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Effect of temperature on the extraction of uranium by TiAP/n-dodecane

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ABSTRACT

The effect of temperature on the extraction of uranium by tri isoamyl phosphate (TiAP) has been studied as a function of nitric acid concentration, temperature and TiAP concentration. The resultant data has been used to derive the enthalpy of extraction of uranyl nitrate using "second law" method. The results are compared with those of tri n-butyl phosphate (TBP) system carried out under identical conditions. The results indicate that the enthalpy of extraction are also exothermic as observed in the TBP system but are distinctly more exothermic in TiAP systems at the acidities measured, while exhibiting similar enthalpies for 0.55 M TiAP solutions.

Keywords: Enthalpy of extraction; Triisoamyl phosphate; Purex process; Second law method

1. Introduction

Spent fuel reprocessing is an important part of the back end of the nuclear fuel cycle and involves the separation of plutonium and uranium from the fission products present in the irradiated fuel. This is normally carried out by aqueous reprocessing using PUREX process [1]. PUREX (plutonium uranium reduction extraction) has been the workhorse for spent fuel reprocessing over the last five decades. PUREX process employs liquid–liquid extraction and typically involves the following steps, 1) chopping the fuel and leaching under boiling conditions with ~10 M nitric acid, 2) adjustment of valency of plutonium to IV state and acidity to between 2 and 3 M, 3) co-extraction of uranium and plutonium with 30% TBP in an inert diluent, 4) partitioning plutonium from uranium by reducing its valency to the inextractable III state and 5) final purification of uranium and plutonium in separate cycles.

TBP has several advantageous properties such as 1) good stability towards thermal, radiation and chemical degradation, 2) ideal physical properties, 3) good selectivity for uranium and plutonium with faster kinetics, 4) economical and easy availability [2,3]. However it suffers from some disadvantages, such as high aqueous solubility, susceptibility for third phase formation and incomplete incinerability due to the formation of residual phosphate during final disposal. The high solubility in aqueous phase demands extensive washing to remove the TBP dissolved in aqueous phase streams such as raffinates and strip products, prior to evaporation, as dissolved TBP would lead to the degradation causing precipitation and accumulation of plutonium leading to losses and also "red oil explosion". Third phase formation is a phenomenon in solvent extraction in which at high metal loading the organic phase splits into two phases. The light phase contains mostly the diluent and the heavy phase contains essentially the metal solvate and free extractant. This heavy phase is called third phase and formation of this phase in counter-current contactors may lead to "flood-

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ing" as well as accumulation leading to criticality as the concentration of plutonium in such heavy phases can be as high as 1.5 M [4]. The third phase phenomenon is especially important and is of high relevance to fast reactor fuel reprocessing where high Pu content fuel is used.

Hence we have taken up a program to study higher homologues of TBP as candidate materials for fast reactor fuel reprocessing and have carried out detailed studies on the extraction of actinides and also on the third phase formation behavior of actinides [5–9]. TiAP a higher, branched chain homologue of tributyl phosphate is being considered as an alternate extractant for spent fuel reprocessing [10]. TiAP retains all the advantages of TBP while overcoming the disadvantages. Its aqueous solubility is very low as compared to TBP [11] Also its is resistant to solvent degradation especially the alpha induced degradation prevalent in high plutonium loaded conditions as experienced in fast reactor fuel reprocessing and does not form third phase with plutonium under ambient conditions. TiAP has been employed for reprocessing high burn up fuel in Russia [12]. Data on the thermodynamic parameters on the extraction of uranium are scarce in the literature and hence an attempt has been made to derive them using the "second law" method and the results are reported here.

2. Materials and method

All chemicals used in the study are of AR grade. Isoamyl alcohol, heptane and pyridine (Rankem Chemicals, India), phosphoryl chloride (Loba Chemie), n-dodecane (Lancaster, England) were procured and used as received. Uranium-233 was obtained from Reprocessing Group, IGCAR. Just prior to use U-233 (in the form of $UO_2(NO_3)_2$) was purified from the daughter products, by extraction using 5% TBP/n-dodecane from 4 M HNO_3, followed by washing of the organic phase and finally stripping of uranium with 0.01 M HNO_3.

