# Calorimetric Measurement of the Enthalpy of Extraction of Uranyl Nitrate by Tri-n-Amyl Phosphate

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Enthalpy of extraction of uranyl nitrate by tri n-amyl phosphate (TAP) and its solutions in n-dodecane has been directly measured by solution calorimetry for the first time. Measurements have been made at  $303\pm1$  K, in both forward as well as the reverse extraction modes. The enthalpies of the accompanying reactions such as the dilution of the uranyl nitrate in the aqueous phase, the hydration of TAP, the mixing of TAP and n-dodecane, the mixing of the metal-solvate (UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>•2TAP) and n-dodecane and mixing of the metal- solvate and TAP have also been independently measured and used to derive both the equilibrium state enthalpies and the standard state enthalpies for the extraction reaction. Two distinct standard states have been used for the organic phase, viz.,1) all solutes infinitely diluted in diluent ( $\Delta$ H\*) and 2) all solutes infinitely diluted in the water saturated extractant ( $\Delta$ H°). The results have been compared with the enthalpies of extraction measured by employing the temperature dependence of the distribution ratio as well as calorimetry reported in the literature for extraction of uranyl nitrate by TAP and TBP.

# Key Words : uranyl nitrate, tri n-amyl phosphate, enthalpy, solvent extraction, solution calorimetry

### I. INTRODUCTION

The thermodynamic parameters like enthalpy, entropy and free energy change of liquid-liquid extraction systems allow an insight into many types of interactions in liquids and into the systematics of the formation of co-ordination adducts in the extraction system studied. The enthalpy of extraction of a metal ion in liquid-liquid extraction can either be measured by the "second law method" or directly by the "first law method" employing calorimeters. The former method is conventionally followed in which the variation of the distribution coefficient with temperature is studied to derive the enthalpy from the slope of  $\log K_d$  Vs 1/T plot. This assumes that K<sub>d</sub> is proportional to "K", the equilibrium constant and also the constancy of activity coefficients in the temperature range of measurement etc. The enthalpies thus measured cannot be reduced to those for standard states. Hence this method has been subjected to severe criticism by Marcus and Kolarik [1,2]. Another option is the direct calorimetric measurement. This method, if corrected for the enthalpies of various side reactions such as hydration of extractant, dilution of the ions in aqueous solution, interactions of extractant/diluent, metal-solvate/extractant and metal-solvate/diluent which also occur during the extraction of the metal ion of interest, can yield the true enthalpy change as well as enthalpy changes corresponding to standard states.

Even though TBP has been used for over four decades in thermal reactor fuel reprocessing, researchers have been looking for safer alternatives for fast rector fuel reprocessing. The problems posed by TBP are the high aqueous phase solubility and susceptibility to form third phase with plutonium. TAP is an ideal choice with respect to both these criteria, as it does not form third phase at ambient temperatures with plutonium and also it has very low aqueous solubility. This paper reports the results of studies carried out on the direct calorimetric measurement of the enthalpy of extraction of uranyl nitrate by various solutions of TAP in n-dodecane as well as neat TAP. The reaction of interest is,

 $(UO_2^{2+})_{aq} + 2 (NO_3^{-})_{aq} + 2 TAP_{org} \Leftrightarrow UO_2(NO_3)_2 \bullet 2 TAP_{org}$ Both forward and reverse extraction modes were used for the enthalpy measurements. Refined correction procedures have been used to obtain standard state enthalpies. The results are compared with the results obtained by the conventional method of temperature dependence of distribution ratio, carried out in our laboratory as well as that reported in literature.

#### **II. EXPERIMENTAL**

All the reagents used were of AR or GR grade. TAP was synthesised and purified prior to use[3]. n-Dodecane (assay 99%, Alfa, Johnson Matthey GmbH, Germany) was used as received. The metal-solvate  $(UO_2(NO_3)_2 \bullet 2TAP)$  was prepared by saturating neat TAP with stoichiometric excess of solid uranyl nitrate hexahydrate crystals in a rotary evaporator with simultaneous vacuum evaporation of the water (of hydration) separating out. The metal-solvate was characterised by estimating the uranium content, which confirmed the formation of the disolvate. The calorimetric measurements were carried out in an isoperibol calorimeter. The details of the calorimeter, the forward and reverse

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extraction reactions, the electrical calibration, cooling correction and post-run data analysis have been described in detail elsewhere[3]. Details of the excess enthalpy measurements for TAP/n-dodecane, TAP/UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>•2TAP, n-dodecane/(UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>•2TAP) have also been dealt in detail elsewhere[4].

