Extraction Behaviour of Gadolinium into the Binary Mixture of Tri-*n*-butyl Phosphate and *n*-Dodecane

S. Ganesh, N. Desigan, N. K. Pandey*, C. Mallika and U. Kamachi Mudali,
Reprocessing group, IGCAR, Kalpakkam 603102

Abstract

The present paper describes, the systematic study of extraction behaviour of gadolinium has been investigated with (0.36-1.1*M*) TBP in *n*-dodecane diluent from different concentration of nitric (1-16*M*) acid medium. The effect of temperature and uranium loading on the extraction of Gd(III) also been examined. The D_{Gd} increases when the TBP concentration increases from 0.0425 to 0.0626 and 0.366 *M* to 1.01 *M* respectively. And D_{Gd} also increases when the acidity of the medium increases from 0.0087 to 0.3121 and 0.97 *M* to 13.5 *M* respectively. But the study of effect of uranium loading and temperature in gadolinium extraction showed that the D_{Gd} decreases down to 0.0253 when 90 *g/L* uranium loading and D_{Gd} decreases down to 0.0184 when $53^{o}C$ temperature respectively. The obtained results clearly indicates that the decontamination factors obtained for Gd is sufficiently high as its distribution in 30% TBP is pretty low under typical PUREX process conditions.

Keywords:

Gadolinium, Solvent extraction, Distribution coefficient, fuel reprocessing, Soluble neutron poison

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*Corresponding author: nkpandey@igcar.gov.in
Fax: +91 4427480126

1. Introduction

The plutonium content in a typical Fast Breeder Reactor (FBR) spent oxide fuel ranges from 10 to 30% by weight depending on various factors. While processing this fuel through aqueous reprocessing methods employing PUREX process; nuclear criticality is an important safety issue to be addressed. To overcome this in the design of process equipment, many possibilities exists viz, designing of poison tube tanks, strategically adding neutron poison sheets in the layout to reduce the effective neutron multiplication factor (k_{eff}) and so on. But all these possibilities take a large toll on the capacity of the plant if they are to be adopted effectively. Alternately, addition of soluble neutron poison was found to be more effective (Marrison et al., 1964, Eggert, 1974). Among all the elements, gadolinium is the best soluble neutron poison because of its high thermal neutron absorption cross section and its chemical compatibility with the PUREX process. As a result it is required only in very small quantity to ensure nuclear criticality safety even when handling higher quantity of fissile material. In addition, the solubility of gadolinium in typical PUREX process streams is high enough to be employed very effectively (Lloyd et al., 1972, Dutta et al., 2006, Vijayalakshmi et al., 2014, Desigan et al., 2012, Baumann, 1980, Gilbert et al., 1985, Rodenas et al., 1990, Rohde and Lewis, 1972, Nichols, 1962). Gadolinium nitrate has been used earlier as a soluble neutron poison to study the criticality safety of uranium (Durazzo and Riella, 2009) and plutonium solutions (Rohde and Lewis, 1972). As the recycled fuel specification sets a very stringent upper limit for neutron poison impurities, it is imperative that the distribution behavior of gadolinium in PUREX solvent is studied. Thus, the primary purpose of the present work is to generate the distribution data for gadolinium at conditions prevalent in FBR fuel reprocessing. Though extensive work has been carried out, the effect of nitric acid concentration at equilibrium both in presence/absence of uranium is yet to be studied in detail. When short cooled FBR spent fuel is reprocessed, due to the higher decay heat of the fuel, the process solutions may get heated up to various temperatures depending on the process conditions. Hence, the effect of temperature on the distribution behavior of gadolinium in TBP-*n*DD/HNO_3 system also has to be established.

