The effect of diluents on the extraction of Sm(III) using *N,N,N',N'*-tetrabutylmalonamide

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Abstract: A study has been made of the extraction of samarium(III) from nitrate solutions using *N,N,N',N'*-tetrabutylmalonamide (TBMA) in a series of diluents. The dependence of the extraction distribution on the concentrations of aqueous nitric acid, lithium nitrate and organic TBMA was investigated. The experimental results showed that the extraction efficiency of TMBA in different diluents for Sm(III) increases in the order: chloroform, carbon tetrachloride, benzene, xylene, toluene, cyclohexane, *n*-hexane, *n*-octane. The stoichiometry of the extracted species conform to $Sm(NO_3)_3 \cdot 3TBMA$ in all the employed diluents. The interaction between extractant or extracted species and diluent is discussed and a quantitative expression relating the extraction constant and the parameters of the diluent has been established.

Keywords: extraction, samarium(III), *N,N,N',N'*-terabutylmalonamide.

INTRODUCTION

Malonamides in organic diluents have been found to be efficient extractants for uranium(VI) and thorium(IV)[1–4] and in the coextraction and separation of transplutonium and trivalent lanthanides.[5,6] To the best of our knowledge, however, there are only a few papers concerning the role of diluents in extractions using N,N'-tetrabutylmalonamide. Many authors have shown that a diluent plays an important role in liquid – liquid extractions.[7–9] The present study was therefore undertaken to extend previous results and to fully evaluate the nature of the interaction with diluent in the extraction of Sm(III) using *N,N,N',N'*-tetrabutylmalonamide. Several polar and nonpolar diluents were employed.

EXPERIMENTAL

Materials

All the employed diluents were purified by fractional distillation. AR Nitric acid and lithium nitrate were used. TBMA was sythesized experimentally as described elsewhere.[6]

Procedure

The preparation of Sm(III) solution and the extraction were similar to those described in a previous paper.[6] The hydrogen ion concentration in the two phases was determined by titration with standard NaOH solution.[10]

RESULTS AND DISCUSSION

Dependence on the concentration of nitric acid in the presence of LiNO$_3$

The extraction of Sm(III) from nitric acid solution in the range of 1.0–8.0 mol dm^{-3} was investigated. The results show that the extractability of Sm(III) from nitric acid solutions by TBMA is very bad ($D < 0.01$). Then the following study was
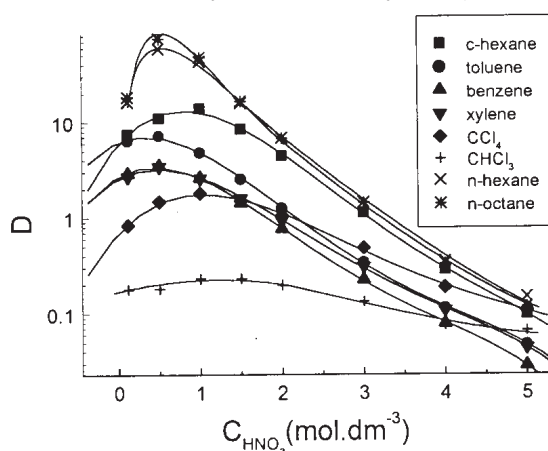

Fig. 1. Effect of nitric acid concentration of the extraction distribution ratio of Sm(III). Aqueous phase: $c_{LiNO_3} = 5.0$ moldm^{-3}. $c_{Sm^{3+}} = 5.00\times10^{-3}$ mol dm^{-3}. Organic phase: $c_{TBMA} = 0.50$ mol dm^{-3}.

conducted in the presence of 5.0 mol·dm^{-3} lithium nitrate in the aqueous phase. The results for the extraction of Sm(III) with TBMA in various diluents are shown in Fig. 1. The trend in the change of the extraction distribution is similar with increasing concentration of nitric acid, however, at the same concentration, the values of the distribution ratios are different. Fig. 1 also shows that, at higher nitric
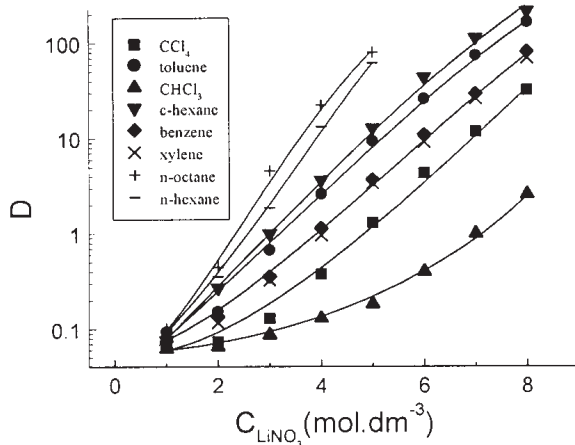

