

Extraction of actinides using *N, N, N', N'*-tetraoctyl diglycolamide (TODGA): a thermodynamic study

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(Received September 5, 2005; accepted in revised form January 19, 2006)

TODGA / Actinides / Thermodynamics / Extraction constant

Summary. The effect of temperature on the extraction behaviour of Am(III), Pu(IV) and U(VI) from nitric acid medium was studied employing *N, N, N', N'*-tetraoctyl diglycolamide (TODGA) in *n*-dodecane. The two-phase equilibrium constants ($\log K'_{ex}$) were calculated and compared with those of other extractants proposed for actinide partitioning, viz. octyl-(phenyl)-*N, N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and *N, N, N', N'*-dimethyl dibutyl tetradecyl malonamide (DMDBTDMA). Thermodynamic parameters, viz. ΔG , ΔH and ΔS for the extraction of actinides by TODGA were also compared with those of CMPO and DMDBTDMA. These studies indicate that the extraction processes of Am(III) and U(VI) are enthalpy driven whereas entropy factor counteracts the extraction. However, in the case of Pu(IV), the extraction process is enthalpy as well as entropy favoured. Role of diluent on the loading of Nd(III) in 0.1 M TODGA has also been investigated.

1. Introduction

Organophosphorus extractants have been extensively used in the separation and recovery of actinides from various aqueous streams in the back end of nuclear fuel cycle. Tri-*n*-butyl phosphate (TBP) is universally employed for the spent fuel reprocessing of Pu in the PUREX process and for the recovery of the ²³³U from irradiated Th in the THOREX process. On the other hand, bifunctional organophosphorus compounds containing P=O and C=O groups like octyl-(phenyl)-*N, N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO, Fig. 1a) have been extensively evaluated for the partitioning of minor actinides from high level waste (HLW) in the TRUEX process [1, 2]. Diisodecyl phosphoric acid (DIDPA, Fig. 1b) and trialkyl phosphine oxide (Cyanex-923, a commercial product where *R* = C₆ and C₈ groups, Fig. 1(c)), have also been extensively investigated for the partitioning of minor actinides from High Active Waste (HAW) at a relatively lower acidity [3–5].

In recent years, completely incinerable substituted diamides have been the focus of numerous studies in the back

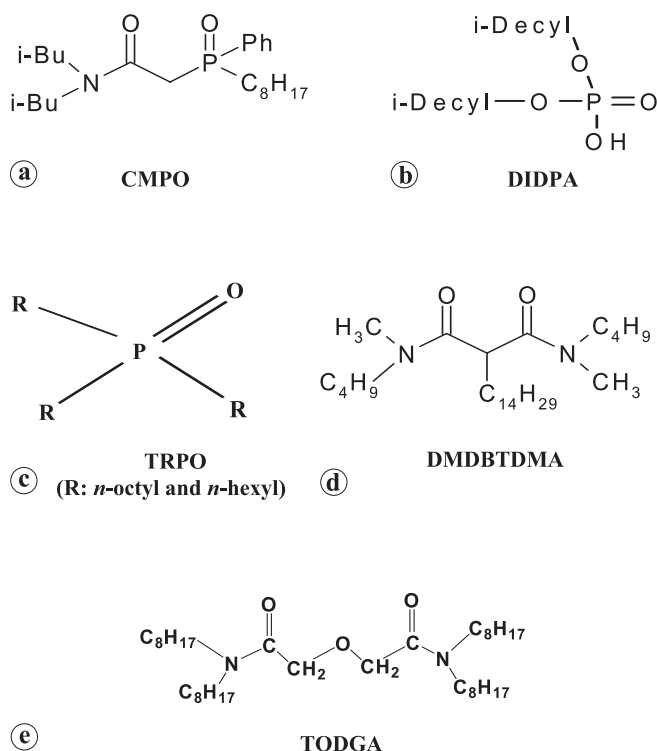


Fig. 1. Structural formulae of extractants.

