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COMPLEXATION OF AMERICIUM(III) WITH A DIAZA-CROWN ETHER

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Abstract—The aqueous phase complexation behaviour of trivalent americium in the presence of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (kryptofix 22) was investigated by employing a solvent extraction tracer technique at a ligand-to-metal ratio as high as 10^5. The extraction behaviour was studied by using a liquid ion exchanger (dinonylnaphthalene sulphonic acid) both in high and low pH regions. Though no observable complexation is detected at low pH (e.g. pH 2.0), measurable complex formation was detected at higher pH values ($\log \beta^L = 6.05 \pm 0.30$).

Size compatibility, a characteristic feature of crown ethers, is predominantly observed for the alkali and the alkaline earth ions[1–3] and is not extendable to the transition metal ions. This is principally due to the preference of the latter for a particular stereochemical arrangement of donor atoms.[4] The trivalent lanthanide ions, on the other hand, have a $4f^n\ 5s^2\ 5p^6$ electronic configuration resulting in a weak crystal field and directional properties. The investigations of their interactions with the macrocyclic ligands, therefore, is a logical extension of the work with alkali and alkaline earth metal ions. Azamacrocycles are known to be particularly effective ionophores for the lanthanide ions in non-aqueous medium.[5,6]

It has been reported earlier that the crown ethers form outer sphere H-bonded complexes rather than encapsulated species with trivalent lanthanide[7,8] and actinide[9] ions in aqueous medium. This is explained on the basis of the higher hydration energies of the trivalent ions. In order to understand the complexation as well as the extraction characteristics of actinides with aza macrocyclic ligands, trivalent americium (a representative trivalent actinide ion) and 1,10-diaza-4,7,13,16-tetraoxa cyclooctadecane otherwise known as kryptofix 22 or simply as K22 (a representative aza macrocyclic ligand, see Fig. 1) were employed in a tracer extraction study in the present work. Dinonylnaphthalene sulphonic acid (DNNS), a liquid cation exchanger, which is immiscible with the aqueous phase has been employed as the organic extractant.

The aqueous phase complexation constant for americium(III) with K22 reported here is the first of its kind for any trivalent actinide ion.

EXPERIMENTAL

Reagents

K22 (procured from E. Merck) and DNNS (obtained from R. T. Vanderbilt Co., U.S.A.) were

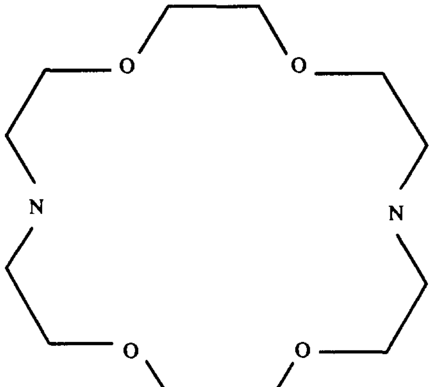

Fig. 1. K22.

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used without further purification. The concentration of DNNS was accurately estimated by titration with a standard alkali in a 50% methanol–water medium. All the other reagents used were of AR grade. ^{241}Am was purified and assayed following a method reported earlier.[10]

Procedure

The solution containing DNNS was equilibrated with 4 M NaCl solution for ~24 h to convert the latter to the sodium form. The extraction studies carried out by forward as well as by reverse extraction method[10] yielded comparable distribution ratio values. However, for convenience sake most of the experiments were carried out using the reverse extraction technique.

The experiments involving the variation of pH were carried out at a fixed DNNS as well as K22 concentration. The organic phase concentration of DNNS was varied in the range of 6.0×10^{-4} to 6.0×10^{-3} M, while the aqueous phase contained a fixed concentration of K22. Experiments were also carried out by varying the concentration of DNNS in the above mentioned concentration range in the absence of K22. The concentration of K22 in the aqueous phase was varied in the range of 1.0×10^{-4} to 1.0×10^{-3} M at a fixed organic phase DNNS concentration. All these experiments were carried out at a fixed pH of 2.0 and a constant ionic strength of 1.0 M maintained by NaCl. The aqueous phase pH in the case of the experiments at higher pH (6.0 or above) was maintained by the use of TRIS-buffer.[11]

The mass balance in all the relevant data points are generally within ±5%. Values with larger deviations are ignored for calculation purpose.