# III. Enthalpy Correction for associated reactions 1. Enthalpy of dilution of uranyl nitrate $(\Delta H_{dil})$

Marcus and Kolarik [1] have measured the enthalpy of dilution of 0.5 M uranyl nitrate with water at 297 K, and reported that the exothermic enthalpy of dilution per mole of uranium in the system varies linearly with the change in the concentration of uranium. Assuming the validity of their data at 303 K and also for the concentration ranges employed in the present studies (a maximum of 0.69 M), the enthalpy of dilution  $\Delta H_{dil}$  is given by the equation,

$$\Delta H_{dil} = q_{dil}/M_U = -(3800 \pm 240) \Delta C_U J.mol^{-1}(mol.L^{-1})^{-1}$$
 (1)

where  $M_U$  is the no. of moles of uranium and  $\Delta C_U$  is the change in the concentration of uranium during dilution  $(C_U^{\text{ini}} - C_U^{\text{fin}})$  in mol.L<sup>-1</sup>. The correction for the heat of dilution is given by the equation,

$$q_{dil} = -(3800*M_U*\Delta C_U)$$
 Joule (2)

It may be noted that in reverse extraction reactions the uranium concentration increases in the aqueous phase with resultant absorption of heat. Unlike the dilution experiments in which the total amount of uranium in the system remains constant, the amount of uranium in the aqueous phase during the extraction process varies from  $M_U^{ini}$  to  $M_U^{fin}$ . Hence a mean value of these has been taken as  $M_U$ , while evaluating corrections for the heat of dilution using equation (2), to derive the enthalpies in both forward and reverse extractions. Usage of the mean value for  $M_U$  is the first refinement that has been adopted while applying corrections for the heat of dilution, over that adopted by Marcus and Kolarik[1].

### 2. Enthalpy of hydration of TAP ( $\Delta H_{hvd}$ )

The exothermic enthalpy of hydration of neat dry TAP was measured at  $303\pm1$ K, in the mole ratio of water to TAP of around 275:1 and it was found to be  $-200\pm30$  J.(mol TAP)<sup>-1</sup>. As the heat of hydration for the solutions of TAP in n-dodecane was insignificantly low, corrections were applied only for the neat TAP extractions.

### 3. Enthalpy of mixing of TAP with dodecane ( $\Delta H_{hyd}$ ) :

This correction is applicable only for extractions with TAP solutions in which the diluent is present and not for the experiments involving neat TAP. The mixing of TAP with non polar n-dodecane is an endothermic reaction. This is due to the energy required to break the weak polar interactions prevailing in TAP to accommodate dodecane molecules. Under the experimental conditions, the diluent and the TAP are initially in a mixed state and during the extraction the consumption of TAP for the formation of metal-solvate will first involve "de-mixing" of TAP and n-dodecane which is obviously an exothermic reaction. Thus for every Y' mole of uranium extracted, 2Y' mole of TAP will "de-mix"

$$= q_{TD} (T+D)^{-1} = \Phi_{TD} (1-\Phi_{TD}) (A+B\Phi_{TD}+C\Phi_{TD}^{2})$$
  
J.mol<sup>-1</sup> (3)

where, A,B and C are 6546.32, -8274.96 and 6082.69 respectively and  $\Phi_{TD} = T/(T+D)$ . During the extraction the concentration of free TAP changes and the correction term for the "de-mixing" reaction is given by the integral,

$$\Delta q_{TD} = \int_{\Phi_{TD}^{\text{fin}}}^{\Phi_{TD}^{\text{fin}}} \Delta H_{TD} (T+D) d\Phi_{TD} , \quad \text{Joule}$$
(4)

The "normalising factor" (the term within the parenthesis in the integral) involves terms T and D in which D is constant whereas T is a variable which can be represented as a function of both D and  $\Phi_{TD}$  as given below,

since 
$$\Phi_{TD} = T/(T+D)$$
,  $\Phi_{TD}T + \Phi_{TD}D = T$  or  $T = \Phi_{TD} D/(1-\Phi_{TD})$  hence the integral takes the form