end of nuclear fuel cycle [6]. Certain distinct advantages, viz. innocuous nature of degradation products, easy stripping and low secondary waste volume, etc. make this class of extractants very attractive [6, 7]. Though *N, N, N', N'*-dimethyl dibutyl tetradecyl malonamide (DMDBTDMA, Fig. 1d) has been reported to be a promising candidate for actinide partitioning, it is a poor extractant for Am(III)/Cm(III) from the HLW at acidity < 3 M HNO₃. In order to increase the efficiency of diamides towards the extraction of Am(III) and Cm(III), efforts are being made towards structural modifications of diamide so as to improve the extractability of these metal ions. It was found that the introduction of one etheric oxygen between the two amide groups (diglycolamide) causes an increase in the extraction efficiency of the minor actinides because of the tridentate nature of the ligand molecule [8, 9]. Recently developed, a tridentate ligand, *N, N, N', N'*-tetraoctyl diglycolamide (TODGA,

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Fig. 1e) has been identified as one of the most powerful extractants being considered for the partitioning of trivalent actinides and lanthanides from HLW solutions [10, 11]. Earlier studies reported from our laboratory as well as elsewhere employing TODGA as the extractant were focused on the distribution behaviour of Am(III), Pu(IV), U(VI), Eu(III), Fe(III), Sr(II) and Cs(I) from pure nitric acid solutions as well as from simulated high-level waste (SHLW) solutions relevant to the PUREX process [10–12]. In view of the presence of α/β emitting radionuclides in HLW, its temperature may rise well above the ambient temperature. So far, no attempt has been made to study the effect of temperature on the extraction behaviour of actinides using TODGA as extractant. The present paper, therefore, deals with the thermodynamics of the extraction of actinides like Am(III), Pu(IV) and U(VI) using TODGA as the extractant. The effect of diluent on the loading of Nd(III) in the organic phase has also been investigated.

2. Experimental

2.1 Reagents and radionuclides

TODGA was synthesised at the Chemistry Department, University of Delhi, Delhi, India. The details of synthesis procedure, analytical data and PMR data are given elsewhere [12]. The diluent, *n*-dodecane, procured from Lancaster, was used without further purification. Other chemicals used were of analytical reagent grade. ^{241}Am was tested for its purity by α as well as by γ -spectrometry. Radiotracer ^{233}U , prepared by irradiation of ^{232}Th in nuclear reactor, was separated by the THOREX process. It was purified by the procedure reported earlier [13]. The purity of the tracer was checked by α -spectrometry. Pu (principally ^{239}Pu) was purified by the reported procedure and its radiochemical purity was ascertained by gamma ray spectrometry for the absence of ^{241}Am [14]. Further, Pu valency in the aqueous phase was adjusted and maintained in the tetravalent state by the addition of 0.05 M NaNO_2 + 0.005 M NH_4VO_3 as the holding oxidant.

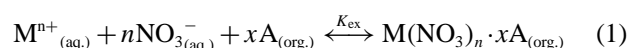
2.2 Distribution studies

A suitable volume of the aqueous phase (generally 1 mL) under desired experimental conditions and spiked with radiotracers, was agitated with an equal volume of pre-equilibrated organic phase (0.1 M TODGA/*n*-dodecane) in stoppered glass tubes for 45 minutes. During these studies, constant temperatures were maintained within $\pm 1^\circ\text{C}$ of the desired value using a thermostated water bath. The two phases were then centrifuged and assayed radiometrically. Estimation of ^{241}Am was carried out by gamma counting using a well type NaI(Tl) scintillation counter. Liquid scintillation counting was followed for ^{233}U and ^{239}Pu employing a toluene-based scintillator containing 0.7% (w/v) PPO (2,5-diphenyl oxazole), 0.03% (w/v) POPOP (1,4-di-[2-(5-phenyloxazolyl)]-benzene) and 10% (v/v) HDEHP (di(2-ethylhexyl) phosphoric acid). The distribution ratio of the metal ion (D_M) was calculated as the ratio of the concentration of metal ions (expressed in terms of counts per unit time per unit volume) in organic phase to that in the

aqueous phase. Loading of Nd(III) in 0.1 M TODGA dissolved in different diluents was carried out from an aqueous phase containing 2 M of Nd(III) at 3 M HNO_3 . The third phase obtained was dissolved by adding the fresh organic phase. In those cases where no third phase formation was observed, repeated loading experiment was performed with fresh aqueous phase each time till the Nd(III) concentration in the organic phase was constant; it was determined by complexometric titration (in acetate buffer at pH 5) employing standard EDTA solution and xylenol orange as indicator [15].