Fig. 2. Effect of lithium nitrate concentration on the extraction distribution ratio of Sm(III). Aqueous phase: $c_{HNO_3} = 0.50$ mol dm^{-3}. $c_{Sm^{3+}} = 5.00 \times 10^{-3}$ mol dm^{-3}. Organic phase: $c_{TBMA} = 0.50$ mol·dm^{-3}.

acid concentrations, the distribution ratios decrease sharply which is due to a decrease in the free extractant caused by the competitive extraction of nitric acid. This implies that the interaction between nitric acid and TBMA is stronger than that between TBMA and diluent, even chloroform.

Effect of the lithium nitrate concentration on the extraction of Sm(III)

The effect of the lithium nitrate concentration on the extraction distribution ratio of Sm(III) in different diluent system is shown in Fig. 2. The distribution ratio of Sm(III) rises significantly with increasing $LiNO_3$ concentration, whereby the co-ion effect plays a crucial role.

Effect of the TBMA concentration on the extraction distribution ratio of Sm(III)

In order to ascertain the nature of the extracted species, D for Sm(III) was determined as a function of TBMA concentration. The results are shown in Fig. 3. The plots of log D *vs.* log c_{TBMA} gave straight lines having slopes near 3 in all the emplyed diluents, which shows that Sm(II) is extracted as trisolvate and the
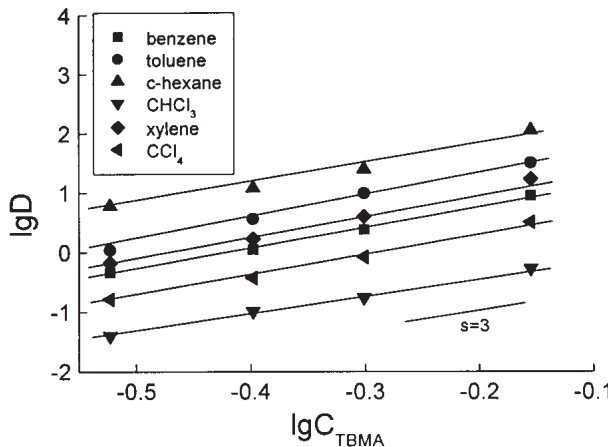

Fig. 3. Effect of TBMA concentration in various diluents on the extraction of Sm(III). Aqueous phase: c_{HNO_3} = 0.50 mol dm^{-3}. $c_{Sm^{3+}}$ = 5.00 × 10^{-3} mol dm^{-3}. Organic phase: c_{LiNO_3} = 5.00 mol dm^{-3}.

stoichiometry of the extracted species is Sm(NO$_3$)3TBMA under the studied conditions. Then the extraction reaction can be represented by:

$$Sm^{3+} + 3NO_3^- + 3TBMA_{(o)} = Sm(NO_3)3TBMA_{(o)} \tag{1}$$

where the subscript (o) refers to the species present in the organic phase, for which the eqilibrium constant, K_{ex}, is:

$$K_{ex} = \frac{[Sm(NO_3)_3 3TBA]_{(o)}}{[Sm^{3+}][NO_3^-]^3[TBMA]_{(o)}^3 \gamma_{Sm^{3+}} \gamma_{NO_3^-}^3} \tag{2}$$

The total Sm^{3+} concentration in the aqueous solution, c_{Sm3+}, can be defined as:

$$c_{Sm3+} = [Sm^{3+}](1 + \beta_1[NO_3^-]) \tag{3}$$

The distribution ratio D can be expressed as:

$$D = \frac{c_{Sm(o)}}{c_{Sm^{3+}}} = \frac{[Sm(NO_3)_3 \cdot 3TBMA]_{(o)}}{[Sm^{3+}](1 + \beta_1[NO_3^-])} \tag{4}$$

Then

$$K_{ex} = \frac{D(1 + \beta_1[NO_3^-])}{[NO_3^-]^3[TBMA]_{(o)}^3 \gamma_{Sm^{3+}} \gamma_{NO_3^-}^3} \tag{5}$$