 $T = \Phi_{TD} D / (1 - \Phi_{TD})$  hence the integral takes the form,

$$\Delta q_{\rm TD} = \int_{\Phi_{\rm TD}^{\rm ini}}^{\Phi_{\rm TD}^{\rm ini}} \Delta H_{\rm TD} \left( \frac{\Phi_{\rm TD} D}{(1 - \Phi_{\rm TD})} + D \right) d\Phi_{\rm TD}$$
(5)

which can be rearranged to yield,

where,

$$\Delta q_{\rm TD} = \int_{\Phi_{\rm TD}^{\rm ini}} \Delta H_{\rm TD} \left( \frac{D}{1 - \Phi_{\rm TD}} \right) d\Phi_{\rm TD}$$
(6)

or, 
$$\Delta q_{TD} = \int_{\Phi_{TD}^{ini}} D \left( A \Phi_{TD} + B \Phi_{TD}^2 + C \Phi_{TD}^3 \right) d\Phi_{TD}$$
 (7)

or, 
$$=D\left(\frac{A}{2}(V^2 - U^2) + \frac{B}{2}(V^3 - U^3) + \frac{C}{2}(V^4 - U^4)\right) J$$
 (8)

$$U = \Phi_{TD}^{ini} = T_{free}^{ini} / (T_{free}^{ini} + D)$$
 and

 $V=\Phi_{TD}^{fin}=T_{free}^{fin}/(T_{free}^{fin}+D)$ , are the initial and final mole fractions of free TAP. The terms D,  $T_{free}^{ini}$  and  $T_{free}^{fin}$  represent the number of millimoles of the diluent, amount of free TAP in the initial and the final states of the system respectively in millimoles. The use of this approach is yet another refinement in applying corrections.

# 4. Enthalpy of mixing of $UO_2(NO_3)_2 \bullet 2TAP$ and n-DD $(\Delta H_{VD})$

The enthalpy of mixing of the metal-solvate with ndodecane was measured at  $303\pm1$  K for metal-solvate mole fractions in the range 0 to 0.14. The reaction was endothermic (q is positive) in the range studied. The heat change that has to be corrected for this mixing reaction in the extraction experiments is given by the equation,

$$\Delta q_{\rm YD} = D \left( \frac{A}{2} \left( \Phi_{\rm YD}^{\rm fin} \right)^2 + \frac{B}{3} \left( \Phi_{\rm YD}^{\rm fin} \right)^3 + \frac{C}{4} \left( \Phi_{\rm YD}^{\rm fin} \right)^4 \right) \ J \quad (9)$$

where, A = 8802.11, B = -30704.5, C = 94439.04 respectively and  $\Phi_{YD}$  is the mole fraction of the metal-solvate defined as,  $\Phi_{YD} = Y/(Y+D)$  where, Y is the

number of millimoles of metal-solvate present in the organic phase.

# 5. Enthalpy of mixing of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>•2TAP and TAP $(\Delta H_{YT})$

The integral enthalpy of mixing of dry TAP and metalsolvate was measured in the range of metal-solvate mole fractions from 0 to 0.164, and found to be exothermic in the range studied. The heat evolved per mole of the mixture as a function of the mole fraction of the metal-solvate  $\Phi_{YT}$ , is given for forward reactions by,

$$\Delta q_{YT} = -T \left( \frac{A}{2} \left( \Phi_{YT}^{\text{fin}} \right)^2 + \frac{B}{3} \left( \Phi_{YT}^{\text{fin}} \right)^3 + \frac{C}{4} \left( \Phi_{YT}^{\text{fin}} \right)^4 \right) \quad J (10)$$

where, A = 9678.7, B = -37821.01 and C = 109893.2, respectively and  $\Phi_{YT}$  is defined as,

$$\Phi_{\rm YT} = Y/(Y+T)$$

where Y is the amount of metal-solvate present in the organic phase in millimoles and T is the average amount of initial and final free TAP in millimoles. For reverse reactions the heat evolved is given by,

$$= -T\left(\frac{A}{2}(U^{2}-V^{2})+\frac{B}{3}(U^{3}-V^{3})+\frac{C}{4}(U^{4}-V^{4})\right) J(11)$$

where U and V represent  $\Phi_{YT}^{fin}$  and  $\Phi_{YT}^{ini}$  respectively.

## 6. Equilibrium State Enthalpy and Reduction to **Standard States**

In this work the various enthalpies are defined as follows, 1) the experimental enthalpy is the measured heat per unit mole of uranium extracted into the organic phase denoted as  $\Delta H_{ini}$ , 2) the equilibrium state enthalpy ( $\Delta H_{corr}$ ) is that corresponding to the equilibrium state, derived after effecting the corrections for the measured heat, from initial state to equilibrium state, 3) the standard state enthalpy  $(\Delta H_{std})$  is one arrived at after deriving the initial and equilibrium states from the standard state applicable.