2.3 Calculation of thermodynamic parameters

In general, the two phase equilibrium representing the extraction of metal ions from nitric acid medium with TODGA (A) can be represented as:



where, the subscripts aq. and org. represent the aqueous and organic phases, respectively. Thus the equilibrium constant for reaction Eq. (1) can be written as:

$$K_{\text{ex}} = \frac{[\text{M}(\text{NO}_3)_n \cdot x\text{A}]_{(\text{org.})} \gamma_{\text{M}(\text{NO}_3)_n \cdot x\text{A}}}{\left\{ [\text{M}^{n+}]_{(\text{aq.})} [\text{NO}_3^{-}]_{(\text{aq.})}^n [\text{A}]_{(\text{org. free})}^x \right\} \times \gamma_{\text{M}^{n+}} \gamma_{\text{NO}_3^{-}}^n \gamma_{\text{A}}^x} \quad (2)$$

where the squared brackets and γ represent the concentrations and the activity coefficients of the respective species, respectively. The equilibrium constants for the extraction of metal ions were calculated using the following approximations: (a) the activity coefficients of the metal ion in the aqueous phase as well as of the metal solvate in the organic phase are assumed to be unity since the concentration of the metal ions is at the tracer level, and (b) $[\text{A}]_{(\text{org. free})}$ is assumed to be equal to the activity of free amide (a_{A}). The activity of nitrate ion ($a_{\text{NO}_3^{-}}$) was used from the literature for the calculation of equilibrium constants [16]. Therefore one can write:

$$K'_{\text{ex}} = \frac{[\text{M}(\text{NO}_3)_n \cdot x\text{A}]_{(\text{org.})}}{[\text{M}^{n+}]_{(\text{aq.})} \{a_{\text{NO}_3^{-}}\}_{(\text{aq.})}^n [\text{A}]_{(\text{org. free})}^x} \quad (3)$$

where K'_{ex} represents the conditional extraction constants of metal ions. The experimentally determined distribution ratio (D_M) is the ratio of the concentration of metal ion in the organic phase to the total concentration of the metal ion in the aqueous phase. Thus the distribution ratio for the equilibrium reaction Eq. (1) can be expressed as,

$$D_M = \frac{[\text{M}(\text{NO}_3)_n \cdot x\text{A}]_{(\text{org.})}}{[\text{M}_t^{n+}]_{(\text{aq.})}} \quad (4)$$

where $[\text{M}_t^{n+}]_{(\text{aq.})}$ represents the total concentration of the metal ion in the aqueous phase. Because of the presence of substantial amount of NO_3^{-} ions, the metal ion species present in the aqueous phase will be M^{n+} , $\text{M}(\text{NO}_3)^{(n-1)+}$, $\text{M}(\text{NO}_3)_2^{(n-2)+}$... *etc.* Thus the total concentration of the metal ion in the aqueous phase can be written as:

$$[\text{M}_t^{n+}]_{(\text{aq.})} = [\text{M}^{n+}] + [\text{M}(\text{NO}_3)^{(n-1)+}] + [\text{M}(\text{NO}_3)_2^{(n-2)+}] + \dots$$

$$[M_t^{n+}]_{(aq)} = [M^{n+}](1 + \beta_1^M[NO_3^-] + \beta_2^M[NO_3^-]^2 + \dots)$$

$$[M_t^{n+}]_{(aq)} = [M^{n+}](1 + \sum \beta_n^M[NO_3^-]^n) \quad (5)$$

where the subscript t refers to the total metal ion concentration in the aqueous phase. Here β_n^M represents the overall stability constant for the given metal complex, which gives the extent of nitrate complexation. Therefore Eq. (3) takes the following form:

$$K'_{ex} = \frac{[M(NO_3)_n \cdot xA]_{(org.)}(1 + \sum \beta_n^M[NO_3^-]^n)}{[M_t^{n+}]_{(aq.)}\{a_{NO_3^-}\}_{(aq.)}^n[A]^x_{(org. free)}} \quad (6)$$

