Thermodynamics of Liquid-Liquid Distribution Reactions. I. The Dioxouranium(VI) Nitrate-Water-Tri-*n*-butyl Phosphate-*n*-Dodecane System

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The heat effect of the extraction of uranyl nitrate from aqueous solution into TBP has been measured. The measurements include both forward and backextractions with neat TBP at 23° ± 1°C, extractions with TBP in dodecane at 23° ± 1°C, and extractions with neat TBP at 5−40°C. Heats of mixing of TBP and of uranyl nitrate bis(TBP) solvate with dodecane, which are endothermic, the heat of dilution of aqueous uranyl nitrate, and the heat of hydration of TBP have also been measured. The thermodynamic functions for the extraction reaction UO_2^{2+} (aq) + 2 NO_3^- (aq) + 2 TBP(org) = $UO_2(NO_3)_2(TBP)_2$(org) have been calculated. The standard state (aq) for the aqueous phase is infinite dilution of all solutes in water. For the organic phase, two distinct standard states (org) are used: infinite dilution of all solutes in dodecane (marked by *) and infinite dilution of all solutes in hydrated TBP (marked by °). The standard state functions are, in kJ mol^{-1}: $\Delta H^* = -54.5$, $\Delta H^\circ = -33.8$, $\Delta G^* = -45.6$, $\Delta G^\circ = -41.0$, and in J K^{-1} mol^{-1}: $\Delta S^* = -30$, $\Delta S^\circ = +24$, and $\Delta C_p{}^\circ = +405$.

The thermodynamics of liquid-liquid distribution systems has been studied for two purposes. On the one hand, knowledge of the interactions with diluents (activity coefficients of solutes in the organic phase) and the thermal effect of the reactions help in the prediction of the performance of practical extraction systems under conditions where they have not yet been studied. On the other hand, understanding of these interactions, enthalpy changes, entropy effects, and changes in partial specific heats permit an insight into many types of interactions in liquids, and into the systematics of the formation of coordination adducts, far exceeding the particular extraction system used. In fact, the distribution system may be used as a probe to study more general interactions in one of the phases *(19, 34)*.

Enthalpy changes for distribution reactions have as a rule been obtained from the temperature dependence of the equilibrium quotient for the distribution reaction. Some authors did not even bother to calculate equilibrium quotients but estimated the enthalpy change from the temperature dependence of the distribution coefficients *(21, 36-40)*. That this procedure is wrong, because of the neglect of the heats of dilution of the reactants to the standard states, need not be emphasized, if it were not for the common practice to do just this—i.e., to determine the temperature dependence of an equilibrium quotient which is a constant only under a particular set of conditions. Equations that should have been used, taking into account these heats of dilution, have been presented *(19)*.

The alternative method, of determining calorimetrically the heat of extraction, while applying corrections for heat effects of dilution and interaction, has been applied in only very few cases *(5, 13, 14, 23-26)*. Although some of the corrections may be somewhat uncertain, this procedure is inherently more accurate, gives directly the major portion of ΔH°, and permits a meaningful evaluation of ΔS°.

The following example illustrates the difficulties with the temperature-dependence method. Extraction of aqueous uranyl nitrate with undiluted tri-*n*-butyl phosphate (TBP) at 0° and 50°C led to $\Delta H = -3615$ cal mol^{-1}, and from data at 25°C, $\Delta G = -4580$ cal mol^{-1} was obtained *(10)* so that ΔS at 25°C is +3.24 cal mol^{-1} deg^{-1}. On the other hand, extraction with 0.05*M* TBP in *n*-dodecane at several temperatures between 0° and 50°C *(42)* led to $\Delta H = -6300$ cal mol^{-1} and at 25°C to $\Delta G = -1840$ cal mol^{-1} and $\Delta S = -15.0$ cal deg^{-1} mol^{-1}. The diluent affects ΔG slightly *(20)*, and as is seen below, also ΔH, but not to the extent shown above, where apparently the sign of ΔS is uncertain.

The present work applies the calorimetric method to this same system, in the presence and the absence of the diluent *n*-dodecane. Overall heat effects measured at given initial and equilibrium concentrations of the reactants are corrected for the various dilution and concentration enthalpy changes, to yield the net enthalpy change $\Delta H_{(1)}$ for the reaction

$$UO_2^{2+}(aq) + 2\,NO_3^-(aq) + 2\,TBP(org) \rightarrow UO_2(NO_3)_2(TBP)_2(org) \quad (1)$$

where all the reactants are at their equilibrium concentrations. The values of $\Delta H_{(1)}$ are then corrected to apply to the standard states defined below, to give the standard enthalpy change for Reaction 1. The standard state for the aqueous solution is infinite dilution of uranyl nitrate, TBP, and, when present *n*-dodecane in water. The standard state for dodecane-diluted TBP is infinite dilution of uranyl nitrate disolvate and of TBP in water-saturated *n*-dodecane. This state is designated with an asterisk, thus $\Delta H_{(1)}{}^*$. The standard state for neat, undiluted, TBP is hydrated TBP *(8, 20, 30)*. This state is designated with a circle, thus $\Delta H^\circ{}_{(1)}$.

The analytical data on the reactant concentrations, together with published activity coefficient data *(6, 7, 28, 29, 33-35)* are used to calculate the standard Gibbs energy change $\Delta G_{(1)}{}^*$ (or $\Delta G_{(1)}{}^\circ$) for Reaction 1, and with $\Delta H_{(1)}{}^*$ (or $\Delta H_{(1)}{}^\circ$) this yields $\Delta S_{(1)}{}^*$ (or $\Delta S_{(1)}{}^\circ$). Finally, from the temperature variation of the calorimetrically determined $\Delta H_{(1)}{}^\circ$, in the range 5-40°C, the standard change in heat capacity $\Delta C_{p(1)}{}^\circ$ for Reaction 1 is calculated. These thermodynamic quantities are then discussed in relation to the chemical interactions in this system.

Experimental

Several designs of calorimetric set-ups for measuring heats of extraction have been published *(13, 15, 16)*. The design used in the present work, Figure 1, permitted higher accuracy than the previous ones, if, as for the present system, large amounts of the reactants can be used. The temperature jump due to the addition of the reactants in the bulb *a* to the liquid in Dewar *b* initially at

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thermal equilibrium, under quasiadiabatic conditions vs. the surroundings, could be measured to ±0.0002°C by means of the Quartz thermometer (Hewlett-Packard Model 2801) probe c. The heat capacity of the equilibrium system C_p(system) was calibrated electrically for each experiment, by means of a heater d, a standard resistor of $R = 0.4979 \pm 0.0001 \Omega$ in series with the heater, and a potentiometric circuit where potentials could be determined to ±0.3%, so that the heat capacity was known to ±0.4%. The heat capacities of the system were in the range 2500–3000 J K^{-1}.

The heat effect for each experiment, q, in joules, was calculated from Equation 2

$$q = vVR^{-1}h^{-1}\Delta t = C_p(\text{system})\,\Delta t \qquad (2)$$

where v is the potential drop, in Volts, across the standard resistor R; V is the drop across the heater, in Volts; h is the rate of temperature increase during the calibration heating, deg $\sec^{-1}$; and Δt is the temperature jump for the reaction, deg. The potential drops were constant during the period of heating, as seen on a recorder. The rate of heating, of the order of 0.05°C/min, was constant and determinable within ±0.1%.