TiAP was synthesized using stoichiometric quantities of isoamyl alcohol, phosphoryl chloride at 0°C. Isoamyl alcohol, pyridine and heptane as solvent were taken in a three neck round bottom flask and placed in an ice bath. Phosphoryl chloride was added drop wise into it and the whole slurry was continuously stirred vigorously. The organic layer is the crude TiAP which was removed and washed to remove pyridinium hydrochloride. Then heptane and other volatile impurities were removed using a rotary evaporator and TiAP finally purified by vacuum distillation.

The purified TiAP was characterized using IR, NMR techniques. Various physical properties were also measured. The density was found to be 0.952 g cm^{-3} at 25°C, refractive index was found to be 1.423 at 30°C and it was found to boil at 105°C at 0.04 millibar pressure.

A solution of 1.1 M and 0.55 M TiAP in n-dodecane was prepared by weighing out appropriate quantity of TiAP in volumetric flask and making up the solution to the mark. It was kept over night to check for volume changes and adjusted accordingly. Then it was washed with 5 M NaOH solution to remove acidic impurities viz., mono isoamylphosphate and diisoamyl phosphate immediately prior to use. The washed TiAP solution was pre-equilibrated with the desired nitric acid to be used in the experiment. 2 ml of the prequilibrated TiAP was taken in equilibration tubes and 2 ml of corresponding nitric acid was added. Finally uranium-233 tracer was added and equilibrated in a specially made thermostatic equilibrator. This equilibrator consists of a double walled glass jacket through which water from a digitally controlled water bath (Julabo) flows. This water jacket is placed on an electromechanical stirrer. Then the equilibration tubes containing the organic and aqueous phase are placed inside the equilibrator. Each of the tubes contains small PTFE coated magnetic stirring bar, which stirred vigorously and there by equilibrating the contents inside. This equilibration was done for nearly 30 min. All the measurements were carried out in duplicate. The tubes were also kept in black polythene bags to avoid any photochemical reaction that will lead to degradation of the extractant.

After the equilibration the phases were allowed to settle by gravitation for phase separation. Then aliquots were taken from organic and aqueous phase directly in scintillation cocktail or after suitable dilution suitably in 5% TiAP/n-DD or 0.1 M HNO_3 respectively. Uranium content was determined by using α-radiometric assay using alpha scintillation counter. Dioxane based cocktail was used. Dioxane was refluxed over NaOH and distilled, scintillation grade PPO, POPOP, Naphthalene and TOPO were used in preparation of cocktail [13,14]. From the values obtained from counting $D_{U(VI)}$ was calculated. All measurements were done in duplicates. These experiments were done in temperature range of 293–333K with 10K interval and nitric acid concentration varying from 0.1 M to 9 M. Enthalpies of extraction at all the different concentration were calculated by the "second law method" using van't Hoff equation. The results were compared with those done with TBP [15] and TAP [16] under identical conditions.

3. Results and discussion

The chemical equilibrium for the extraction of U(VI) by TiAP is given as follows [5]

$$UO_2^{2+} + 2NO_3^- + 2TiAP \Leftrightarrow UO_2(NO_3)_2 \cdot 2TiAP \qquad (1)$$

The equilibrium constant of this reaction can be written as

$$K = \frac{(UO_2(NO_3)_2 \cdot 2TiAP)}{(UO_2^{2+})(NO_3^-)^2(TiAP)^2} \qquad (2)$$

This equation can also be represented in terms of concentration and activity coefficients

$$K = \frac{(\mathrm{UO_2(NO_3)_2 \cdot 2TiAP}) \cdot \gamma_{(\mathrm{UO_2(NO_3)_2.2TiAP})}}{(\mathrm{UO_2^{2+}})(\mathrm{NO_3^-})^2(\mathrm{TiAP})^2 \cdot \gamma_{\mathrm{UO_2^{2+}}}\gamma^2_{\mathrm{NO_3^-}}\gamma^2_{\mathrm{TiAP}}} \tag{3}$$