From Eqs. (4) and (6), following expression can be obtained.

$$K'_{ex} = \frac{D_M(1 + \sum \beta_n^M[NO_3^-]^n)}{\{a_{NO_3^-}\}_{(aq.)}^n[A]^x_{(org. free)}} \quad (7)$$

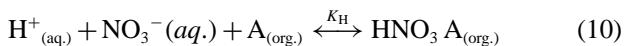
Assuming that the values of the term $(1 + \sum \beta_n^M[NO_3^-]^n)$ do not change significantly in the chosen temperature range [17, 18], then the Van't Hoff equation can be used to calculate the enthalpy change (ΔH) associated with the extraction process.

$$\frac{(\Delta \log K)}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \quad (8)$$

where R is the gas constant and thus,

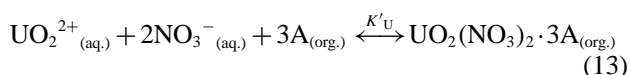
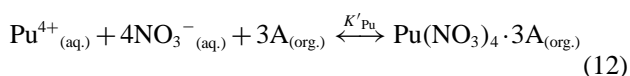
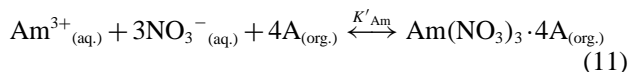
$$\Delta H = -R \times 2.303 \times \text{slope} \quad (9)$$

Because HNO_3 is also extracted to a small extent by neutral ligand TODGA, it was necessary to determine the concentration of the free ligand. Earlier studies have demonstrated that TODGA extracts HNO_3 predominantly by the following equilibrium reaction,



where K_H represents the basicity of the extractant. Assuming that the above equilibrium reaction does not change with the temperature selected for the present work, the concentration of the free ligand $[A]_{(org. free)}$ was calculated from the basicity of the extractant (Basicity of TODGA, $K_H = 4.1$) [12].

The ligand variation studies carried out in our laboratory as well as elsewhere for Am(III), Pu(IV) and U(VI) employing TODGA/*n*-dodecane have shown the predominant extracted species in the organic phase as: $Am(NO_3)_3 \cdot 4TODGA$, $Pu(NO_3)_4 \cdot 3TODGA$ and $UO_2(NO_3)_2 \cdot 3TODGA$, respectively [10]. With the knowledge of stoichiometry of the extracted species, the extraction equilibria for Am(III), Pu(IV) and U(VI) by TODGA can be written as:



Assuming that the stoichiometry of the extracted species does not change in the temperature range employed in the present studies [19], the extraction constant for Am(III), Pu(IV) and U(VI) for the above equilibrium reactions can be calculated on the basis of Eq. (7) as follows:

$$K'_{Am} = \frac{D_{Am} \cdot (1 + \sum \beta_n^{Am}[NO_3^-]^n)}{\{a_{NO_3^-}\}_{(aq.)}^3 \cdot [A]^4_{(org. free)}} \quad (14)$$

$$K'_{Pu} = \frac{D_{Pu} \cdot (1 + \sum \beta_n^{Pu}[NO_3^-]^n)}{\{a_{NO_3^-}\}_{(aq.)}^4 \cdot [A]^3_{(org. free)}} \quad (15)$$

$$K'_{U} = \frac{D_U \cdot (1 + \sum \beta_n^U[NO_3^-]^n)}{\{a_{NO_3^-}\}_{(aq.)}^2 \cdot [A]^3_{(org. free)}} \quad (16)$$