The whole assembly (Figure 1) was located in a water bath regulated to ±0.01°C. The heat of stirring was constant at a constant stirring speed (which was in the range of 100–400 rpm, read on revolution counter f), and together with heat leaks amounted to a constant rate of temperature change before and after reagent addition of 0.002–0.010°C/min, known within ±2%. The temperature jump was read at the steepest point, and the time for equilibration was 1–3 min. For extraction experiments this jump was ca. 0.2–0.5°C, determined to within 0.0003°C.

The overall error for a single determination of the heat change (which ranged from 12 J for some heats of dilution to 1600 J for some heats of extraction) was ±0.6 J (±0.15 cal) or ±0.6%, whichever is greater. This compares favorably with the precision of 1–2% in the work of Nikolaev and Afanasev *(3, 23, 24)* and of >1.7 J in the work of Kettrup *(14)* and Kletenik *(15)*. An improved design for use with smaller volumes, of the order of 100 ml, which is under construction, will increase the precision to ±0.1 J for a single determination.

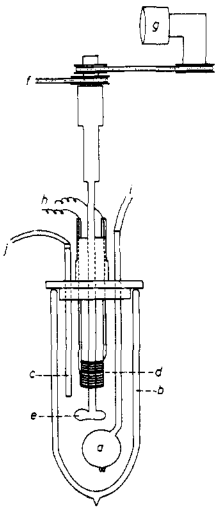

Figure 1. Calorimeter: a, bulb of ca. 50-ml volume with a capillary outlet; b, Dewar vessel of 800-ml capacity; c, probe of Quartz thermometer; d, Pt wire heater of ca. 30 Ω wound on a perforated glass cylinder; e, glass stirrer; f, pulley and belt to stirring motor; g, revolution rate counter; h, lead wires to 6-V constant voltage source; i, tubing to air-filled automatic piston buret; j, lead to Quartz thermometer

The chemicals used were of analytical grade: uranyl nitrate hexahydrate (Merck), which analyzed as $UO_2(NO_3)_2(H_2O)_{5.91}$, tri-*n*-butyl phosphate (Merck), and *n*-dodecane (Fluka), the latter >99% pure by gas chromatography, the impurities being other saturated hydrocarbons. All analyses were made by weight, as were the additions of reagents. Only uranium was analyzed for, and this was done coulometrically for aqueous solutions, the results being expressed in mg U/gram solution, with an accuracy of ±0.25% or better. Organic phases were first diluted about fivefold with chloroform, to decrease the distribution coefficient, and then stripped with a known amount of 0.01*M* nitric acid, which was then analyzed as above. Residual uranium in the chloroform phase was analyzed spectrofluorometrically, and this correction, known to ±3% and never exceeding 0.5% of the uranium in the organic phase sample, was added to the main amount determined in the strip solution.

Densities, necessary for calculating molar concentrations needed in the computation of equilibrium constants on the molar scale, were determined by weighing volumetric flasks equilibrated at the proper temperature. The precision attained, ±0.001 g/cm^3, was sufficient for the purpose.

The main difficulty with the analytical method was the coextraction of water with the uranyl nitrate. This had to be accounted for in order to calculate the number of moles of uranium extracted into the organic phase, Y, since only the initial, but not the *equilibrium*, total amounts of the phases were known. The coextracted water could be determined in the following manner: Let U, T, D, and W be the total number of moles of uranyl nitrate, TBP, dodecane, and water, respectively, present in the sysem. Initially there are only U and W moles of the respective components in the aqueous phase weighing $A = 394.03\,U + 18.01\,W$ grams and D and T moles in the organic phase weighing $Q = 170.34\,D + 266.32\,T$ grams (mutatis mutandis for the reextraction experiments). The equilibrium uranium content of the aqueous phase is x mg/g and that of the organic phase is y mg/g. It is assumed that there is a negligible loss of TBP and dodecane to the aqueous phase, so that the equilbrium weight of the organic phase is

$$Q_{\text{eq}} = [Q + 18.01\,W^{\text{tr}}]/[1 - (0.39403/238.03)\,y] \qquad (3)$$

where W^{tr} is the number of moles of water coextracted, and $0.39403\,y/238.03$ is the weight of uranyl nitrate per gram organic phase. The number W^{tr} is sufficiently small to constitute only a <3% correction on the equilibrium weight of the organic phase, hence may be estimated with sufficient accuracy by equating it to the number of moles of free TBP, T_{fr}, assuming that TBP not bound in the uranyl nitrate disolvate is bound to water as $TBP \cdot H_2O$ for undiluted TBP, and to $0.5T_{\text{fr}}$ for 1 and 2*M* TBP *(6, 8, 20, 30)*. The number T_{fr} is obtained from $T_{\text{fr}} = T - 2\,Y$, and Y is obtained from $Y = yQ_{\text{eq}}/238030$, where one iteration is sufficient to give the final value. The values of Q_{eq} calculated from Equation 3 could be used to confirm the uranium mass balance:

$$(A + Q - Q_{\text{eq}})\,x + Q_{\text{eq}}y = 238030\,X + 238030\,Y = Ax = 238030\,U \qquad (4)$$

within ±1.15% for some 16 extraction experiments.

Results

Heat effects of extraction. Extraction experiments were made at 23° ± 1°C with both neat TBP, and with TBP diluted with dodecane at 0.5, 1.0, and 2.0*M*. Further experiments, with neat TBP, were made at several temperatures between 5° and 40°C. Several experiments were made where the uranium was initially in the organic phase, and was reextracted into water. This organic phase had the approximate composition of the disolvate, but was contaminated with some excess of TBP and some water, due to the way of its preparation, from stoichiometric amounts of uranyl nitrate hexahydrate and TBP. The results of these experiments are shown in Table I.

In this table the quantity Y should be understood in its algebraic sense—i.e., as the change in the number of moles of uranium in the organic phase between the initial and the final states. The last three experiments in Table I are thus reextraction experiments where heat was absorbed from the system so that its temperature fell. In these experiments the initial uranium concentration of the organic phase was y° = 223.7 mg/g. The temperature t represents that of the equilibrium system after the temperature jump, but before any calibration heating. The concentration of neat TBP, C_T°, varies with the temperature because of the known changes in its density. As mentioned in the introduction, the measured heat effects, q, include not only the enthalpy change for the chemical reaction (1), but also additional terms for dilution and mixing, and must be corrected accordingly.

Heat of dilution of uranyl nitrate. The heat of dilution of 0.50*M* aqueous uranyl nitrate with water was measured in two independent series of experiments, in good agreement. In one series both the heat effects of the addition of water to the uranyl nitrate solution, and of the addition of the solution to water were measured; in the other, only the latter. The results are shown in Figure 2, where it is seen that the heat evolved on dilution (q is positive) per mole of uranium in the system is proportional to the change in uranium concentration between the initial state and the final state. The best straight line that can be passed through the points has the formula

$$q_{\text{dil}} = (3800 \pm 240)U(-\Delta C_U) \text{ J} \qquad (5)$$

where U is the number of moles of uranium in the system, and ΔC_U is the (negative) change in concentration. Because of the linearity of the relationship, it is assumed to hold for whatever initial and final concentrations are obtained in extraction experiments, provided they are both <0.5*M*, the limit to which Equation 5 was tested. The quantity $q_{\text{dil}}/U\Delta C_U$ can be equated to the standard molar heat of dilution $\Delta H_{\text{dil}}^\circ$, which is −3800 J mol^{-1} (mol/l.)$^{-1}$ [or −0.91 kcal mol^{-1} (mol/l.)$^{-1}$].