2. Experimental

Reagents and Instrumentation

Nitric acid used for the experiments was 70% Analytical grade of Fischer make. TBP was from Fluka and *n*-dodecane from Aldrich. Gadolinium used in the form of $Gd(NO_3)_3 \cdot 6H_2O$ which is 99.9% (REO) chemically pure from Alfa Aesar. The gadolinium in the stock solution was analyzed by ICP-AES (Hennebruder et al., 2004) which was then used for calibrating the spectrophotometric method for gadolinium estimation (Ganesh et al., 2014). Stock solution of uranyl nitrate was prepared and standardized by Davies Gray method (Davies and Gray, 1964). Free acidity was estimated by potentiometry (Ganesh et al., 2011). All other reagents used for the experiments were of analytical grade (99.9%) from Sigma Aldrich and Merck. Fiber optic aided spectrophotometric technique with 1 *cm* path length dip type probe was used to measure absorbance. Chemlabs, Bangalore, make Micro-07; pH/mV meter coupled with glass electrode was used for pH measurements.

Procedures

Solvent extraction was carried out with equal volume of solvent and aqueous in a centrifugal vial of 50 *mL* volume with sufficient free board volume for effective mixing using a vortex shaker of Heidolph Reax made at a speed of 1700 *rpm* for 30 minutes. The two phases were then allowed to disengage completely. After phase separation, the acidity and gadolinium concentration were measured, with appropriate dilution if necessary. The free acidity of both phases was estimated using titration with standard sodium carbonate. Gadolinium estimation in both phases using spectrophotometry using Alizarin Red S as chromogenic reagent. All the measurements were carried out in duplicate and their average was used for the calculation of distribution coefficients. The distribution coefficient of gadolinium (D_{Gd}) was determined by the ratio of concentration of gadolinium in organic to aqueous phase at equilibrium. For studying the temperature effect on gadolinium distribution, the experiments were carried out in a double walled glass container with provisions for mechanical mixing and external jacket for temperature control is shown in Fig.1. In all the experiments, mixing was carried out for 30 minutes which was sufficient for the equilibrium to be established, and then allowed to settle for about 5 minutes for phase separation. The aqueous to organic volume ratio was maintained at unity for all the experiments reported in this article. Experimental values were within ±5%.

3. Results and discussion

The extraction behaviour of Gd(III) in TBP-HNO_3 system is very similar to the trivalent lanthanides (Bednarczky and Siekierski, 1989) and have 3TBP molecules coordinated to $Gd(NO_3)_3$ in the extracted species. The overall chemical reaction is represented by the following set of equation (Desigan et al., 2012):

$$Gd^{3+}_{aqu} + 3NO_3^{-}{}_{aqu} + 3TBP_{org} \rightleftharpoons Gd(NO_3)_3 \cdot 3TBP_{org} \tag{1}$$

The apparent equilibrium constant, which is defined as the product of the equilibrium constant and the activity coefficients raised to appropriate power of stoichiometric coefficients as per Eq.(1) is represented as follows:

$$K_{Gd} = \frac{[Gd(NO_3)_3 \bullet 3TBP]}{[Gd^{3+}][NO_3^{-}]^3[TBP_f]^3} \tag{2}$$

The distribution coefficient of gadolinium is defined as,

$$D_{Gd} = \frac{[Gd(NO_3)_3 \bullet 3TBP]}{[Gd^{3+}]} \tag{3}$$

$$K = \frac{D_{Gd}}{[NO_3^-]^3[TBP_f]^3} \tag{4}$$

$$\ln K + 3\ln[TBP_f] = \ln \frac{D_{Gd}}{[NO_3^-]^3} \tag{5}$$

$$\ln K + 3\ln[NO_3^-] = \ln \frac{D_{Gd}}{[TBP_f]^3} \tag{6}$$

Classical slope analysis techniques of the data obtained from this work were performed. A plot of ln [TBP_f] vs ln [$D_{Gd}/[NO_3^-]_3$ results in a straight line with the slope as the stoichiometric co-efficient of TBP and intercept as ln K which is represented in Fig 2. The results indicates that, the slope of the line was 2.735 which conformed that almost 3TBP molecules coordinated to $Gd(NO_3)_3$ in the extracted species. The influences of concentration of Gd, TBP, HNO_3, U and temperature on the distribution coefficient of gadolinium are discussed below.