# (1) Correction for equilibrium states

The equilibrium state enthalpy for example is derived as follows,  $\Delta H_{corr} = q_{corr} / Y'$ 

$$q_{corr} = q_{ini} - (q_{dil} + \Delta q_{hyd} + \Delta q_{TD} + \Delta q_{YD} + \Delta q_{YT}) \quad (12)$$

# (2) Correction for standard state

The standard state enthalpies are derived from,

$$\Delta H_{std} = q^{std} / Y', \text{ where,}$$

$$q^{std} = q_{ini} - (q_{dil}^{std} + q_{hvd}^{std} + q_{TD}^{std} + q_{YD}^{std} + q_{YT}^{std}) \qquad (13)$$

where Y' in the equations (12) and (13) represents the millimoles of uranium transferred from aqueous phase to the organic phase or vice versa and  $q_{ini}$  is the experimentally measured heat and the integrals for various corrections are evaluated between the initial and equilibrium states for  $(\Delta H_{corr})$ . the procedure for deriving the standard state enthalpies are details below.

### (a) Correction for dilution of uranyl nitrate

Using Hess' law of heat summation,  $q_{dil}^{std} + q_2 + q_3 = 0$ , where  $q_{dil}^{std}$ , q2 and q3 are enthalpy changes associated with the reactions (for going from one state to another) depicted below, proceeding in the anti-clockwise direction. It follows from the above,  $q_{dil}^{std} = -(q2+q3)$  or  $q_{dil}^{std} = q3'-q2$  where q3' (reverse of q3) is enthalpy change for the reverse reaction in which uranyl nitrate solution is taken from the initial state to the standard state.



The standard state enthalpy is derived as follows, from equation (1),

$$\begin{aligned} q_{dil} &= -(3800 * M_U * \Delta C_U), \quad \text{Joule} \\ \text{where } \Delta C_U &= C_{\text{ini}} \cdot C_{\text{fin}} \text{ and since here } C_{\text{fin}} = C_{\text{std}} = 0, \\ q3' &= -3800 * C_{\text{ini}} * V_{\text{ini}} * (C_{\text{ini}} \cdot C_{\text{std}}) \\ &= -3800 * C_{\text{ini}} * V_{\text{ini}} * (C_{\text{ini}} - 0) \end{aligned}$$

and similarly,

 $q2 = -3800 * C_{eq} * V_{eq} * (C_{eq} - 0),$ therefore,

 $q_{dil}^{std} = q2-q3'$ 

= 
$$-3800 * C_{ini} * V_{ini} * (C_{ini}-0) - (-3800 * C_{eq} * V_{eq} * (C_{eq}-0))$$
 and since  $V_{ini} = V_{eq} = V_{aq}$ , on simplification,

$$q_{dil}^{std} = -3800 * V_{aq} * (C_{ini}^2 - C_{eq}^2)$$
 J (15)

#### (b) Correction for the hydration of TAP

In forward extraction reactions, in the initial state the entire TAP is in dry condition and in the equilibrium state the excess unreacted TAP is in hydrated form. The standard state correction applicable is,

$$\begin{array}{l} q_{hyd}^{std} \; = \; q2\text{-}q3' \\ -200\,(\,T_{free}^{\,ini}\,\,) - (-200\,(T_{free}^{\,ini}\,\,-T_{free}^{\,eq}) \; = \; -200\,T_{free}^{\,eq} \end{array}$$

where  $T_{free}^{eq}$  is the amount of unreacted excess free TAP in moles.

In reverse extractions, in both the initial and the equilibrium states, the excess unreacted TAP is present in hydrated form. Free TAP generated by partial stripping of uranium from the organic phase gets hydrated and thus the net heat evolved is given by,

$$q_{hvd}^{std} = -(200 (T_{free}^{eq} - T_{free}^{ini})) \text{ Joule}$$
(16)

# (c) Correction for TAP/ n-dodecane interaction

The correction term  $q_{TD}^{std}$ can be represented after simplification by the simplified expression,

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$$= D\left(\frac{A}{2}(X^{2} - Y^{2}) + \frac{B}{3}(X^{3} - Y^{3}) + \frac{C}{4}(X^{4} - Y^{4})\right) J(17)$$

where A, B, C are the fitting constants,  $Y = \Phi_{TD}^{ini}$  and  $X = \Phi_{TD}^{eq}$  are respectively the mole fractions of the initial and equilibrium state free TAP, used in equation (3) and D is the amount of diluent present in the system in millimoles.