Heat of hydration of TBP. Although TBP does not form a very stable monohydrate, it does interact with an excess of water with the evolution of heat. Experiments were made at 24° ± 1°C with addition of neat or diluted TBP to a large excess of water. The amount of heat evolved per mole of TBP, q_{hyd}/T was not large, but quite significant. On the contrary, the amount of heat evolved when a similar weight of water or of dodecane was added to the water in the Dewar was insignificant: $\Delta t <$ 0.0003°C was observed—i.e., $q < 1$ J. The heat of hydration of TBP (Figure 3) can be summarized by

$$q_{\text{hyd}} = [(210 \pm 50) + (85 \pm 15)\,C_T^\circ]\,T = -\Delta H_{\text{hyd}}\,T \text{ J} \qquad (6)$$

The standard heat of hydration of undiluted TBP is thus $\Delta H_{\text{hyd}}^\circ$ = −520 ± 50 J mol^{-1} (or −0.12 kcal mol^{-1}), while the standard partial heat of hydration of TBP at infinite dilution is ΔH_{hyd}^* = −210 J mol^{-1} (or −0.05 kcal mol^{-1}). The heat of hydration is thus concentration de-

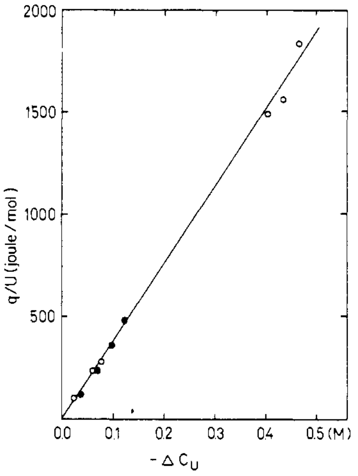

Figure 2. Heat of dilution of aqueous uranyl nitrate
● initial concentration 0.503*M*; ○ initial concentration 0.501*M*, represent two independent series of experiments

Table I. Heat Effects and Composition of Equilibrium Phases for Extraction of Uranyl Nitrate with TBP in Dodecane

No.	C_T° (*M*)	*t*, °C	*x*°, mg/g	*x*, mg/g	*y*, mg/g	*Y*, mmoles	*q*, J
222	0.50	23.0	103.1	98.2	85.5	16.61	595.0
223	0.50	24.1	78.0	73.6	73.0	13.79	500.2
215	1.00	20.7	102.9	95.7	80.8	14.72	521.3
216	1.00	23.9	95.7	90.3	81.3	14.62	514.2
217	1.00	24.7	90.3	87.7	78.4	14.27	479.4
228	2.00	22.8	79.3	70.2	126.0	26.64	786.6
232	2.00	23.6	72.9	65.0	112.8	24.05	729.0
218	3.66	24.0	87.9	71.0	175.0	48.01	1501.2
219	3.66	24.5	82.4	66.2	176.7	50.46	1531.2
221	3.66	22.7	84.1	66.7	181.0	51.66	1578.9
234	3.71	6.8	55.9	41.0	146.8	38.87	1477.2
233	3.69	14.2	67.2	52.2	161.5	41.84	1433.2
224	3.62	32.4	70.0	56.5	149.0	36.26	979.2
225	3.60	38.4	63.1	49.4	142.6	36.33	910.3
230	3.42	22.2	0.0	17.62	46.5	−43.4	−1097.8
231	3.42	22.9	0.0	17.57	42.3	−44.6	−1155.6
235	3.42	22.8	0.0	5.56	7.12	−14.1	−338.0

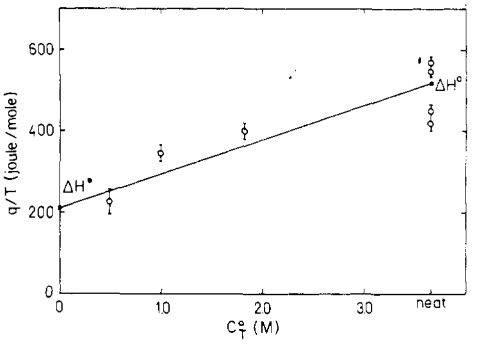

Figure 3. Heat of hydration of TBP diluted with dodecane

pendent, and the heat evolved between two states of (free) TBP in extraction experiments is (f = final and i = initial states):

$$\Delta q_{\text{hyd}} = (-\Delta H_{\text{hyd}\ f})T_f - (-\Delta H_{\text{hyd}\ i})T_i \quad (7)$$

In the application of Equation 7, only free, initially unhydrated, TBP must be considered, so that neat TBP at 25°C has $C_T^\circ = 3.66M$ rather than the equilibrium value of hydrated TBP, 3.43M *(20)*. A comparison with values in the literature is in place here. For the single-phase solution of one mole of water in 80 moles of TBP, the molar heat of reaction $\Delta H = +590$ J (mol water)$^{-1}$ has been found *(12)*, while for undisclosed concentrations, the values +200 to +550 have been given *(1)* which have the opposite sign to the heat of reaction in the two-phase system (total moles water:total moles TBP ~ 200) studied here. More comparable is the exothermic heat found *(13)* for stoichiometrically equivalent amounts $\Delta H_{\text{hyd}} = -400$ J (mol TBP)$^{-1}$ and for the two-phase system (total water:total TBP = 5) $\Delta H_{\text{hyd}} = -670$ J (mol TBP)$^{-1}$. Our value lies in between the two values given by Kettrup and Specker *(14)* which, however, should not be different, since the addition of excess water to the fully hydrated equilibrium system should be without any thermal effect. None of the other determinations was claimed to be more accurate than ours.

Heat of mixing of TBP and dodecane. The mixing of a polar substance such as TBP with an inert liquid such as dodecane is an endothermic reaction, because of the energy needed to break up the polar interactions. Experiments were made at 24° ± 1°C of mixing TBP and dodecane in the TBP-mole fraction ranges N_T from 0.00 to 0.22 and 0.75 to 1.00. The heat absorbed (q_T is negative) per mole of mixture is strongly dependent on the composition, as follows:

$$\Delta H_T{}^E = -q_T(T + D)^{-1}N_T{}^{-1}(1 - N_T)^{-1} = 8950 - 14100\, N_T + 11800\, N_T{}^2 \text{ J mol}^{-1} \quad (8)$$

The curve of $\Delta H_T{}^E N_T(1 - N_T)$ against N_T (Figure 4a) has a maximum of +1250 J mol^{-1} (300 cal mol^{-1}) at $N_T = 0.40$. When in an extraction experiment the concentration of free TBP changes, the heat change will be

$$\Delta q_T = -\int_{N_{Ti}'}^{N_{Tf}'} \Delta H_T{}^E D dN_T' =$$

$$-8950\, D(N_{Tf}' - N_{Ti}')\{1 - 0.787\,(N_{Tf}' + N_{Ti}') + 0.439\,[(N_{Tf}')^2 + N_{Tf}'\,N_{Ti}' + (N_{Ti}')^2]\}\text{ J} \quad (9)$$

where $N_T' = T_{\text{fr}}/(T_{\text{fr}} + D)$ is the mole fraction of free TBP, disregarding in the denominator the presence of uranium and water in the organic phase. In fact, in a separate experiment it was found that the presence of water does not affect the heat of mixing to any measurable extent, while the presence of uranium is taken into account in a suitable heat-of-mixing term (see below).