Effect of metal ion concentration

Extraction behaviour of various gadolinium concentrations (1-5 *g/L*) from nitric acid solution of fixed concentration of 3.5*M* into TBP of three different concentrations (10, 20 and 30% by volume in *n*-dodecane) was investigated. The results are presented in Fig.3 which clearly indicates that the D_{Gd} decreases with increase in gadolinium concentration for a given TBP concentration and also it increases as a function of TBP for a given Gd concentrations at equilibrium. As the gadolinium concentration used in this study was very less, which was arrived at based on criticality safety calculations for the fissile material concentrations prevailing in typical fast reactor fuel reprocessing conditions, its loading is much lesser than the saturation limit of gadolinium loading. Hence, with increase in Gd concentration D_{Gd} decreases. Fig.4 shows, D_{HNO3} as a function of [Gd] for 10, 20 and 30% TBP. It can be noted that D_{HNO3} increases with increasing [Gd]. This is because Gd has very low extractability than nitric acid. Nitric acid is getting extracted in TBP phase.

Effect of nitric acid concentration

Extraction behaviour of gadolinium with 30% TBP (1.1M) in *n*-dodecane from nitric acid of varying concentration (1-13.5 *M*) was investigated. Results indicate that the D_{Gd} increases marginally up to 4.5*M* HNO_3, then drops down slightly from 4-8*M* and again increases with increase in nitric acid concentration as shown in Fig.5. As the typical acidity employed in FBR fuel reprocessing is about 4-6 *M*, the results assures better decontamination of Gd(III) as its D_{Gd} value is pretty low in this acidity range. The increase of D_{Gd} value beyond 8 *M* acidity clearly shows that the change of extraction mechanism. This increase may be due to some higher charged complex formation between Gd(III) and nitrate ions which is more extractable by TBP. This behaviour could be useful for a possible separation of Gd from raffinate of the PUREX process. Further speciation studies are required to be carried out in this range for understanding this phenomenon.

Effect of uranium concentration

As uranium is the major content in any nuclear reactor's spent fuel which is also the most extractable species by TBP, the distribution behaviour of Gd(III) in TBP in the presence uranium as U(VI) was studied which would indicate the feasibility of Gd decontamination under typical PUEX process conditions. Thus experiments were carried out at a constant nitric acid concentration of 3.8 *M* and 2 *g/L* of Gd(III) at various concentration of U(VI) up to 90 *g/L* and D_{Gd} was determined in each case. The results as indicated (Fig.6) reveal that D_{Gd} decreases with increasing U(VI) concentration from 5 to 100 *g/L*. The value of the distribution coefficient is very low (0.025) when the organic phase is 100% saturated with uranium. The U(VI)-TBP complex which is more soluble in the organic phase than its Gd(III) counterpart, is getting stabilized more in the TBP phase than the Gd(III)-TBP complex. This effect shows that Gd(III) is not extracted in the extraction of uranium and plutonium in the

PUREX process. Thus it can be concluded confidently that Gd decontamination during FBR fuel reprocessing is highly feasible.

Effect of temperature

When short cooled FBR spent fuel is reprocessed, due to the higher decay heat of the fuel, the process solutions may get heated up to various temperatures depending on the process conditions. Hence the effect of temperature on the distribution behavior of gadolinium in TBP/*n*-dodecane/HNO_3 system was studied by changing temperature between $13^{o}C$ and $53^{o}C$ at 1.1*M* TBP concentration and fixed nitric acid concentration of 3.89*M*. Though the actual temperatures during the process conditions may not reduce below 28^{o}C, lower temperatures were chosen for the sake of completion. It can be seen from Fig.7 that D_{Gd} decrease with temperature. Thus, it can be inferred that when processing very short cooled fuel, Gd(III) decontamination would not pose any problem. The Van't Hoff equation (Berthod and Carda-Broch, 2004) can be used to calculate the enthalpy change associated with extraction of gadolinium which is written as

