation of the uranyl nitrate solvate (H_c). The experiments were carried out directly in the calorimeter. After completion of the initial period of the calorimetric experiment, a weighed portion of saturated aqueous uranyl nitrate solution was introduced into the calorimetric beaker. At the end of the experiment the organic phase was analyzed, and the composition of the aqueous phase was calculated. The heat of solvation (H_c) was calculated from formula (2) and the data of Tables 1 and 2. As is seen from the data of Table 3, H_c is 6300±380 cal/mol, which indicates the chemical nature of the interaction between uranyl nitrate and TBP, something that is not observed, as we have shown (5), in the H_2O—TBP system.

As indicated earlier, H_c is the thermal effect of reaction (1). A number of authors have calculated this quantity from the temperature change of the equilibrium constant of this reaction: 3400-4660 cal/mol at an ionic strength

aqueous phase from 1.2 to 0.2 (6), 6300 cal/mole (7), 3610 cal/mole (8). In work (7) concentration equilibrium constants were used and activity coefficients were not taken into account; however, the result of the calculation agrees well with the heat found by us calorimetrically. The thermal effects given in work (6) approach the value H_c found by us when the ionic strength is decreased. The large scatter of the calculated results (6–8) is probably connected with the difficulty of allowing, in the calculation, for changes in the activity coefficients, especially in the organic phase; all the more so since solutions of uranyl nitrate solvates in excess TBP (Table 1) are not regular, as is often assumed (1). Consequently, calorimetry should be regarded as the only reliable method for determining the thermal effects in extraction.

Table 1

No.	TBP charge, %	Solvate charge, g	$UO_2(NO_3)_2$ content in solution, wt. %, before experiment	$UO_2(NO_3)_2$ content in solution, wt. %, after experiment	Mole fraction $UO_2(NO_3)_2$, N	Thermal effect of a single experiment, cal	H_{soln}, cal/mole solution	$A = \frac{H_{soln}}{N(1-N)}$
1	28.56	6.73	0	8.45	0.0625	6.50	57	975
2	28.56	6.67	8.45	14.2	0.119	10.55	140	1330
3	28.56	6.55	14.2	18.3	0.167	15.00	248	1780
4	28.56	6.55	18.3	21.4	0.210	12.50	328	1970
5	—*	6.50	21.4	24.9	0.290	7.45	542	2630

* Before the beginning of the experiment, part of the solution (17.60 g) was removed from the calorimeter.

Table 2

No.	Weight of solution before experiment, g	Added H_2O, g	$UO_2(NO_3)_2$ content in solution, wt. %, before experiment	$UO_2(NO_3)_2$ content in solution, wt. %, after experiment	Thermal effect of a single experiment, cal	H_{dil}, cal/mole $UO_2(NO_3)_2$	$M_{H_2O} M_{UO_2(NO_3)_2}$
1	42.15	5.52	53.6	47.5	25.82	448	24.8
2	47.67	6.53	47.5	41.7	15.94	725	30.4
3	54.20	6.65	41.7	37.2	9.06	885	36.9
4	60.85	18.53	37.2	28.5	8.40	1030	55.0

Table 3

No.	Weight of solution before experiment, g	Added solution*, g	Taken for analysis, g	$UO_2(NO_3)_2$ transferred into TBP in this experiment, g	$UO_2(NO_3)_2$ transferred into TBP in this experiment, moles	Thermal effect of a single experiment, cal	Heat of solvation in this experiment, cal	H_c, cal/mole $UO_2(NO_3)_2$
1	38.25	3.221	2.059	1.398	0.00355	30.13	22.48	6340
2	39.41	3.163	1.996	1.862	0.00473	32.80	23.85	5730
3	40.58	3.021	2.314	1.236	0.00314	35.75	27.65	6840
							Average: 6300$±$380 (6%)	

* 54 wt. % $UO_2(NO_3)_2$ in water.

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