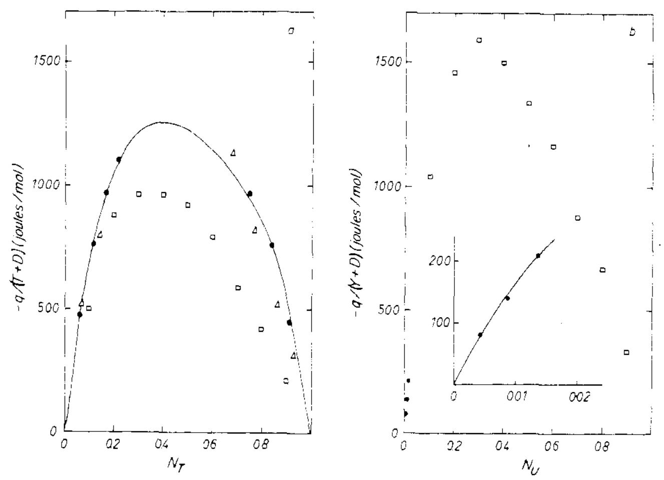

Figure 4. Heat of mixing of dodecane with TBP (a), and with the solvate (b), per mole of mixture: ● present work, □ ref. *33*, △ ref. *9*

Other authors *(3, 9, 22, 33, 41)* have studied the heat of mixing of TBP with diluents, but not with dodecane. Schwabe and Wiesener *(41)* studied triisobutyl phosphate and found an almost symmetrical curve of $\Delta H^E N(1 - N)$ for mixing with hexane, with a maximum of +880 J mol^{-1}, while Rozen et al. *(33)* found for TBP and hexane a skew curve similar to that found here for dodecane, with a maximum of +960 J mol^{-1} at $N_T = 0.35$ (Figure 4). For decane, Fomin and Rudenko *(9)* again found a similar skew curve (Figure 4) with a maximum of ca. +1150 J mol^{-1} at $N_T \sim 0.4$. A similar trend of increasing maxima in the curve, between n-heptane, n-nonane, and n-decane (but with uniformly about 10% lower values than the previous studies) was found by Afanasev et al. *(3)*. Thus the present values for dodecane continue the trend found between hexane and decane. For other hydrocarbons (isooctane, cyclohexane, decalin, benzene, toluene, and xylene) there are only qualitative data *(22)* pointing in the same direction of endothermic heats of mixing.

Heat of mixing of the disolvate with dodecane. The mixing of uranyl nitrate-TBP solvate with dodecane again is an endothermic reaction *(33)*. In this case only dilute solutions were studied, since the extraction experiments with diluted TBP yielded a maximal mole fraction $N_U' = Y/(Y + D)$ of 0.17. At 24°C, the heat absorbed (q_U is negative) per mole of mixture depends on the composition as follows:

$$\Delta H_U{}^E = -q_U(Y + D)^{-1}(N_U')^{-1}(1 - N_U')^{-1} = 15100 - 27000\, N_U' \text{ J mol}^{-1} \quad (10)$$

The curve of $\Delta H_U{}^E N_U'(1 - N_U')$ against N_U' (Figure 4b), when continued to higher mole fractions of the solvate agrees well with the data of Rozen et al. *(33)* who studied the mixing with hexane. As before, the curve for dodecane is expected to be somewhat higher than for hexane, $\Delta H_U{}^E$ for the latter diluent is describable in terms of a cubic equation with somewhat lower coefficients. The heat chage due to this mixing reaction in extraction experiments is

$$\Delta q_U = -\int_{N_{Ui}'}^{N_{Uf}'} \Delta H_U{}^E D dN_U' =$$

$$-15100\, D(N_{Uf}' - N_{Ui}')\,[1 - 0.945\,(N_{Uf}' + N_{Ui}')]\text{J} \quad (11)$$

provided that $N_U' = Y/(Y + D) \leq 0.17$ is the mole fraction of the solvate in the organic phase, disregarding any water and excess TBP present. Again, a separate experiment has shown that water has no measurable effect on the heat of mixing of the solvate and dodecane, while the effect of excess TBP is considered separately, as will now be described.

Heat of mixing of the solvate and TBP. Solutions of uranyl nitrate bis(TBP) solvate in TBP are nonideal *(34)*, although both are polar substances, but the mutual interactions are very intricate. A few experiments were made to ascertain the heat effect, in which the solvate was mixed with solutions of TBP in dodecane of various compositions. The heat effects due to the mixing of the solvate with dodecane, and to the change in the mixing of TBP with dodecane, were calculated according to the equations in the previous sections, assuming them to be independent, and subtracted from the observed heat effect: $q_M = q_{\text{obsd}} - \Delta q_U - \Delta q_T$, and the remainder is ascribed to the mixing of TBP and the solvate. It is interesting to note that both the observed heat effect, as well as the corrected value q_M, change sign when going from small $N_U' = Y/(Y + T)$, where the reaction is exothermic, to large N_U' (>0.1), where it is endothermic. The data are compared in Figure 5 with values calculated from literature data *(2, 4)* showing reasonable agreement. In one study *(2)* the integral heat of solution of uranyl nitrate dihydrate in undiluted TBP was measured in the dilution range $T{:}Y = 16.3$ to 195, corresponding to N_U' from 0.002 to 0.058. If the constant value −36.0 kJ/mol is assigned to the reaction

$$UO_2(NO_3)_2(H_2O)_2(s) + 2\,TBP(l) = UO_2(NO_3)_2(TBP)_2(l) + 2\,H_2O(l) \quad (12)$$

and subtracted from the observed values, the rest represents the heat of dilution of the solvate with excess TBP, as shown in Figure 5—since the effect of water is negligible, as shown in a separate experiment, where water was added to a solvate–TBP mixture. In the other study *(4)* the mixing of the disolvate with TBP (undiluted) was studied directly, at 25°C, but at a higher concentration range. The data of the present study can be represented by

$$\Delta H_M{}^E = -q_M(T + Y)^{-1}(N_U')^{-1}(1 - N_U')^{-1} = -8000 + 70000\,N_U' - 88000(N_U')^2 \text{ J mol}^{-1} \quad (13)$$

which for an extraction experiment leads to a correction term

$$\Delta q_M = -\int_0^{N_U'} \Delta H_M{}^E T_{fr} dN_U' = 8000\,T_{fr}N_U'[1 - 4.40\,N_U' + 3.68(N_U')^2]\text{ J} \quad (14)$$

while for reextraction experiments, the limits of integration are reversed: $N_{Ui}' = N_U'$ and $N_{Uf}' = 0$.