$$\frac{d(\ln D_{Gd})}{d(1/T)} = -\frac{\Delta H}{R} \qquad (7)$$

where, R is ideal gas constant. The values of $\ln(D_{Gd})$ are plotted against 1/T in Fig.8. The slope of the straight line obtained in this plot when multiplied with R, gives enthalpy of extraction process. From Fig.8, the slope of line was found to be 1292.566 for 3.89 *M* nitric acid concentration. Therefore, the apparent standard enthalpy of the extraction reaction is 24.74 *kJ/mol*. Therefore, the extraction of gadolinium from nitric acid medium with TBP is an exothermic reaction.

Conclusions

The extraction behaviour of gadolinium using various concentrations of TBP was studied and the influence of parameters like nitric acid concentration, uranium loading and temperature were established. The results clearly show the significant effect of uranium thereby rendering better gadolinium decontamination during the actual processing. Also the decrease in gadolinium distribution at higher temperature indicates better gadolinium decontamination when processing short cooled FBR spent fuel. Thus to sum up it can be concluded that gadolinium can be employed in FBR fuel reprocessing by aqueous route to ensure nuclear criticality safety and the typical PUREX process chemistry offers greater flexibility in decontamination gadolinium from reaching the final product thereby enabling it to meet the fresh fuel specification with respect to neutron poison impurity content.

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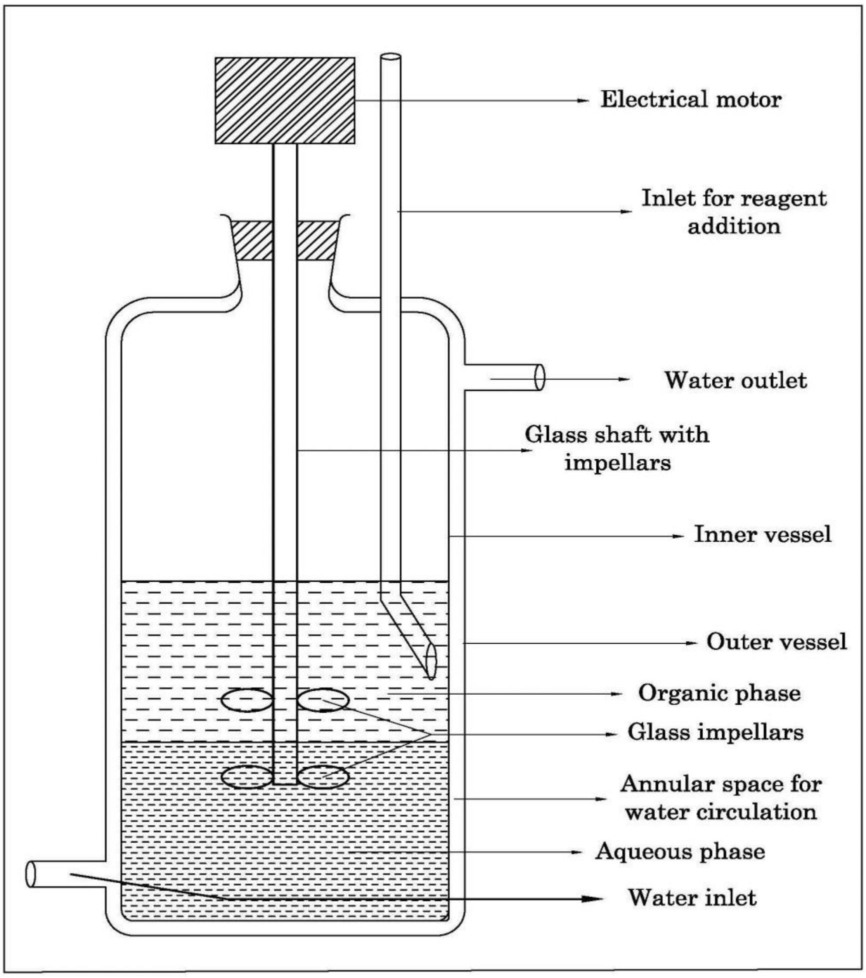