The Gibbs energy change (ΔG) associated with the extraction process of the above metal ions can be calculated from the value of the extraction constant (K'_{ex}), employing the following equation,

$$\Delta G = -RT \times 2.303 \times \log K'_{ex} \quad (17)$$

From the knowledge of the Gibbs energy change (ΔG) and the enthalpy change (ΔH), entropy change (ΔS) of the system is calculated from Gibbs's Helmholtz equation,

$$\Delta G = \Delta H - T \Delta S \quad (18)$$

3. Results and discussion

3.1 Effect of temperature on distribution of metal ions

Table 1 lists the D_M values for Am(III), Pu(IV) and U(VI) by 0.1 M TODGA/*n*-dodecane from 1 M HNO_3 at different temperatures (15–45 °C). It is clear that the extraction of these metal ions decreased with increase in the temperature, suggesting the exothermic nature of the extraction equilibria. Similar observations have been reported earlier for the extraction of Am(III), Pu(IV) and U(VI) with DMDBTDMMA, CMPO and other neutral organophosphorus extractants like tri-*n*-butyl phosphate (TBP), tri-*n*-amyl phosphate (TAP) [20–25]. The extraction constant ($\log K'_{ex}$) for Am(III), Pu(IV) and U(VI) by TODGA was calculated employing Eqs. 14, 15 and 16, respectively. However to enable such calculations, it is essential to evaluate the value of $(1 + \sum \beta_n^M[NO_3^-]^n)$ for each of the metal ions. In the present work, the values of these complexation factors for Am(III), U(VI) and Pu(IV) at 1 M

Table 1. Distribution ratio of metal ions at different temperatures; Aqueous phase: 1 M HNO_3 ; Organic phase: 0.1 M TODGA/*n*-dodecane.

| Temperature (K) | D_M | | |
|-----------------|---------|--------|-------|
| | Am(III) | Pu(IV) | U(VI) |
| 288 | 55.62 | 75.69 | 0.53 |
| 298 | 23.84 | 58.61 | 0.27 |
| 308 | 7.37 | 25.02 | 0.15 |
| 318 | 1.77 | 17.64 | 0.08 |

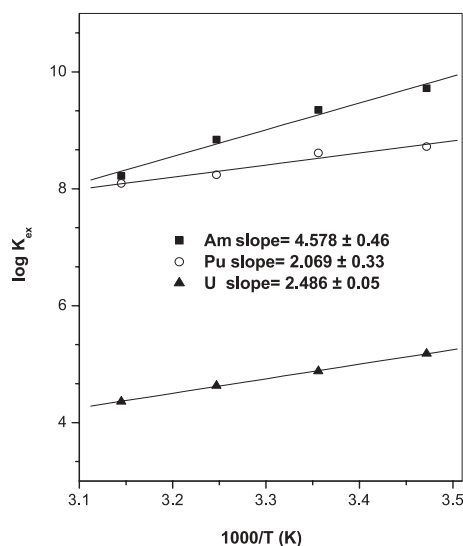
Table 2. Extraction constants ($\log K'_{\text{ex}}$) for actinide ions at 25 °C from nitrate medium for different extractants; Diluent: *n*-dodecane.

| Extractants | Extraction constant ($\log K'_{\text{ex}}$) | | | Reference |
|-------------|---|----------------|----------------|--------------|
| | Am(III) | Pu(IV) | U(VI) | |
| TODGA | 9.4 ± 0.04 | 8.6 ± 0.03 | 4.9 ± 0.01 | Present work |
| CMPO | 5.7 ± 0.04 | 4.7 ± 0.10 | 2.8 ± 0.09 | [21,31] |
| DMDBTDMA | 1.3 ± 0.06 | 5.4 ± 0.02 | 2.2 ± 0.04 | [7] |