Enthalpies of extraction. It is now possible to convert the observed heat effects of the extraction experiments, q in Table I, to molar enthalpy changes for Reaction 1, according to

$$\Delta H_{(1)} = -[q - q_{\text{dil}} - \Delta q_{\text{hyd}} - \Delta q_T - \Delta q_U + \Delta q_M]/Y \quad (15)$$

The values of $\Delta H_{(1)}$ are shown in Table II. For the experiments carried out at 23° ± 1°C, they are plotted against $C_T°$ in Figure 6, while for those experiments carried out with neat TBP at varying temperatures they are plotted against t in Figure 7.

To obtain standard enthalpies of extraction, it is necessary to convert the enthalpy changes listed in Table II, and valid for the equilibrium states of the system, to those at the standard states. The procedure chosen was

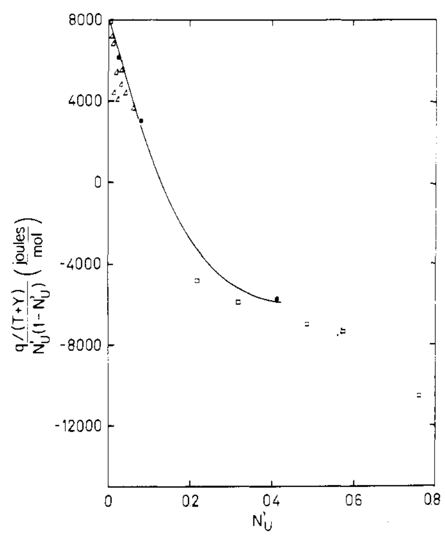

Figure 5. Heat of mixing of TBP with the solvate per mole of mixture divided by $N_U'(1 - N_U')$: ● present work, △ ref. 2, □ ref. 4

Table II. Enthalpy Changes for Extraction of Uranyl Nitrate with TBP in Dodecane

No.	q, J	q_{dil}, J	Δq_{hyd}, J	Δq_T, J	Δq_U, J	Δq_M, J	$\Delta H_{(1)}$, kJ/mol
222	595.0	+34.0	−0.9	+180.2	−214.0	~0	−36.1
223	500.2	+17.6	−0.9	+179.5	−182.8	~0	−35.7
215	521.3	+42.7	−3.3	+147.5	−169.0	−15.5	−35.2
216	514.2	+27.2	−3.3	+146.0	−167.5	−15.5	−36.0
217	479.4	+12.1	−3.3	+138.7	−163.3	−15.1	−35.8
228	786.6	+32.3	−12.1	+129.9	−208.6	−12.1	−32.2
232	729.0	+26.0	−12.1	+123.7	−194.0	−15.5	−33.2
218	1501.2	+60.7	−42.7			−35.6	−31.7
219	1531.2	+58.3	−44.8			−39.0	−30.9
221	1578.9	+56.5	−44.8			−46.1	−31.2
234	1477.2	+28.5	−38.1			+9.6	−38.0
233	1433.2	+41.4	−39.0			−12.6	−34.5
224	979.2	+36.4	−33.9			+7.1	−28.2
225	910.3	+31.0	−34.8			+16.7	−24.8
230	−1097.8	−12.1	+26.8			+211.8	−30.5
231	−1155.6	−12.6	+27.6			+209.2	−31.0
235	−338.0	−1.3	+9.6			+60.4	−29.0

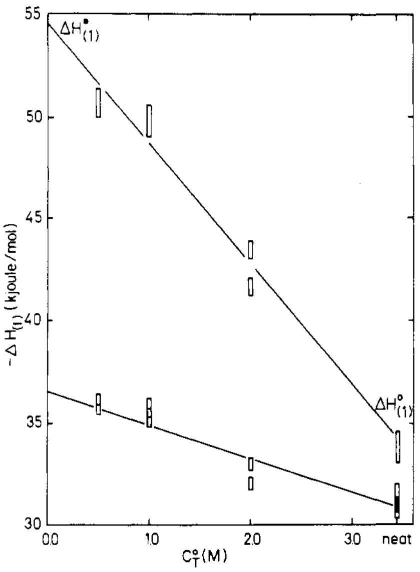

Figure 6. Enthalpy of extraction at 23° ± 1°C of uranyl nitrate with TBP in dodecane as a function of the initial TBP molarity

Filled symbols pertain to reextraction experiments. Lower curve gives $\Delta H_{(1)}$ from Table II; the upper curve gives the values corrected to standard conditions for heat of dilution in the aqueous phase, heat of hydration of TBP, heat of mixing of the solvate with dodecane, and heat of mixing of the solvate with TBP, Equations 7, 9, 13, and 16

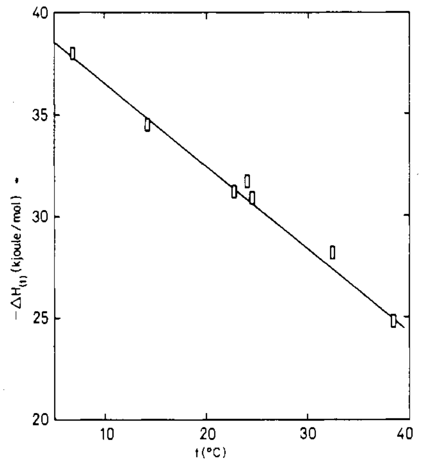

Figure 7. Enthalpy of extraction of uranyl nitrate with undiluted TBP as a function of the temperature

to calculate the heat changes of Equations 5, 7, 11, and 14 between the limits of the equilibrium states and the standard states, per mole of uranium, add the results algebraically to the $\Delta H_{(1)}$, and plot the corrected enthalpies against $C_T{}^\circ$ as the upper curve of Figure 6. In this way the difficulty of the absence of free TBP in the experiments with 0.5*M* TBP was avoided. Extrapolation to $C_T{}^\circ = 0$ yields the value of $\Delta H_{(1)}{}^*$. The standard enthalpy change of transfer of uranyl nitrate bis(TBP) solvate at infinite dilution from (hydrated) TBP to dodecane is

$$\Delta H^{\mathrm{tr}} = \Delta H_{(1)}{}^* - \Delta H_{(1)}{}^\circ \qquad (16)$$

The values of $\Delta H_{(1)}{}^*$, $\Delta H_{(1)}{}^\circ$ and ΔH^{tr} are shown in Table IV.

Gibbs energies of extraction. The equilibrium constant expression for Reaction 1 is

$$K_{(1)} = (\mathrm{UO_2(NO_3)_2(TBP)_2\,org})/\mathrm{UO_2{}^{2+}\,aq}) \times$$

$$(\mathrm{NO_3{}^-\,aq})^2(\mathrm{TBP\,org})^2 = [\mathrm{UO_2(NO_3)_2(TBP)_2\,org}] \times$$

$$\gamma_S/4\,[\mathrm{UO_2{}^{2+}\,aq}]^3\,\gamma_\pm{}^3[\mathrm{TBP\,or\,free}]^2\,\gamma_T{}^2 \qquad (17)$$

where round parentheses denote activities (on any scale), while for the second equation, square brackets denote molalities; γ, molal activity coefficients; the subscripts *S* and *T*, the solvate and free TBP, respectively, in the organic phase; and ±, uranyl nitrate in the aqueous phase. From the equilibrium composition data in Table I it is possible to calculate directly the equilibrium quotients $Q_{(1)}{}^m$ and the use of activity coefficients for the aqueous phase *(7, 29)* makes possible the conversion of these equilibrium quotients to "effective constants," $\bar{K}_{(1)}$ often used in the Russian literature:

$$K_{(1)} = Q_{(1)}{}^m\gamma_S/\gamma_\pm{}^3\gamma_T{}^2 = \bar{K}_{(1)}{}^m\gamma_S/\gamma_T{}^2 \qquad (18)$$

Concentrations on the molal scale are expressed per kg dodecane for the diluted solutions and per kg TBP for the undiluted ones. To make comparisons with other published data, also effective constants on the molar scale, denoted $\bar{K}_{(1)}{}^c$ have been calculated, utilizing density data that have been obtained for all initial and equilibrium solutions. The values of $\bar{K}_{(1)}{}^m$ and $\bar{K}_{(1)}{}^c$ are shown in Table III.