Fig.1 Schematic diagram of Lewis cell

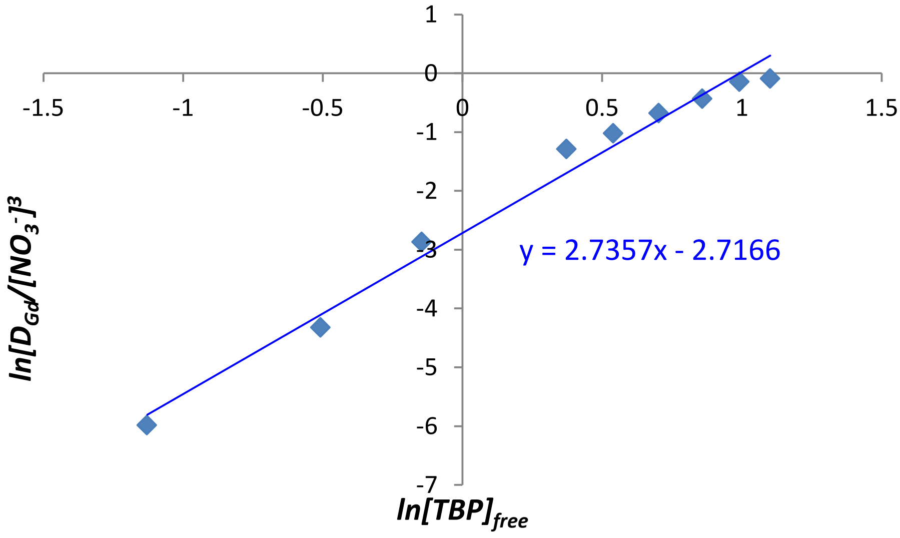

Fig.2 Validation of salvation number of TBP stoichiometry for Gd extraction

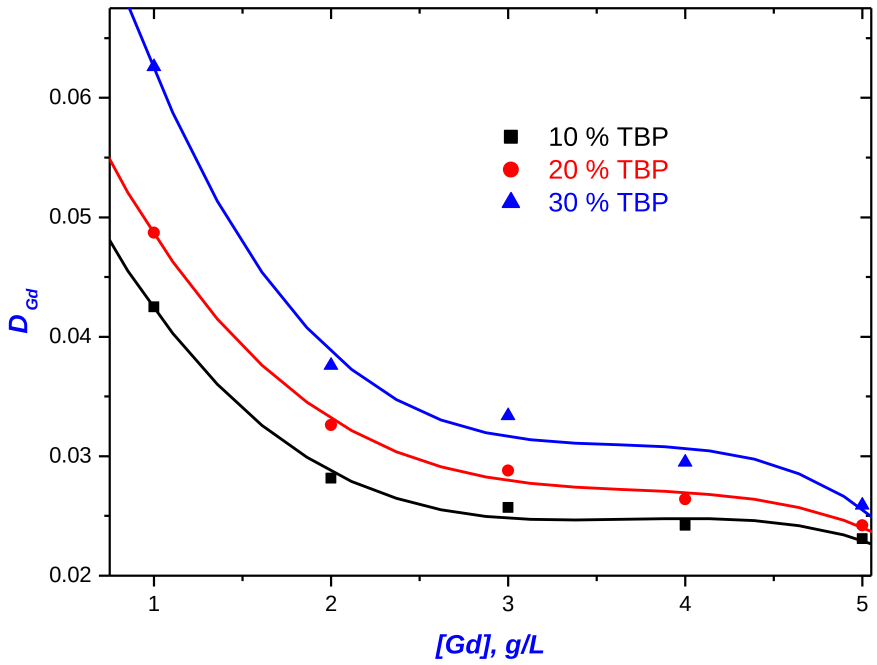

Fig.3 Variation of D_{Gd} as a function of Gadolinium concentration (1-5 *g/L*) with different concentration of TBP from 3.5*M* nitric acid.