If one assumes that the activity coefficients of the extractant and the nitric acid concentration are constant and the activity coefficients are negligibly dependent on temperature then we can write

$$K' = \frac{(\mathrm{UO_2(NO_3)_2 \cdot 2TiAP})}{(\mathrm{UO_2^{2+}})(\mathrm{NO_3^-})^2(\mathrm{TiAP})^2} \tag{4}$$

The aqueous phase contains various nitrate complexes of U(VI), viz., $\mathrm{UO_2(NO_3)^+}$, $\mathrm{UO_2(NO_3)_2}$, $\mathrm{UO_2(NO_3)_3^-}$ etc. If T_u is the total concentration of U(VI) in the aqueous phase at equilibrium then we can write

$$T_u = (\mathrm{UO_2^{2+}})(1+\beta_n[\mathrm{NO_3^-}]^n) \tag{5}$$

where β_n is the overall stability constant for the following reaction.

$$\mathrm{UO_2^{2+}} + n(\mathrm{NO_3^-}) \xrightarrow{\beta_n} (\mathrm{UO_2(NO_3)})_n^{(2-n)+} \tag{6}$$

Now putting T_u in the above equation, K' can be written as

$$K' = \frac{(\mathrm{UO_2(NO_3)_2 \cdot 2TiAP})\left(1+\sum_1^n \beta_n[\mathrm{NO_3^-}]^n\right)}{(\mathrm{UO_2^{2+}})(\mathrm{NO_3^-})^2\,(\mathrm{TiAP})^2} \tag{7}$$

Eq. (7) can be also be simplified to

$$K' = \frac{D_{\mathrm{U(VI)}}\left(1+\sum_1^n \beta_n[\mathrm{NO_3^-}]^n\right)}{(\mathrm{NO_3^-})^2(\mathrm{TiAP})^2} \tag{8}$$

Fig. 1 depicts the variation of the distribution ratio for the extraction of nitric acid by 1.1 M TiAP/n-dodecane, as a function of equilibrium aqueous phase acidity at different temperatures. It can be seen that the distribution ratios do not vary significantly with temperature. Assuming the concentration of free TiAP remains constant over the temperature range studied and also assuming the factor, $(1 + \beta_n\ [\mathrm{NO_3^-}]_n)$ remains constant from 293K to 333K, the van't Hoff equation given below can be used to derive the enthalpy of extraction

$$\frac{\Delta \log K'}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \tag{9}$$

Putting the value of K' in the above equation and by further reducing the equation we get

$$\frac{\Delta \log D_{\mathrm{U(VI)}}}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \tag{10}$$

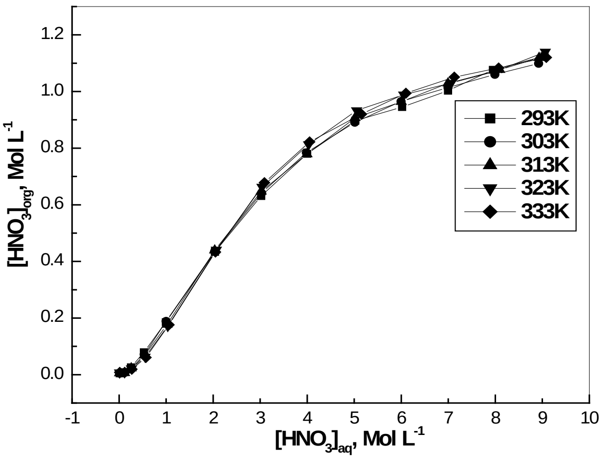

Fig. 1. Effect of temperature on the extraction of nitric acid by 1.1 M TiAP/n-dodecane at different temperatures (293–333K).

A plot of log $D_{\mathrm{U(VI)}}$ vs. log $(1/T)$ yields a straight line with a slope equal to $-\Delta H/2.303R$.

The $D_{(\mathrm{U(VI)})}$ values plotted as a function of equilibrium aqueous phase acidity at various temperatures for both 1.1 M and 0.55 M TiAP are depicted in Fig. 2 and Fig. 3, respectively. It can be seen that all temperatures $D_{(\mathrm{U(VI)})}$ initially increases with acidity attains a maximum and then decreases. The D values at any acidity for a given concentration of TiAP are also lower at higher temperature indicating the exothermic nature of the extraction of uranyl nitrate by TiAP.