The activity coefficients γ_S and γ_T for binary solutions of TBP and of the solvate in the diluent *n*-hexane (both dry, and in the presence of an aqueous phase) can be

Table III. Equilibrium Constants and Gibbs Energy Change for Extraction of Uranyl Nitrate with TBP in Dodecane

No.	$C_T{}^\circ$, *M*	*t*, °C	$\bar{K}_{(1)}{}^m$, kg^{4}mol^{-4} [a]	$\bar{K}_{(1)}{}^c$, l^{4}mol^{-4}	$\Delta G_{(1)}$, kJ/mol
222	0.50		...	[b]	...
223	0.50		...	[b]	...
215	1.00	20.7	19.3	38.4	−44.9
216	1.00	23.9	25.6	44.3	−45.8
217	1.00	24.7	22.8	38.2	−45.5
228	2.00	22.8	21.0	45.3	−45.8
232	2.00	23.6	19.7	44.1	−45.5
218	3.66	24.0	19.0	17.6	−40.4
219	3.66	24.5	25.3	25.0	−41.4
221	3.66	22.7	28.2	27.1	−41.4
234	3.71	6.8	57.1	56.9	−40.5
233	3.69	14.2	37.9	37.3	−40.6
224	3.62	32.4	21.5	21.0	−41.7
225	3.60	38.4	29.1	28.2	(−43.3)
230	3.42	22.2	57	72	(−43.3)
231	3.42	22.9	54	65	(−43.2)

[a] For the first five experiments involving dodecane the units are (kg water)^3 (kg dodecane)mol^{-4}, while for the other experiments the units are (kg water)^3 (kg TBP) mol^{-4}. [b] For these experiments the equilibrium organic phase had $\bar{C}_U$ = 0.325*M* (no. 222) and 0.273*M* (No. 223), so that no free TBP is present, and no $\bar{K}_{(1)}{}^c$, $\bar{K}_{(1)}{}^m$ or $\Delta G_{(1)}$ can be calculated.

estimated from the data in the literature *(6, 28, 33)*. As expected, the ratio γ_S/γ_T^2 varies considerably less than each of them individually, but it is then assumed that γ_S and γ_T are independent of each other, and that *n*-dodecane would give values for the ratio similar to those obtained for *n*-hexane. A simpler procedure is to estimate the quantity $dil = y_T^2/y_S = \bar{K}_{(1)}^c/K_{(1)}^c$ as a function of $\bar{C}_U$ and $\bar{C}_T°$ from the data of Rozen et al. *(35)*. It turns out that *dil* is independent of $\bar{C}_T°$, from 20% TBP in kerosene (~dodecane) to neat TBP, and gives a smooth plot against $\bar{C}_U$ for different $\bar{C}_T°$. In the range of the concentrations encountered in the experiments tabulated in Table III, *dil* varies from 0.76 to 0.96, so that even if temperature variations of *dil* are ignored, the possible errors in its estimates lead to rather small errors in $\Delta G_{(1)}^c$.

To avoid difficulties from the choice of concentration scales, the cratic part of the Gibbs energy change *(31)* has been subtracted, to leave only the unitary part, or in other words, $\Delta G_{(1)}$ has been calculated as $-RT \ln K_{(1)}^N$, where $K_{(1)}^N$ is the equilibrium constant on the mole fraction scale.

$$K_{(1)}^N = K_{(1)}^c(1000/V_{\mathrm{H_2O}})^3(1000/V_{\mathrm{dod\ or\ TBP}}) \qquad (19a)$$

$$= K_{(1)}^m(1000/M_{\mathrm{H_2O}})^3(1000/M_{\mathrm{dod\ or\ TBP}}) \qquad (19b)$$

where $V_{\mathrm{H_2O}}$ and $M_{\mathrm{H_2O}}$ are the molar volume and weight of water, and V_{dod} and V_{TBP}, and M_{dod} and M_{TBP} are the molar volumes and weights of dodecane and TBP respectively. The values of $\Delta G_{(1)}$ are given in Table III.

It is seen that $\Delta G_{(1)}$ is independent of the concentration of TBP in the diluent, and that an average value $\Delta G_{(1)}^*$ given in Table IV describes equilibrium (1), with the standard states of infinite dilution of all solutes in water and in dodecane. Similarly, for neat TBP, $\Delta G_{(1)}$ is independent of the uranium concentration, and in the range 5–40°C, also of temperature, giving the $\Delta G_{(1)}°$ of Table IV with the standard state of infinite dilution of all solutes in water and in (hydrated) TBP. The reservation must be made that the variation of the activity coefficients of the solutes with the temperature has been neglected. The standard Gibbs energy of transfer of uranyl nitrate bis(TBP) solvate at infinite dilution from TBP to dodecane shown in Table IV is

$$\Delta G^{\mathrm{tr}} = \Delta G_{(1)}^* - \Delta G_{(1)}° \qquad (20)$$

Entropies of extraction. From the standard Gibbs energies and standard enthalpies for the extraction reaction it is now possible to calculate the standard entropies for 23° ± 1°C:

$$\Delta S_{(1)}^* = (\Delta H_{(1)}^* - \Delta G_{(1)}^*)/T \qquad (21a)$$

$$\Delta S_{(1)}° = (\Delta H_{(1)}° - \Delta G_{(1)}°)/T \qquad (21b)$$

and the standard entropy change for the transfer of uranyl nitrate bis(TBP) solvate at infinite dilution from (hydrated) TBP to dodecane

$$\Delta S^{\mathrm{tr}} = \Delta S_{(1)}^* - \Delta S_{(1)}° \qquad (22)$$

shown in Table IV.

Heat capacity change of extraction. The heat capacity change for the extraction reaction can be obtained as $\Delta C_{p(1)} = d(\Delta H_{(1)})/dt$ from the slope of the curve of Figure 7. Since the corrections for the heats of dilution and the heats of mixing were obtained only at 23° ± 1°C, there is some uncertainty in the result, which is not the *standard* change in heat capacity. The value obtained for extraction with neat TBP is shown in Table IV.

Discussion

For evaluating the calorimetric method for obtaining the thermodynamic quantities for the extraction reaction it is instructive to compare briefly the sources of error in this method with those inherent in the other method, namely the temperature coefficient of the distribution constant.

