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PHYSICAL CHEMISTRY OF SOLUTIONS

Extraction of U(VI) with *N,N'*-Dimethyl-*N,N'*-Dioctylmalonamide from Nitrate Media[1]

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Abstract—The extraction of uranyl nitrate with the novel extractant *N,N'*-dimethyl-*N,N'*-dioctylmalonamide (DMDOMA) from aqueous sodium nitrate (and nitric acid) was investigated. The extraction mechanism was established and the stoichiometry of the main extracted species confirms to $UO_2(NO_3)_2 \cdot$ DMDOMA. The IR spectral study was also made of the extracted species. Methyl substituent improves the extraction ability of malonamide for U(VI) compared with that of *N,N,N',N'*-tertrabutylmalonamide (TBMA).

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INTRODUCTION

The extraction and partition of lanthanides and actinides are important in the hydrometallurgy, nuclear reprocessing and so on [1, 2]. *N*,*N'*,*N*,*N'*-tetraalkyldiamides have been reported to be potential extractants of actinides and also considered as an alternate choice in place of TBP in the nuclear fuel reprocessing [3–6]. It is now recognized that extraction behavior varies widely depending on the nature of the alkyl groups on the diamide framework. For $(RR'NCO)_2CH_2$, if R is a small group (typically methyl) and R' a bigger one, the stereochimical around the carbonyl oxygen atoms is kept to minimium and the lipophilic character of the ligands is attained by the presence of a higher chain-alkyl or arkyl groups at R'. Costa [7], Spjuth [8], Musikas [9] and Nakamura [10] had reported the extractability of some unsymmetrical diamides for U(VI) and Ln(III). Our approach to investigating structure-function relationships for binding diamides to f-bolck metals builds upon the study of the extraction with various diamides choosing different alkyl substituents. We had reported the extraction of U(VI) with *N,N'*-dimethyl-*N,N'*-dioctylsuccinylamide in our previous paper [11], here presented the extraction of U(VI) from sodium nitrate with DMDOMA, which shows good affinity for U(VI) than that of TBMA.

EXPERIMENTAL

Reagents

The extractant DMDOMA was obtained by the reaction of *N*-methyloctylamine with diethyl malonate. The unsymmetrical *N*-methyloctylamine was prepared by reduction of *N*-methyloctylamide using $NaBH_4$ as reducing agent and acetic acid as catalyzer in THF. DMDOMA was purified by distillation under vacuum. The final products were characterized by elemental analysis, IR and ^{1}HNMR measurement.

Compound(*N,N'*-dimethyl-*N,N'*-dioctylmalonamide): yield 72%, pale yellow oil, bp 205~208°C/2~4 mm Hg; IR (KBr, cm^{-1}) 1660.1 (C=O); δ_H (300 MHz, DMSO), 0.86 (6H, t, C–CH_3), 1.245 (20H, s, –CH_2–), 1.447 (4H, m, –CH_2–C–N–), 2.781, 2.889 (6H, t, N–CH_3), 3.166–3.329 (4H, m, N–CH_2–), 3.449 (2H, d, OC–CH_2–CO). Elem. Anal. Calcd. for $C_{21}H_{42}N_2O_2$: C 71.14%, H 11.94%, N 7.90%. Found: C 70.45%, H 11.87%, N 7.71%.

Other agents employed in this work were all A.R. grades.

Extraction and Analytical Procedures

Equal volumes of organic and aqueous phases were agitated for 30 minutes (enough for equilibrium) at 25°C under the desired experimental conditions. The two phases were then centrifuged and assayed by taking known aliquots (0.05–0.1 mL) from the aqueous phases. The concentrations of U(VI) in the sample were determined by Arsenazo-III visible spectrophotometric analysis and that in organic phase obtained by subtracting the aqueous concentrations from the total initial aqueous concentration of U(VI). The distribution ratio (*D*) was calculated as the ratio of the concentration of U(VI) in organic phase to that in aqueous phase. If not stated otherwise, c_U was 5.00×10^{-3} mol dm^{-3}, c_{amide} 0.10 mol dm^{-3}, c_{HNO_3} 0.01 mol dm^{-3}.

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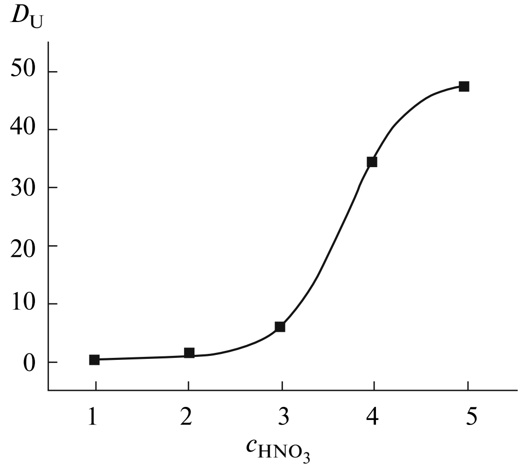

Fig. 1. Effect of HNO_3 concentration on the extraction of U(VI); $c_U = 5.0 \times 10^{-3}$ mol dm^{-3}, $c_{DMDOMA} = 0.10$ mol dm^{-3}.