HNO_3 used were obtained from the literature [21, 24, 25]. Table 2 compares the $\log K'_{\text{ex}}$ values for Am(III), Pu(IV) and U(VI) for TODGA, DMDBTDMA and CMPO from nitrate medium. In general, it was observed that $\log K'_{\text{ex}}$ values (for each of these extractants) followed the order of their basicity (K_{H}), *i.e.* TODGA(4.1) > CMPO(2.0) > DMDBTDMA(0.32). In case of TODGA and CMPO, the $\log K'_{\text{ex}}$ values were found to follow the order: Am(III) > Pu(IV) > U(VI); the corresponding order for DMDBTDMA was: Pu(IV) > U(VI) > Am(III). This is a quite unusual observation with respect to the extraction of trivalent ions by TODGA and CMPO. This behaviour can be explained in terms of the stoichiometry of the extracted species of metal ions, *viz.* for DMDBTDMA: $\text{Am}(\text{NO}_3)_3 \cdot 3\text{DMDBTDMA}$, $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{DMDBTDMA}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DMDBTDMA}$; for TODGA: $\text{Am}(\text{NO}_3)_3 \cdot 4\text{TODGA}$, $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{TODGA}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{TODGA}$; and for CMPO: $\text{Am}(\text{NO}_3)_3 \cdot 3\text{CMPO}$, $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{CMPO}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CMPO}$ [7, 10, 26]. In case of TODGA and CMPO, higher solvation number for Am(III) as compared to U(VI) and Pu(IV) could be responsible for enhancement in the organophilicity of the complexes leading to higher $\log K'_{\text{ex}}$ values. On the other hand, in case of DMDBTDMA, the order of $\log K'_{\text{ex}}$ values was governed by the ionic potential of these metal ions. However, it is desirable to study the structural aspects of the corresponding complexes to gain an insight of the denticity and the arrangement of TODGA molecules around the metal ions. Recently diglycolamides have been reported to coordinate as bidentate ligands to Cm(III) similar to CMPO and DMDBTDMA [27].

3.2 Thermodynamic parameters (ΔG , ΔH and ΔS)

Figure 2 gives the variation of $\log K'_{\text{ex}}$ as a function of temperature ($1/T$). The slope of the plot has been used for the calculation of ΔH employing Eq. (9). Table 3 lists the calculated thermodynamic parameters, *viz.* ΔG , ΔH and ΔS for the extraction of Am(III), Pu(IV) and U(VI) by TODGA. The data show that the Gibbs energy change ($-\Delta G$) follows the order: Am(III) > Pu(IV) > U(VI). More negative ΔG value for Am(III) shows that the formation of tetra-

**Fig. 2.** Variation of $\log K'_{\text{ex}}$ with temperature; Organic phase: 0.1 M TODGA/*n*-dodecane; Aqueous phase: 1 M HNO_3 .

solvated Am(III)–TODGA complex is thermodynamically more favoured as compared to tri-solvated complexes of Pu(IV) and U(VI). Similarly, higher exothermic enthalpy value ($-\Delta H$) for Am(III) suggests the stronger binding of TODGA with Am(III) as compared to Pu(IV) and U(VI) in the metal complex.

In general, the enthalpy and entropy changes in the complexation of metal ions are associated largely with the change in the hydration of these cations [28, 29]. Complexation results in decrease in the hydration of metal ions which increases the entropy as a result of increase in the randomness of the system. On the other hand, dehydration process of the metal ions makes an endothermic enthalpy contribution ($+\Delta H$) as a result of the breakage of ion-water and water-water bonding in the hydrated species. Consequently, higher exothermic enthalpy change in case of Am(III) (Table 3) is due to less hydration of the metal ion as compared to U(VI) and Pu(IV). The over all enthalpy change depends on several contributing factors, such as, (i) dehydration of metal ions (ΔH_1), (ii) formation of neutral extracted species (ΔH_2), and (iii) dissolution of metal complex in the organic phase (ΔH_3). The values of ΔH_3 should be more exothermic for Am(III) as the solubility of the tetra-solvated species in the organic phase is more as compared to tri-solvated Pu(IV) and U(VI) complex. Consequently, more exothermic ΔH was observed in Am(III) extraction. Positive entropy contribution during the extraction process of Pu(IV) with TODGA (Table 3) reflects the net gain in the degree of freedom when the extractant molecule replaces relatively large number of water molecules from the primary coordination sphere of the metal nitrate complex. On the other

Table 3. Thermodynamic parameters for the extraction of metal ions at 25 °C; Aqueous phase: 1 M HNO_3 ; Organic phase: 0.1 M TODGA/*n*-dodecane.