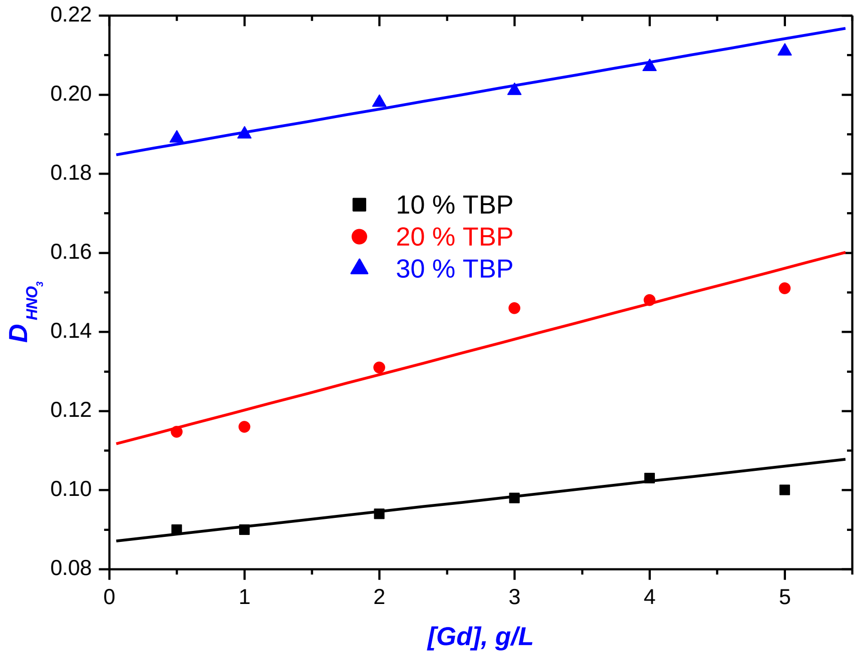

Fig.4 Variation of D_{HNO3} in presence of Gd (1-5 g/L) with different TBP concentration at 3.5M nitric acid