# (d) Correction for $UO_2(NO_3)_2 \bullet 2TAP$ and n-dodecane interaction

As discussed earlier,

$$q3' = \int_{\Phi_{YD}^{ini}}^{0} \Delta H_{YD}^{E} (Y+D) d\Phi_{YD}, \quad \text{Joule} \quad (18)$$

similarly,

$$q2 = \int_{\Phi_{YD}^{eq}}^{0} \Delta H_{YD}^{E} (Y+D) d\Phi_{YD}, \quad \text{Joule} \quad (19)$$

hence  $q_{\text{STD}}$  can be represented after simplification by the equation,

$$= D\left(\frac{A}{2}(M^2 - N^2) + \frac{B}{3}(M^3 - N^3) + \frac{C}{4}(M^4 - N^4)\right) J(20)$$

where A, B, C, are fitting constants,  $N = \Phi_{YD}^{ini}$  and  $M = \Phi_{YD}^{eq}$  respectively the mole fractions of the metal solvate in the initial and final states as referred in equation (8).

# (e) Correction for $UO_2(NO_3)_2 \bullet 2TAP$ and TAP interaction

The correction for the interaction of the metalsolvate and TAP for the reaction q3' can be represented as follows,

$$q3' = \int_{\Phi_{YT}^{ini}}^{0} \Delta H_{YT}^{E} (T+Y) d\Phi_{YT}, \quad \text{Joule} \quad (21)$$

similarly,

$$q2 = \int_{\Phi_{YT}^{eq}}^{0} \Delta H_{YT}^{E} (T+Y) d\Phi_{YT}, \quad \text{Joule} \quad (22)$$

hence  $q_{YT}^{std}$  can be represented after simplification by the equation,

$$= -T\left(\frac{A}{2}(P^{2} - Q^{2}) + \frac{B}{3}(P^{3} - Q^{3}) + \frac{C}{4}(P^{4} - Q^{4})\right) (23)$$

where A, B, C the fitting constants,  $Q = \Phi_{YT}^{ini}$  and  $P = \Phi_{YT}^{eq}$  respectively and mole fractions of the metal solvate used in equation (10). The above equation is applicable for both forward and reverse extraction reactions. While for forward reactions  $\Phi_{YT}^{ini} = 0$ , for reverse extractions both  $\Phi_{YT}^{ini}$  and  $\Phi_{YT}^{eq}$  have non zero values.

# **IV. RESULTS AND DISCUSSION**

Figure 1 depicts the derived standard state enthalpies as a function of TAP concentration. A least squares fitted line has been drawn through the derived standard state enthalpy points and been extrapolated to both Y axes to get  $\Delta H^*$  and  $\Delta H^\circ$ . It can be seen that the enthalpy at infinite dilution in n-dodecane ( $\Delta H^*$ ) is more exothermic (-24.9kJ.mol<sup>-1</sup>) than the

enthalpy at infinite dilution in hydrated neat TAP ( $\Delta$ H°) is -20.7kJ.mol<sup>-1</sup>. This is in contrast to the standard state enthalpies reported by Marcus and Kolarik[1], which indicated more exothermic $\Delta$ H<sup>\*</sup>(-54.5kJ.mol-1) as compared to  $\Delta$ H° (-33.8 kJ.mol<sup>-1</sup>). We do not have any explanation for this trend. Nevertheless, calorimetric measurements on the enthalpy of extraction of nitric acid by TBP, uranyl nitrate by tri isoamyl phosphate have confirmed the trend observed.

Also included in the figure are the enthalpies derived by extrapolation to "zero" acidity measured by us [6] for different TAP concentrations. The enthalpy derived by extrapolating these to "zero" TAP concentration (-21kJ.mol<sup>-1</sup>) is seen to coincide with  $\Delta H^*$  obtained by calorimetry. Siddall's [6] enthalpy value of -26.4kJ.mol<sup>-1</sup> is seen to be more exothermic but has been measured at 3M nitric acid.



**Figure 1** : Enthalpies of extraction of uranyl nitrate at various TAP concentrations,

 $\Delta$  : Enthalpy by distribution ratio method

- O : Enthalpy by calorimetry
- □ : Enthalpy reported by Siddall [6]

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