The values of activity coefficients under the studied conditions were not found in the literature, Let

$$K = K_{ex}\gamma_{Sm^{3+}}\gamma_{NO_3^-}^3 = \frac{D(1 + \beta_1[NO_3^-])}{[NO_3^-]^3[TBMA]_{(o)}^3} \tag{6}$$

where $\beta_1 = 0.74$ for Sm(III).[11]

Amides interact with the acid according to the following mechanism:

$$H^+ + NO_3^- + nTBMA_{(o)} = HNO_3 \cdot nTBMA_{(o)} \tag{7}$$

Studies show that the stoichiometry of the predominant species is 1:1 (HNO$_3$·Amide) at lower aqueous acidity (about 3 mol dm^{-3}).[3] Therefore,

$$[TBMA]_{(o),free} = c_{TBMA} - [TBMA]_{bound} \tag{8}$$

where $[TBMA]_{bound} = [HNO_3 \cdot TBMA]_{(o)} = [H^+]$. Then, one obtains

$$[TBMA]_{(o),free} = c_{TBMA} - [H^+]_{(o)} \tag{9}$$

The extraction studies of nitric acid were carried out under the same conditions as for the extraction of metal ions. The results are given in Table I.

TABLE I. Distribution of nitric acid in the two-phase system
$c_{HNO3} = 0.50$ mol dm^{-3}, $c_{LiNO3} = 5.00$ mol dm^{-3}, $c_{TBMA} = 0.50$ mol dm^{-3}

Diluent	Equilibrium [HNO$_3$]$_{aq}$ (mol dm^{-3})	Equilibrium [HNO$_3$]$_{(o)}$ (mol dm^{-3})	D nitric acid	[TBMA]$_{(o,free)}$
Benzene	0.254	0.246	0.969	0.254
Toluene	0.234	0.266	1.14	0.234
Xylene	0.244	0.256	1.05	0.244
Cyclohexane	0.255	0.245	0.961	0.255
n-Hexane	0.223	0.267	1.15	0.223
n-Octane	0.203	0.297	1.46	0.203
CCl$_4$	0.357	0.143	0.401	0.357
CHCl$_3$	0.287	0.213	0.742	0.287

The values of K, calculated from Eq. (6) using the free TBMA concentration are listed in Table II. Examination of Table II shows that the extraction efficiency of TBMA for Samarium(III) in different diluents increases in the order: chloroform, carbon tetrachloride, xylene–benzene, toluene, cyclohexane, n-hexane, n-octane. The lower values of D in the chloroform system may be attributed to the strong interaction between molecules of TBMA and chloroform through hydrogen bonding, $C=O - - HCCl_3$.

TABLE II. Values of K in different diluent systems

Diluent	c-Hexane	Toluene	Benzene	Xylene	CCl_4	$CHCl_3$	n-Hexane	n-Octane
K	23.29	22.04	6.79	7.06	0.88	0.24	153.86	269.56

Effect of diluent from the viewpoint of the thermodynamics of the interactions

The extraction process of Sm(III) is considered by a Born-Harber type of cycle. The change in the Gibbs free energy is the sum of four terms which represent the change in the Gibbs free energy for the dehydration of Sm^{3+} and NO_3^- (ΔG_1), for the desolvation of TBMA (ΔG_2), for the reaction of Sm^{3+}, NO_3^- and TBMA (ΔG_3), and for the dissolution of the complex $Sm(NO_3)_3 \cdot 3TBMA$ into the organic phase (ΔG_4). The magnitude and sign of the net change in the Gibbs free energy depend on the contributions of the changes in Gibbs free energy in these processes. It can be found that the values of ΔG_1 and ΔG_3 are independent of the kind of diluent. If the concentrations of aqueous acid and salt remain constant, *i.e.*, the activities of the species in the aqueous phase are kept constant, the observed change in the Gibbs free energy can be expressed as:

$$\Delta G = \Delta G_2 + \Delta G_4 + constant \qquad (10)$$

Based on the relationship

$$\Delta G = -RT \ln K_{ex} \qquad (11)$$

one obtains

$$\ln K_{ex} = -\Delta G_2/RT - \Delta G_4/RT + constant \qquad (12)$$

which shows that the difference in the extraction constants in various diluent systems can be attributed to the difference in the solvation of the extractant and the extracted complex.