| Metal ion | $\log K'_{\text{ex}}$ | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol/K) |
|-----------|-----------------------|------------------------|------------------------|-------------------------|
| Am(III) | 9.4 ± 0.04 | -53.6 ± 0.2 | -87.6 ± 8.8 | -114.1 ± 5.5 |
| Pu(IV) | 8.6 ± 0.03 | -49.1 ± 0.2 | -39.6 ± 6.3 | 31.9 ± 3.5 |
| U(VI) | 4.9 ± 0.01 | -27.9 ± 0.1 | -47.6 ± 0.9 | -66.1 ± 2.5 |

Table 4. Loading of Nd(III) by 0.1 M TODGA in different diluents at 25 °C; Aqueous phase = 315 mg/mL of Nd at 3 M HNO₃.

| Diluents | Dielectric constant | Nd- Loading (M) |
|--------------------|---------------------|-----------------|
| <i>n</i> -dodecane | 2.01 | 0.008 |
| Toluene | 2.4 | 0.041 |
| 1-Octanol | 10.3 | 0.049 |
| 1,2-dichloroethane | 6.7 | 0.041 |
| Nitrobenzene | 34.8 | 0.039 |

hand, negative entropy changes ($-\Delta S$) in case of Am(III) and U(VI) extraction could be due to the loss of translational and rotational entropy of TODGA upon complexation in the bulky extracted species, *viz.* Am(NO₃)₃·4TODGA and UO₂(NO₃)₂·3TODGA. Negative entropy change also suggests the presence of few water molecules in the hydrated Am(III) and U(VI) as compared to Pu(IV).

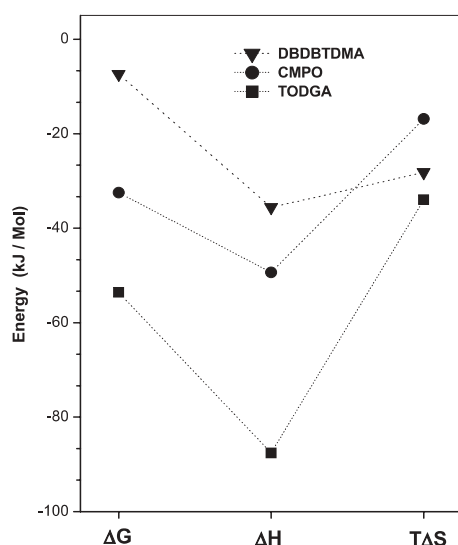
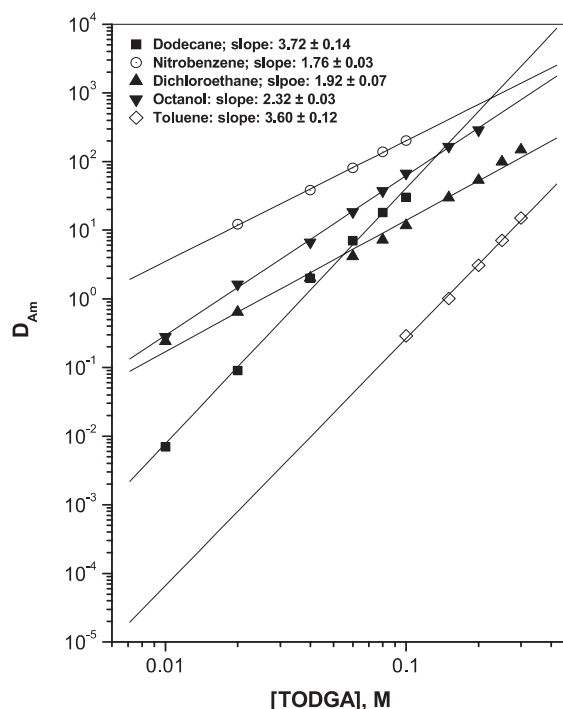
Figure 3 compares the thermodynamic parameters for the extraction of Am(NO₃)₃ by TODGA, DMBDMDMA [20] and CMPO [21]. The order of Gibbs energy change ($-\Delta G$) and enthalpy change ($-\Delta H$) for the extraction of Am(NO₃)₃ by different extractants was: TODGA > CMPO > DMBDMDMA. This figure clearly demonstrates that TODGA is a better extractant for trivalent actinide as compared to the commonly proposed extractants for actinide partitioning, *viz.* CMPO (TRUEX solvent) and DMBDMDMA (DIAMEX solvent). In case of TODGA, less favorable entropy may arise due to loss of rotational and vibrational entropy of the large TODGA molecule when it binds strongly to the Am(NO₃)₃ complex.