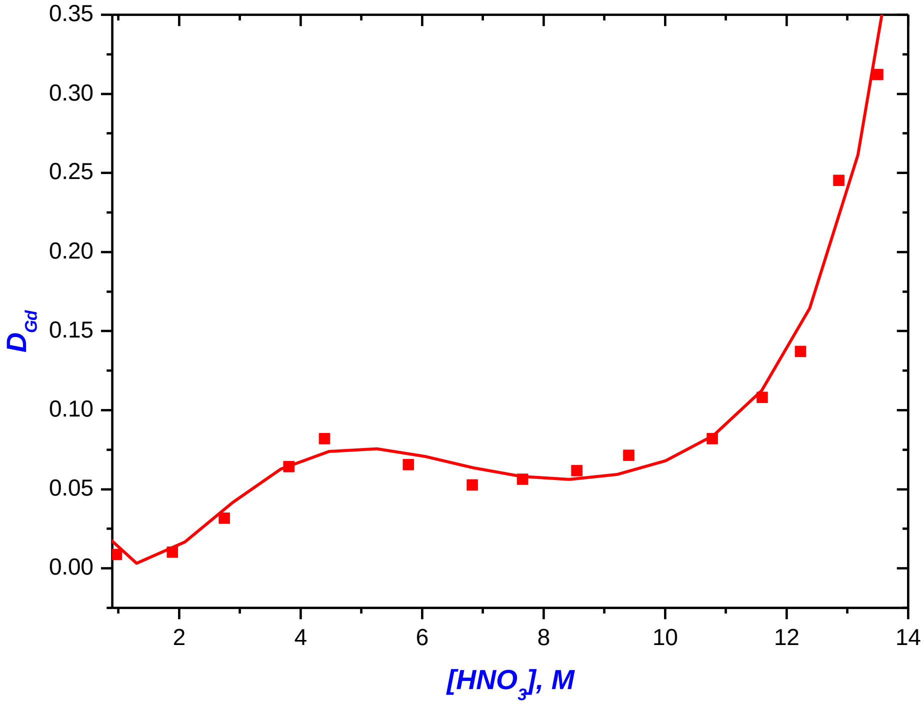

Fig.5 Variation of D_{Gd} as a function of nitric acid concentration

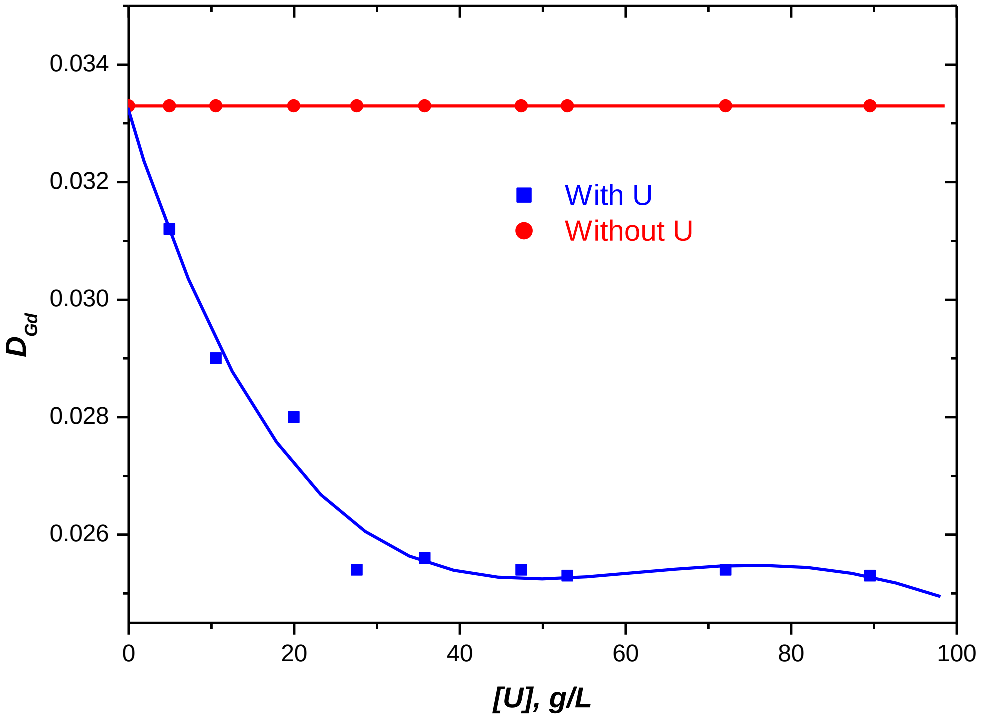

Fig.6 Effect of uranium on the extractability of gadolinium