In the former method the heat effect of the extraction reaction *q* is obtained directly, in the present work with a precision of ±0.6% or ±3 J, a figure which could probably still be improved on. A major difficulty arose with the determination of the extent of the extraction reaction, because of coextraction of water. The fact that only uranium was analyzed for, on the one hand, and the fact that all concentrations were expressed on a weight basis and that the analytical precision was as good as ±0.25% on the other, led to a precision in *Y* of ±0.4%. A more complete analysis of the equilibrium phases should improve this precision. Other errors are more serious, particularly in the heats of mixing of the solvate and of TBP with the diluent, which contribute appreciably to $\Delta H_{(1)}$, but in a mutually compensating manner. The quantity $q_T - q_S$ is 4–10% of *q*, and makes the accuracy of the $\Delta H_{(1)}$ for solutions of TBP in dodecane inferior to that for neat TBP. Except for the reextraction experiments, the magnitude of the sum of the other correction terms is only ~3% of *q*, and of minor significance for the accuracy of $\Delta H_{(1)}$. The same comments pertain to the calculation of $\Delta H_{(1)}°$, but for $\Delta H_{(1)}^*$, the importance of the heat of mixing terms becomes so great that appreciable uncertainties (systematic errors) could be due to this. In the present work q_T was obtained relatively accurately (Figure 4*a*) and in good agreement with others' work (done on lower hydrocarbon diluents), but q_S, and the assumption of independence of these two terms from each other (inherent in the calculation of q_M) and from the presence of water (checked experimentally at one or two points only) could be improved. Even so, the random and systematic

Table IV. Thermodynamic Quantities for the Reaction UO_2^{2+}(aq) + 2 NO_3^-(aq) + 2 TBP(org) = $UO_2(NO_3)_2$ (org) at 23°C

Organic phase:	Dodecane	TBP	Transfer
Enthalpy change,			
kJ mol^{-1}	$\Delta H_{(1)}^* = -54.5 = 1.5$	$\Delta H_{(1)}° = -33.8 \pm 0.5$	$\Delta H^{\mathrm{tr}} = -20.7 \pm 1.6$
(kcal mol^{-1})	(−13.0 ± 0.4)	(−8.1 ± 0.1)	(4.9 ± 0.4)
Gibbs energy change,			
kJ mol^{-1}	$\Delta G_{(1)}^* = -45.6 \pm 0.2$	$\Delta G_{(1)}° = -41.0 \pm 0.5$	$\Delta G^{\mathrm{tr}} = -4.6 \pm 0.5$
(kcal mol^{-1})	(−10.9 ± 0.05)	(−9.8 ± 0.1)	(−1.1 ± 0.1)
Entropy change,			
J K^{-1} mol^{-1}	$\Delta S_{(1)}^* = -30 \pm 5$	$\Delta S_{(1)}° = +24 \pm 2$	$\Delta S^{\mathrm{tr}} = -54 \pm 5$
(cal K^{-1} mol^{-1})	(−7.2 ± 1.2)	(+5.7 ± 0.6)	(−13.0 ± 1.3)
Heat capacity change,			
J K^{-1} mol^{-1}		$\Delta C_{p(1)} = +405 \pm 35$	
(cal K^{-1} mol^{-1})		(+97 ± 8)	

errors in $\Delta H_{(1)}^*$ and $\Delta H_{(1)}^\circ$ are sufficiently low (see Table IV and Figure 6), that combined with $\Delta G_{(1)}^*$ and $\Delta G_{(1)}^\circ$, obtained with reasonable accuracy and precision, they lead to meaningful derived quantities such as $\Delta S_{(1)}^*$, $\Delta S_{(1)}^\circ$, ΔH^{tr}, and $\Delta C_{p(1)}$.

The major criticism against the temperature coefficient method, already mentioned in the introduction, is that it has never been carried out properly. The thermodynamic equilibrium constant for Reaction 1 has been estimated in various ways *(20)* for both standard states of infinite dilution in dodecane or in (hydrated) TBP at but one temperature. All attempts to estimate the temperature dependence have been made on the equilibrium quotient $Q_{(1)}$. From Equation 18

$$d \ln K_{(1)}/d(1/T) = d \ln Q_{(1)}/d(1/T) + d \ln \gamma_S/d(1/T) - 3\, d \ln \gamma_\pm/d(1/T) - 2\, d \ln \gamma_T/d(1/T) \qquad (23)$$

The temperature dependence of $\gamma_\pm$ has been nominally studied by Komarov et al. *(17)* However, their work is a neat example of circular arguments, since they derive their $\gamma_\pm$ from distribution data with TBP. These give them $Q_{(1)}$ values at six temperatures between 10° and 50°C, extrapolation to zero concentrations of solutes gives $K_{(1)}$ values, and finally, a fit of log $\gamma_\pm$, obtained from Equation 18 and the above data, with the expression $-A(C_U)^{1/2}/[1 + 2.85(C_U)^{1/2}]^{-1} + 0.257\, C_U$, in effect compels the values to obey the Debye-Hückel expression for A and its temperature variation. There is thus here no independent determination of $d \ln \gamma_\pm/d(1/T)$ at all. The activity coefficients of the solutes in the organic phase have been determined only at 25° or so, *(6, 28, 33, 35)* and although considerable heat effects have been observed for the binary solutions, *(3, 9, 22, 33)* no direct measurements of the variation of the partial vapor pressure of the solvent (which lead to the activity coefficients of the solutes) with temperature have been made. Therefore, the quantity

$$\Delta H_{(1)}' = -R d \ln Q_{(1)}/d(1/T) =$$
$$(\Delta H_{(1)}^{*\text{ or }\circ} + R d \ln \gamma_S/d(1/T) - 3\, d \ln \gamma_\pm/d(1/T) -$$
$$2\, d \ln \gamma_T/d(1/T) \qquad (24)$$

is seen to differ from the standard enthalpy change.

One estimate of $\Delta H_{(1)}'$ of -15.4 kJ mol^{-1} for neat TBP is found in the literature *(10)* which is less than a half of $\Delta H_{(1)}^\circ$, showing that the sum of the activity coefficient terms in Equation 24 has a considerable negative value. The calorimetric estimate *(23)* $\Delta H_{(1)} = -26.8 \pm 1.6$ kJ mol^{-1} is much nearer our value. It has been described as "in essence, the heat of Reaction 1" *(23)* but although the wording suggests this to be the *standard* enthalpy change, the paper contains too few details to permit a confirmation of this. Also, the scatter of the results (three experiments), is larger than the above limit of error (±6%) given by the authors.

For hydrocarbon diluent systems there are several estimates of $\Delta H_{(1)}'$, ranging from -18 (*21*), through -19.8 (*32*), -21.7 ± 0.8 (*18*), -22.2 (*27*), -25.1 (*45*), to -26.8 ± 0.8 (*42*) all in kJ mol^{-1}. In some of these studies, nitric acid was present in the system (*21, 27, 42, 45*) and although this was stated as corrected for either by extrapolation to zero concentration (*21, 27, 45*) or by keeping its concentration constant (*42*), this added complication makes the values a less satisfactory estimate even of $\Delta H_{(1)}'$. The studies not involving nitric acid (*18, 32*) were made at appreciable uranium concentrations, so that the temperature coefficients of the activity coefficients should be important, but perhaps not sufficiently large to explain the difference between the work of Komarov et al. (*18*) ($C_T^\circ = 0.02$–$0.2M$, $C_U = 0.15$–$0.40M$, and $\bar{C}_U = 10^{-4}$–$1.5 \times 10^{-2}M$, *n*-decane as diluent) and the present work. However, it should be noted that in converting from $\Delta H_{(1)}$ for the equilibrium state (Table II, and lower curve in Figure 6) to $\Delta H_{(1)}^*$ for the standard state of infinite dilution of all solutes in the diluent, the organic phase is diluted simultaneously in both TBP and the solvate, so that both endothermic heats of mixing are reckoned in the same direction, and they no longer cancel each other. This produces the very large change from lim $\Delta H_{(1)}$ $C_T \rightarrow 0$ to $\Delta H_{(1)}^*$. The calorimetric estimate *(13, 14)* of $\Delta H_{(1)}$, made for isooctane as a diluent, gave -26.4 ± 0.8 (or, in the original thesis *(13)* -26.4 ± 3.4) kJ mol^{-1} for a concentration of $C_T^\circ = 0.1M$, but with no corrections for the heat effects for mixing, dilution, etc., being in effect the value q/Y. Since the concentrations of the initial and equilibrium solutions were not given in detail, it is impossible to correct from this q/Y to $\Delta H_{(1)}$, not to speak of $\Delta H_{(1)}^*$.