A generalized equation for $\Delta G^o_{B,solv}$ of the solute B, has been established as being:

$$\Delta G^o_{B,solv} = A_0 + A_\pi \pi^* + A_\alpha \alpha + A_\beta \beta + A_\delta \delta^2 \qquad (13)$$

in which the solvatochromic parameters, π^* is for polarity-polarizability, α is for hydrogen bond donation, β is for hydrogen bond acceptance basicity and δ is the square root of the

cohesive energy density (called the solubility parameter).[2,3] The values of the parameters are listed in Table III.

Substituting Eq. (13) into Eq. (12) yields:

$$\ln K_{ex} = B_0 + B_\pi \pi^* + B_\alpha \alpha + B_\beta \beta + B_\delta \delta^2 \tag{14}$$

Using Multiple Regression Program to process the data in Table III, for the eight studied dilutents one onbtaines the one can get the relationship:

$$\ln K = 45.87 + 29.18\,\pi^* - 11.5\alpha - 7.71\beta - 0.171\delta^2 \tag{15}$$

the value of the correlation coefficient of which is 0.986.

TABLE III. Selected properties and solvatochromic parameters of some solvents[12,13]

Substance	π^*	α	β	$\delta/(J/mL)^{1/2}$	ε
n-Hexane	-0.04	0	0	15.0	1.88
n-Octane	0.01	0	0	15.4	1.95
c-Hexane	0.00	0.00	0.00	15.8	2.02
Benzene	0.59	0.00	0.10	18.8	2.28
Toluene	0.54	0.00	0.11	18.3	2.38
Xylene	0.43	0.00	0.12	18.1	2.27
Carbon tetrachloride	0.28	0.00	0.10	17.6	2.24
Chloroform	0.58	0.20	0.10	18.9	4.90

A closer examination of Eq. (15) leads to the conclusion that higher values of π^* of the diluents favor the extraction and, on the contrary lower values of α, β and δ hinder the extraction.

TABLE IV. Concentration at which a third phase appears. $c_{LiNO_3} = 5.00$ mol.dm^{-3}

Diluent	*c*-Hexane	*n*-Hexane	*n*-Octane	Xylene	CCl$_4$
Initial c_{HNO_3}/mol dm^{-3}	1	0.5	0.5	4	3
Initial c_{LiNO_3}/mol dm^{-3}	6	3	3	–	–
Initial $c_{TBMP(o)}$/mol dm^{-3}	–	0.2	0.2	–	–

It is also noteworthy that a third phase is formed under the studied conditions, especially in the aliphatic hydrocarbon systems. The minimum concentration at which a third phase appears is given in Table IV. The tendency to form a third phase is a follows: *n*-octane > *n*-hexane > *c*-hexane > CCl$_4$ > xylene.

CONCLUSION

A study has been made of the extraction of samarium(III) from nitrate solutions using *N,N,N',N'*-tetrabutylmalonamide (TBMA) in a series of diluents. The

experimental results showed that the extraction efficiency of Sm(III) by TBMA increases in the order: chloroform, carbon tetrachloride, benzene, xylene, toluene, cyclohexane, *n*-hexane, *n*-octane. The stoichiometry of the extracted species corresponds to $Sm(NO_3)_3 \cdot 3TBMA$ in all the employed diluents. The interaction of the extractant or extracted species with the diluent has been discussed and a quantitative expression relating the extraction constant with the parameters of diluent was established and presented by Eq. (15) which shows that increasing values of π^* of the diluents favor the extraction and, on the contrary, increasing values of α, β and δ hinder the extraction.

ИЗВОД

УТИЦАЈ РАСТВАРАЧА НА ЕКСТРАКЦИЈУ Sm(III) КОРИШЋЕЊЕМ *N,N,N',N'*-ТЕТРАБУТИЛМАЛОНАМИДА

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Проучавана је екстракција самаријум(III) из нитратних раствора коришћењем *N,N,N',N'*-тетрабутилмалонамида (ТВМА) у низу раствара. Проучавана је зависност екстракционе расподела од концентрације водених раствора азотне киселине, литијум нитрата и органске ТВМА. Експериментални резултати су показали да се ефикасност екстракције ТВМА са Sm(III) у различитим растварачима повећава по редоследу: хлороформ, угљен-тетрахлорид, бензен, ксилен, толуен, циклохексан, *n*-хексан, *n*-октан. Стехиометрија екстраховане врсте је $Sn(NO_3)_3 \cdot 3TBMA$ са свим коришћеним растварачима. Разматрана је интеракција екстрактаната или екстраховане врсте са растварачем и утврђен је квантитативни однос између константе екстракције и параметара растварача.

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