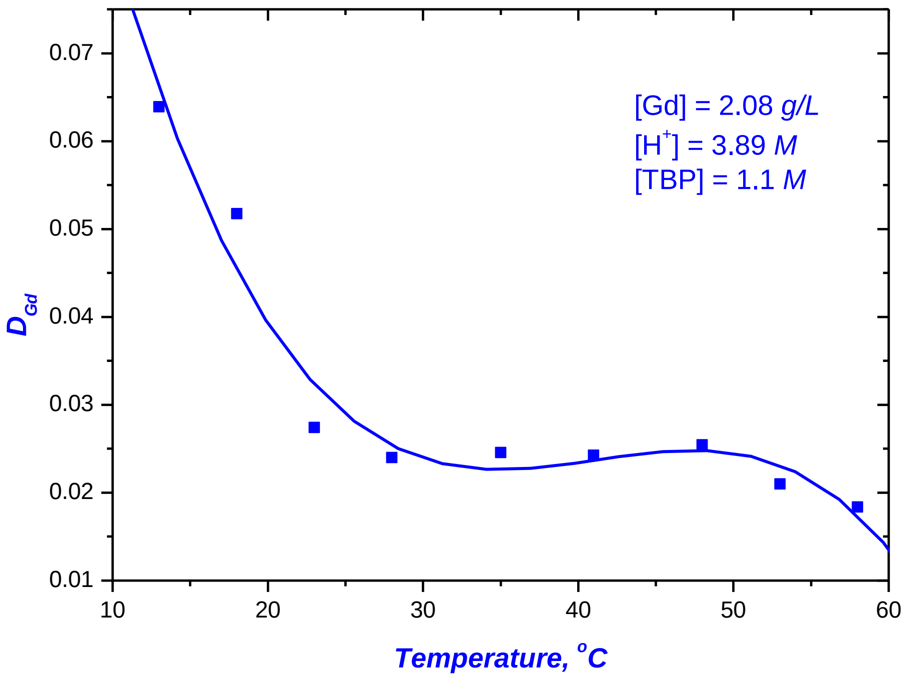

Fig.7 Variation of D_{Gd} as a function of temperature

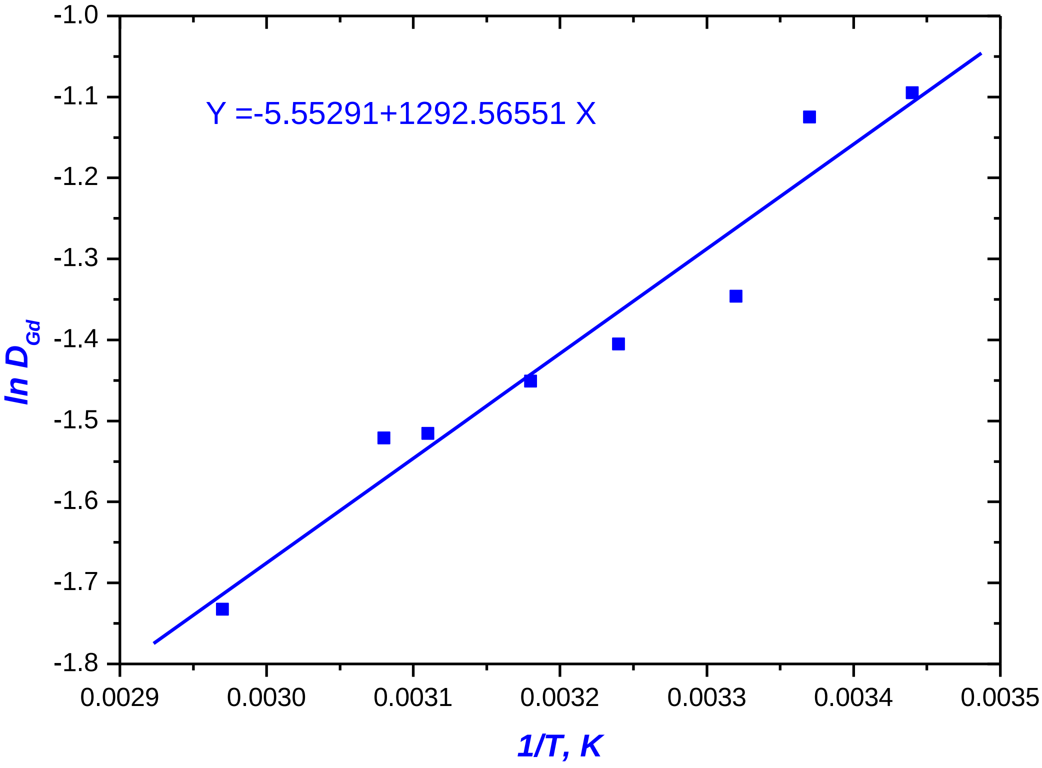

Fig.8 Vant Hoff’s plot to determine the enthalpy of extraction