3.3 Effect of diluent on Nd(III) loading

Earlier studies have revealed that the limiting organic concentration (LOC) for Nd(III) is quite low (~ 0.008 M at 3 M HNO₃) by 0.1 M TODGA/*n*-dodecane [11]. A systematic study was, therefore, carried out to determine the LOC of Nd(III) using 0.1 M TODGA dissolved in diluents of varying dielectric constant, *viz.* *n*-dodecane, toluene, 1-octanol,

1,2-dichloroethane and nitrobenzene. Table 4 gives the LOC values of Nd(III) for 0.1 M TODGA dissolved in different diluents. The order of Nd(III) loading observed for different diluents was: *n*-dodecane < nitrobenzene < toluene \sim 1, 2-dichloroethane < 1-octanol. No direct correlation was observed between Nd(III)-LOC values and dielectric constant of the diluents. In case of 1-octanol, relatively higher Nd-LOC value (~ 0.05 M) conformed to a disolvated species, *viz.* Nd(NO₃)₃·2TODGA. This observation was further supported by the ligand variation studies for Am(III) in 1-octanol where disolvated species of Am(III) was observed. Ligand variation studies for Am(III) by TODGA dissolved in different diluent are given in Fig. 4. This figure shows that for polar solvents like nitrobenzene and 1-octanol, disolvated Am(III) species is extracted, whereas higher solvation number was observed for non-polar solvents like *n*-dodecane.

Earlier studies have suggested that the Nd(III)-TODGA complex is composed of two extractant molecules bonded through tridentate fashion with some water molecules in the inner coordination sphere, and depending on the solvent used, some TODGA molecules could be organized in the outer sphere. According to EXAFS study, the Nd(III)-TODGA complexes extracted in various solvents or in third phase matrix (in *n*-dodecane) exhibit the same inner sphere structure of Nd(III) [30]. Consequently, it is suggested that in Nd(III)-TODGA complex, two TODGA molecules are involved in the inner coordination sphere in 1-octanol, nitrobenzene and dichloroethane. On the other hand, in case of *n*-dodecane and toluene two TODGA molecules are present in the outer sphere of the complex, in addition to the two molecules in the inner sphere. This behaviour was attributed to the interaction of the polar solvent with TODGA which was subsequently confirmed by IR spectrum where

**Fig. 3.** Thermodynamic parameters for the extraction of Am(NO₃)₃ by different extractants; diluent: *n*-dodecane; Temperature: 25 °C.**Fig. 4.** Variation of D_{Am} with TODGA concentration in different diluents; Aqueous phase: 1 M HNO₃, Temperature: 25 °C.

$\sim 30\text{ cm}^{-1}$ down shift in the $> \text{C}=\text{O}$ stretching frequency was observed for TODGA / 1-octanol solution. A similar effect was not observed when *n*-dodecane was used as the diluent.

4. Conclusions

Temperature variation studies suggest that the extraction process of Am(III), Pu(IV) and U(VI) by TODGA is exothermic in nature. Extraction process of Am(III) and U(VI) is enthalpy driven whereas entropy factor counteracts the extraction. However, in the case of Pu(IV), the extraction process is enthalpy and entropy favoured. Ligand variation studies carried out in different diluents suggest that the extracted species of Am(III) changes with the diluent. Loading studies in different diluents suggest that the nature of diluent as well as the stoichiometry of the extracted species affect the Nd(III) loading in the organic phase. At 3 M HNO_3 , loading of Nd(III) by 0.1 M TODGA dissolved in different diluents varies in the order: 1-octanol $>$ toluene \sim 1, 2-dichloroethane $>$ nitrobenzene $>$ *n*-dodecane.

References

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