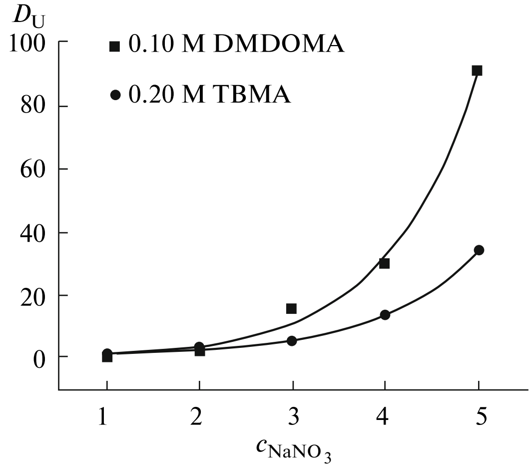

Fig. 2. Effect of $NaNO_3$ concentration on the extraction of U(VI); $c_U = 5.00 \times 10^{-3}$ mol dm^{-3}, $c_{DMDOMA} = 0.10$ mol dm^{-3}, $c_{H^+} = 0.01$ mol dm^{-3}.

Preparation and Characterization of Extracted Species

The extracted species were prepared, presumedly identical to those existing in the extracts. The extractant solutions were shaken with a concentrated solution of $UO_2(NO_3)_2$, centrifuged and the organic phase separated. The organic solvents were removed by evaporation and FT-IR spectra of the residuals were recorded on an FTS-165 Spectrometer in the range 400–4000 cm^{-1}. The samples were used in the spectrometer between potassium bromide windows. The scan times and the resolution were 60 and 2 cm^{-1}, respectively.

RESULTS AND DISCUSSION

Effect of Nitric Acid Concentration on the Extraction of U(VI)

The extraction of U(VI) with 0.10 mol dm^{-3} DMDOMA from nitric acid solutions in the range of 1.00–5.00 mol dm^{-3} at 298 K has been investigated (Fig. 1). The results show that the distribution ratio of U(VI) increases with the increase in the concentration of HNO_3.

Effect of Sodium Nitrate Concentration on the Extraction of U(VI)

The effect of sodium nitrate concentration in the presence of 0.01 mol dm^{-3} HNO_3 on the distribution ratio of U(VI) is shown in Fig. 2. The distribution ratio of U(VI) increases significantly with increasing $NaNO_3$ concentration in which the co-ion effect plays a crucial role. Compared with the result of the extraction of *N,N,N′,N′*-tetrabutylmalonamide (TBMA] [12, 13], we find that the adoption of unsymmetrical substituted alkyl does improve the extractability of malonamides markedly, which indicates that the two straight long chain alkyls adjacent to nitrogen atom in malonamide extractants bring big steric hindrance effect in the formation of the extracted species of uranyl ion.

Effect of the Concentration of Extractant on the Extraction of U(VI)

The variation in the distribution ratio of U(VI) with DMDOMA in toluene is given in Fig. 3. The log-log plots of the distribution ratio vs. the initial extractant concentration show that the lines have a slope of nearly 1. It implies that the stoichiometrics of the extracted species in toluene is $UO_2(NO_3)_2 \cdot$ DMDOMA, which is distinct from the result of the extraction of U(VI) with TBMA which forms $UO_2(NO_3)_2 \cdot 2TBMA$ [12].

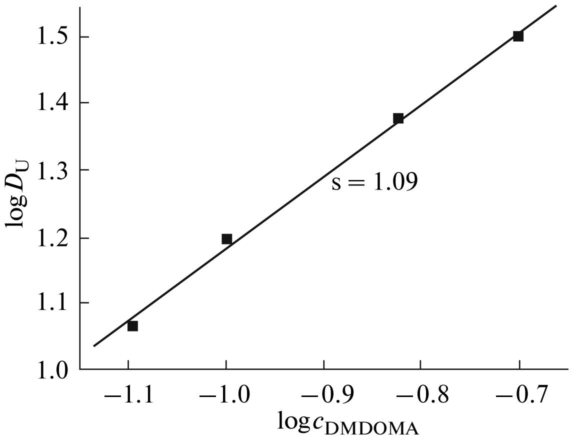

Fig. 3. Effect of extractant concentration on the extraction of U(VI); $c_U = 5.00 \times 10^{-3}$ mol dm^{-3}, $c_{H^+} = 0.01$ mol dm^{-3}, $c_{NaNO_3} = 3.00$ mol dm^{-3}.