It is also interesting to observe that the acidity corresponding to the maximum $D_{(\mathrm{VI})}$ decreases with the increase in temperature. At any temperature the initial increase can be attributed to the increased salting by the increasing nitrate ion concentration and the later decrease is due to both the formation of anionic nitrate complex and also due to competition from nitric acid extraction by

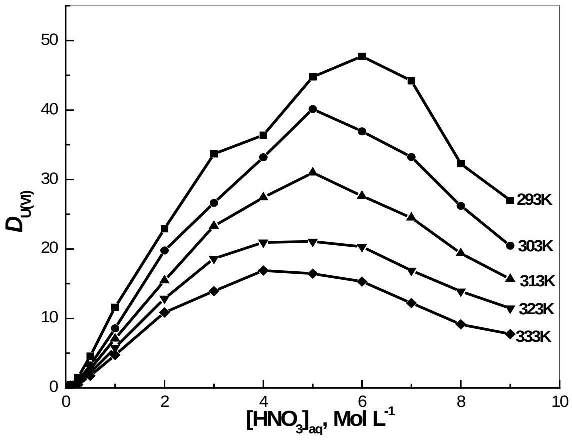

Fig. 2. Effect of equilibrium aqueous phase acidity and temperature on the extraction of $\mathrm{UO_2^{2+}}$ by 1.1 M TiAP/n-dodecane.

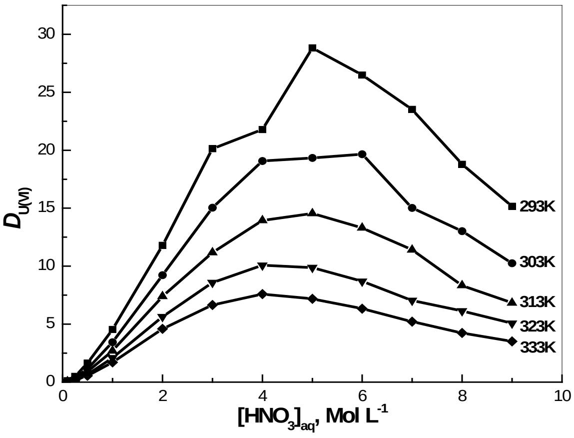

Fig. 3. Effect of equilibrium aqueous phase acidity and temperature on the extraction of UO_2^{2+} by 0.55 M TiAP/n-dodecane.

TiAP. This shifting of maxima towards lower acidity may be due to the increased formation of anionic complexes of uranium at high temperatures.

Using linear least squares fitting of the data points of the plot “log $D_{U(VI)}$ vs. $1/T$”, the enthalpies of extraction derived from the slope are depicted in Figs. 4 and 5, respectively, as a function of equilibrium aqueous phase nitric acid concentration for 1.1 M and 0.55 M TiAP/n-dodecane. Also included in the figures for comparison are the corresponding enthalpies of extraction of uranyl nitrate by identical concentrations of TBP [15] and TAP [16] reported in literature under identical equilibrium aqueous phase acidities. A comparison of the enthalpies of extraction by 1.1 M and 0.55 M TiAP is depicted in Fig. 6.

The results indicate that the enthalpy of extraction of uranyl nitrate by TiAP is exothermic at all acidities and temperatures and also for both the concentrations of the extractant studied.

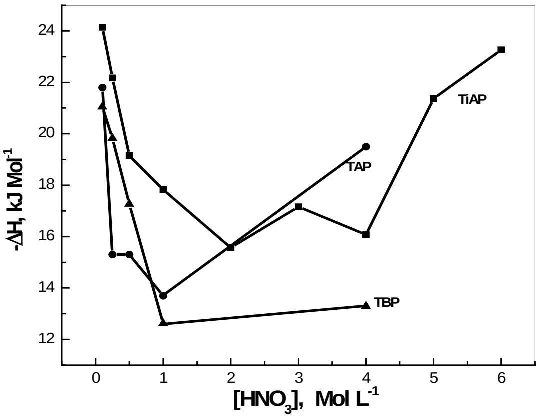

Fig. 4. Enthalpy of extraction of U(VI) as a function of aqueous phase acidity for 1.1 M TiAP/n-DD, 1.1 M TAP/n-DD and 1.1 M TBP/n-DD.