An evaluation of the equilibrium constants for this system, thus also of $\Delta G_{(1)}^*$ and $\Delta G_{(1)}^\circ$, has been made separately *(20)*. These constants are log $(K_{(1)}^c)^* = 2.25 \pm 0.08$ and log $(K_{(1)}^c)^\circ = 1.75 \pm 0.02$. These have to be converted to the respective mole-fraction values in order to avoid the cratic part. No special precision or accuracy is claimed for the present data, Table III, since the emphasis has been put on the calorimetric data. For dodecane, the present study has log $K_{(1)}^c$ about 0.1 units lower than the best published value for kerosene *(20)*, while for neat TBP it is about 0.2 units lower. This corresponds to a discrepancy of about 0.5 and 1.1 kJ mol^{-1} respectively, about twice the standard deviation, and not necessarily significant. As regards the Gibbs energy of transfer, which from the literature data is $\Delta G^{\mathrm{tr}} = -3.3 \pm 0.5$ kJ mol^{-1}, compared with the present value of -4.6 ± 0.5 kJ mol^{-1}, the discrepancy is, again, hardly significant, though accentuated by taking the difference.

The values of $\Delta S_{(1)}$ reported in the literature are all too negative *(18, 21, 27, 42)* or not sufficiently positive *(10)* by the cratic term $R\,[\ln (1000/V_{\mathrm{H_2O}})^3(1000/V_{\mathrm{dil\ or\ TBP}})]$. If the unitary parts of the entropies of extraction reported in the literature are calculated, not only that for neat TBP *(10)* but also those for diluted TBP turn out to be positive, in the range +50 to +124 J K^{-1} mol^{-1}. Since they are based on unreliable $\Delta H_{(1)}'$ values, and not very reliable $\Delta G_{(1)}$ values, these high positive values should be discounted. On the other hand, the values of $\Delta C_{p(1)}$ reported in the literature +147 *(42)* and +310 *(27)* J K^{-1} mol^{-1}, obtained from $d^2 \log Q_{(1)}/dT^2$, are of the right sign and the latter of nearly correct magnitude. Again, the calorimetrically determined value should be preferable, even though the correction factors used, valid for 23° ± 1°C rather than for the range of measurement of $\Delta H_{(1)}$, from 5° to 40°C, detract from its accuracy.

A final comparison that ought to be made is between $\Delta H_{(1)}^\circ$ determined in the present work, and the difference between the heats of solution of uranyl nitrate in water and in TBP:

$$\Delta H_{(1)}^\circ = \Delta H_{\mathrm{soln}}^\circ(\text{in TBP}) - \Delta H_{\mathrm{soln}}^\circ(\text{in H}_2\text{O}) \qquad (25)$$

Such comparisons, between enthalpies of extraction and the difference between the enthalpies of solution in the two separate phases, have been only rarely made *(11, 25)*. For anhydrous uranyl nitrate, the heat of solution in an infinite amount of water was found to be -49.9 ± 0.7 kJ mol^{-1} *(43)*, while the heat of solution in dry TBP at dilutions of 1:3500 to 1:10000 was found *(44)* to be -81.1 ± 0.7 kJ mol^{-1}, the difference of -31.2 ± 1.0 kJ mol^{-1} corresponding quite nicely to the value found in the present work of $\Delta H_{(1)}^{\circ} = -33.8 \pm 0.5$ kJ mol^{-1}. The extraction value of $\Delta H_{(1)}^{\circ}$ pertains to hydrated TBP, while the heat of solution value pertains to dry TBP, but the effect of the addition of water is small *(12)*, hence the small difference. Somewhat less accurate values for $\Delta H_{(1)}^{\circ}$ calculated from Equation 25 are obtained if the heats of solution of uranyl nitrate hydrates are compared, since for solutions of the hydrate in excess TBP, the interaction of the liberated water with the TBP must be corrected for. The data of Katzin et al. *(12)* yield for Equation 25 -19.6 and -21.3 kJ mol^{-1} for the hexahydrate and the dihydrate respectively. Corrected for liberated water with heat of solution data given by these authors *(12)* the figures become -23.1 and -22.5 kJ mol^{-1} respectively, still lower than the direct value or that calculated from heats of solution of the anhydrous salt. The dilutions used (1:80 for TBP and 1:180 for water) are, however, lower than in the work just quoted, but not sufficiently so to explain the difference. From the data of Vdovenko et al. *(43, 44)* for the dihydrate, the absurdly high value of $\Delta H_{(1)}^{\circ} = -49$ kJ mol^{-1} is obtained, but whereas the heats of solution for aqueous solutions obtained by Vdovenko et al. agree quite well with those obtained by Katzin et al., this is not the case for the dihydrate in TBP. The most probable value could be calculated from the present extraction data, and is right in between the values given by these two groups of authors.

Finally, a few words on the chemical significance of the thermodynamic data. The appreciable increase in heat capacity for the transfer of uranyl nitrate from the aqueous solution to TBP has already been commented on by Siddall *(42)*. Configurational and vibrational modes of energy absorption must be more pronounced in the bulky solvate than in the dissociated and tightly hydrated ions in the aqueous phase.

The negative (unitary) entropy change for extraction into dodecane is due to the association of five particles to form one complex particle. Although several water molecules from the hydration shell of the uranyl cation are released in this process, they are not set completely free, since in joining the bulk water they participate in the water structure, so that their full positive contribution is not realized. On the other hand the bulky solvate possibly produces additional disorder in the neat TBP by disrupting the orderly arrangement of the dipoles of the TBP molecules, an effect that cannot be present at infinite dilution in dodecane. This could explain the positive (unitary) entropy observed in neat TBP, although the magnitude of the entropy of transfer seems to be rather large for this effect.

The enthalpy of extraction is the balance between the heat of removal of the ions from their aqueous environment and the heat effect of the formation of uranyl nitrate bis(TBP) solvate. Since the low dielectric constant media permit the association of the ions, a major source for the exothermic heat is the coulombic energy, while the solvation—i.e., coordinate bond formation between the TBP and the uranium—helps to more than offset the loss of hydration energy. The considerable positive heat of transfer from dodecane to TBP can again be ascribed to the work required to disrupt the arrangement of the TBP dipoles by the bulky solvate in the latter solvent.

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