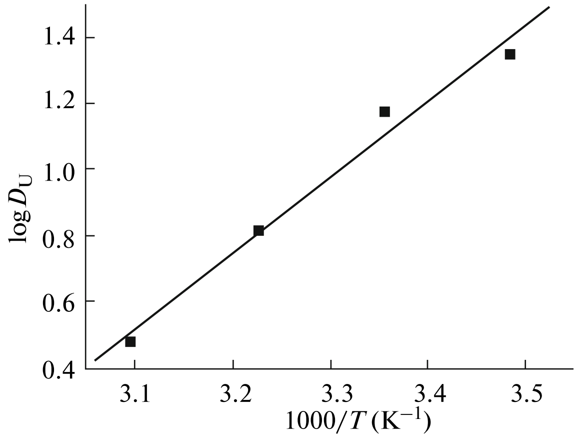

Fig. 4. Dependence of extraction of U(VI) on the experimental temperature; $c_{DMDOMA} = 0.10$ mol dm^{-3}, $c_U = 5.00 \times 10^{-3}$ mol dm^{-3}, $c_{NaNO_3} = 3.00$ mol dm^{-3}, $c_{H^+} = 0.01$ mol dm^{-3}.

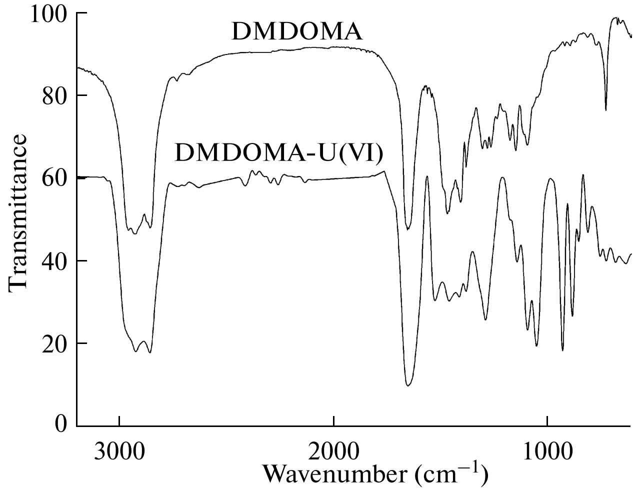

Fig. 5. IR spectra of the extractant loaded uranyl nitrate.

Hence the equilibrium expression, written as the solvating reaction of U(VI) is given as follows

$$
\begin{aligned}
&UO_2^{2+} + 2NO_3^- + DMDOMA_{(O)} \\
&= UO_2(NO_3)_2 \cdot DMDOMA_{(O)}
\end{aligned}
\quad (1)
$$

in which the equilibrium constant for U(VI), K_{ex}, is

$$
K_{ex} = \frac{[UO_2(NO_3)_2 \cdot DMDOMA]_{(O)}}{[UO_2^{2+}] \cdot [NO_3^-]^2 \cdot [DMDOMA]_{(O)}}. \quad (2)
$$

From Fig. 3 we can obtain the values of K_{ex} through equation (2), which is 17.25 ± 0.75 mol^{-3}dm^9.

Influence of Temperature on the Extraction of U(VI)

Figure 4 illustrates the influence of temperature on the values of *D*. The extraction distribution ratio decreases with the increase in the temperature, which shows that the extraction reaction is exothermic. The log*D* values increase linearly with the increase in $1/T$. The change in enthalpy, ΔH, associated with reaction (1), can be evaluated by means of the Van't Hoff Equation. The value of ΔH obtained from Fig. 4, is –44.23 ± 4.20 kJ mol^{-1}.

IR Spectra Analysis of the Extracted Species

An analysis of the spectra (Fig. 5) of the loaded organic phase in the C=O stretching region (1550–1760 cm^{-1}) was carried out using a curve fitting procedure. The broad band of C=O consists of three subbands and the peaks are at 1593.1, 1629.6 and 1659.5 cm^{-1}, respectively. Compared with the IR spectra of free extractants, the carbonyl group (C=O) stretching vibration of the extracted species is shifted from about 1660 to 1593.1 and 1629.6 cm^{-1}, which implies that the amide ligand directly coordinates to the uranyl ion through its carbonyl group. The appearance of bands at about 1046, 1281 and 1520 cm^{-1} can be attributed to the coordinated nitrate ions [14, 15]. An additional band described as the U–O stretching vibration of the uranyl ion is noted at 926 cm^{-1}.

CONCLUSIONS

U(VI) can be extracted effectively from nitric acid solution employing toluene as diluent by the new unsymmetrical diamide, *N,N'*-dimethyl-*N,N'*-dioctylmalonamide. The stoichiometry of the extracted species in toluene is $UO_2(NO_3)_2 \cdot$ DMDOMA. The value of ΔH for the extraction is –44.23 ± 4.20 kJ mol^{-1}. The adoption of unsymmetrical substituted alkyl does improve the extractability of malonamides markedly compared with symmetrical extractant whose substituents possess similar number of carbon atoms.

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