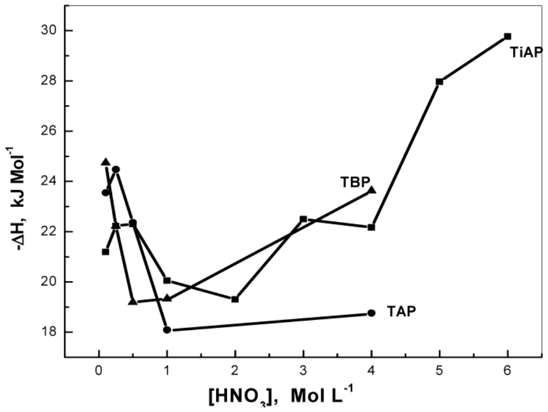

Fig. 5. Enthalpy of extraction of U(VI) as a function of aqueous phase acidity for 0.55 M TiAP/n-DD, 0.55 M TAP/n-DD and 0.55 TBP/n-DD.

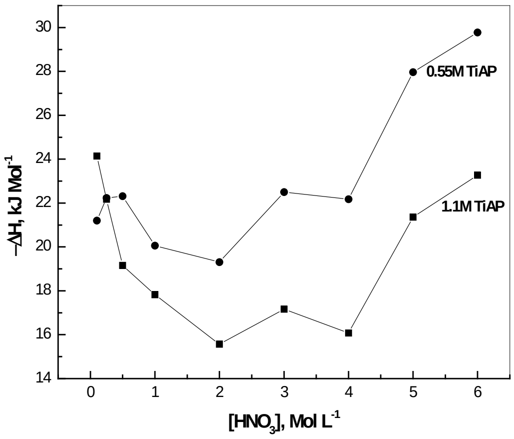

Fig. 6. Comparison of enthalpy of extraction of UO_2^{2+}using 1.1 M and 0.55 M TiAP.

The overall enthalpy change in an extraction process consists of enthalpy changes associated with (a) dehydration of actinide ion (ΔH_1), (b) the formation of neutral extractable complex of the actinide ion (ΔH_2) and [c] solvation of the neutral complex in organic phase (ΔH_3) [17]. The magnitude and sign of ΔH depends on the magnitude and sign of these three components. As $UO_2(NO_3)_2 \cdot 2TiAP$ is the only species formed so ΔH_2 can be assumed to be constant and exothermic. But both ΔH_1 and ΔH_3 are dependent on the concentration of nitric acid. ΔH_1 decreases with the increase in nitric acid concentration, due to the decrease in water activity. ΔH_3 depends on the acidity of the organic phase which depends on the nitric acid concentration.

In the plot presented the enthalpy becomes less exothermic with increase in nitric acid concentration up to 1 M and then becomes increasingly exothermic. It is possible that in U(VI)–TiAP system, up to 1 M nitric acid, the change in ΔH_1 is not significant since the variation in water activity is very little and the ΔH is influenced only by a change in ΔH_3, while at higher acidities, the influence of water activity predominates and the overall enthalpy change becomes more exothermic with increase in acidity. The plot also compares the data reported in literature for 1.1 M TAP and 1.1 M TBP solutions in n-dodecane, derived from experiments conducted in similar condition. From the results, it can be concluded that increase in the carbon chain length from butyl and amyl or branching within the amyl group does not result in any significant variation in the trend.

4. Conclusion

The extraction of uranyl nitrate by TiAP solutions in n-dodecane has been studied as a function of temperature, equilibrium aqueous phase acidity as well as extractant concentration. The enthalpy of extraction has been derived using second law method and the trends observed have been explained based on the constituent enthalpies contributing to the overall enthalpy. The enthalpy of extraction of uranium by TiAP has been found to be exothermic and also follow a similar trend exhibited by TBP and TAP. However it will be useful if detailed studies on the radiation (especially alpha induced), thermal and acid degradation behaviour are carried out on TiAP in comparison with TBP systems prior to utilization in fast reactor fuel reprocessing.

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