CALCULATIONS

The two phase equilibrium involving Am^{3+}, NaDNNS (sodium form of DNNS) and K22 is represented as

$$\mathrm{Am^{3+}} + \mathrm{K22} + (\mathrm{NaDNNS})_{n,\mathrm{org}} \overset{K_{\mathrm{ex}}}{\rightleftharpoons} \{\mathrm{Am(K22)(DNNS)}_n\mathrm{Na}_{n-3}\}_{\mathrm{org}} + 3\mathrm{Na}^+ \quad (1)$$

Thus,

$$K_{\mathrm{ex}} = \frac{[\mathrm{Am(K22)(DNNS)}_n\mathrm{Na}_{n-3}]_{\mathrm{org}}[\mathrm{Na}^+]^3}{[\mathrm{Am}^{3+}][\mathrm{K22}][\mathrm{NaDNNS}]_{n,\mathrm{org}}} \quad (2)$$

The subscript org refers to species in the organic phase and those without subscript refer to the species in the aqueous phase. The charges are omitted henceforth for simplicity.

Assuming the co-extraction of americium as well as AmL with NaDNNS into the organic phase, the presence of chloro, hydroxy and K22 complexes in the aqueous phase and neglecting the presence of polymeric species, the distribution ratio, D, in the presence of the ligand K22 and D_0 in its absence are expressed as

$$D = \frac{[\mathrm{Am(K22)(DNNS)}_n\mathrm{Na}_{n-3}]_{\mathrm{org}} + [\mathrm{Am(DNNS)}_n\mathrm{Na}_{n-3}]_{\mathrm{org}}}{[\mathrm{Am}]\left\{1 + \sum_i \beta_i^{\mathrm{Cl}}[\mathrm{Cl}]^i + \sum_j \beta_j^{\mathrm{OH}}[\mathrm{OH}]^j + \sum_k \beta_k^{\mathrm{K22}}[\mathrm{K22}]^k\right\}} \quad (3)$$

$$D_0 = \frac{[\mathrm{Am(DNNS)}_n\mathrm{Na}_{n-3}]_{\mathrm{org}}}{[\mathrm{Am}]\left\{1 + \sum_i \beta_i^{\mathrm{Cl}}[\mathrm{Cl}]^i + \sum_j \beta_j^{\mathrm{OH}}[\mathrm{OH}]^j\right\}} \quad (4)$$

From eqs (2)–(4) one can deduce

$$\frac{D - D_0}{[\mathrm{K22}]} = K_1 - K_2 D \quad (5)$$

where

$$K_1 = \frac{K_{\mathrm{ex}}[\mathrm{NaDNNS}]_{n,\mathrm{org}}}{(1+X)[\mathrm{Na}]^3} \quad (6)$$

and

$$K_2 = \frac{\beta^{\mathrm{L}}}{(1+X)} \quad (7)$$

In eqs (6) and (7) X denotes

$$\sum_i \beta_i^{\mathrm{Cl}}[\mathrm{Cl}]^i + \sum_j \beta_j^{\mathrm{OH}}[\mathrm{OH}]^j$$

The aqueous complexation constant of Am^{3+} with K22, β^{L}, was determined using eqs (5) and (7).

RESULTS AND DISCUSSION

Studies at low pH (<3.0):

*Effect of DNNS concentration.*The extraction of metal ions in the presence of liquid ion exchangers such as DNNS and didodecylnaphthalene sulphonic acid (DDNS) are known to be operative through a micellar mechanism.[12] The extraction process involves the exchange of the replaceable cations of the extractant with the metal ion of interest. In the present extraction system, a dependency of -2.7 for the logarithm of distribution ratio ($\log D$) of americium(III) on the $\log[Na^+]$ suggested the following extraction equilibrium:

$$Am^{3+} + (NaDNNS)_n \rightleftharpoons AmNa_{n-3}(DNNS)_n + 3Na^+ \quad (8)$$

The dependency of $\log D$ on log [DNNS] is a straight line plot of unity slope (Fig. 2) confirming the micellar mechanism of extraction. This dependence in the presence of 10^{-4} M of K22 remains unaltered though the absolute D values decrease. The slope value shows increasing deviation from unity with further increase of K22 concentration. For a given concentration of K22 (1×10^{-3} M) the slope varies from 1 to 3 as the concentration of DNNS is varied from 1×10^{-2} to 5×10^{-4} M. At still higher ligand concentration (1×10^{-2} M), the slope value is 2.2 even in the DNNS concentration range of 1×10^{-2} to 3×10^{-3} M. The decrease in the absolute D values with the increase of ligand concentration could be explained either by considering (i) the formation of hydrophilic americium(III)–K22 complex species or by (ii) the co-extraction of the protonated form of K22 along with americium(III) as ion-pairs with DNNS towards the organic phase. On the basis of the reported p*K*a values of K22[13] there is very little possibility of the formation of americium(III)–K22 complex species at pH 2.0. In addition, the deviation from unity slope observed at high K22 concentration cannot be explained by considering the formation of these complex species alone. The nature of the extractable species i.e., $AmNa_{n-3}(DNNS)_n$ does not undergo any change in this case. On the other hand, due to the co-extraction of the $K22(H)_2Na_{n-2}(DNNS)_n$ species, the abscissa in Fig. 2 does not represent the equilibrium concentration of DNNS. This is particularly true for larger K22 concentration of 1×10^{-2} and 1×10^{-3} M. The deviation from unity slope is related to the varying degrees of decrease of DNNS concentration caused by its interaction with the protonated form of K22. It is possible that with the equilibrium concentration of DNNS dropping below 1×10^{-5} M, even the micelle mechanism may not be operative and the nature of the extractable species change over to $Am(DNNS)_3$.[12]

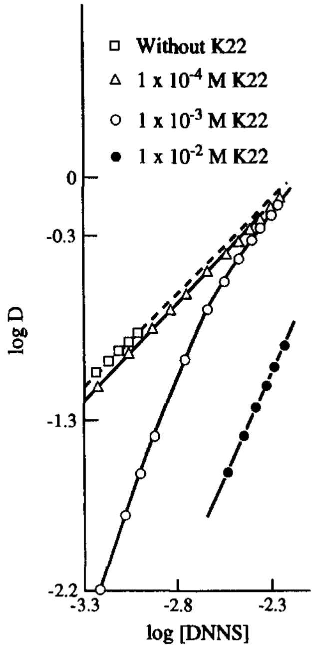

Fig. 2. DNNS concentration variation plots at a fixed pH of 2.0 and ionic strength of 1.0 M.

Effect of ligand concentration. The variation of $\log D$ with the logarithm of ligand concentration at pH 2.0 and DNNS concentration of 0.01 M is a straight line plot of -1 slope. This suggests the formation of a 1 : 1 species of $[K22(H)_2]^{2+}$ with the DNNS micelle as shown in the following equation:

$$K22(H)_2^{2+} + (NaDNNS)_{n,org} \rightleftharpoons K22(H)_2(DNNS)_nNa_{n-2} + 2Na^+ \quad (9)$$

Effect of pH. The distribution ratio, for a given concentration of K22 and DNNS, is independent of pH in the range 1.9 to 3.1. The observed value of $D = 0.806 \pm 0.043$ for $[DNNS] = 6.0 \times 10^{-2}$ M and $[K22] = 1.0 \times 10^{-3}$ M. It suggests that there is no complexation of americium(III) with the ligand in this pH range. As mentioned above this is in conformity with the reported p*K*a value of the ligand.[13]

Studies at high pH (> 6.0)

It was thought desirable to carry out distribution experiments at higher pH values (> 6.0) which may facilitate the complexation by diaza-crown ether. In contrast to the low pH experiments, the D values (Table 1) are enhanced significantly under these conditions. This is ascribed to the extraction of synergistic species containing K22 as well as DNNS. This enhancement is several fold larger compared with that observed with crown ether for lanthanides in similar extraction systems.[14]

As expected, D/D_0 values increase with K22 concentration from 1×10^{-5} to 1×10^{-3} M as well as with the increase of pH from 6.0 to 8.0 (Fig. 3). These values decrease if the ligand concentration

Table 1. Distribution data in the higher pH region as a function of K22 concentration, [DNNS] = 0.01 M; [NaCl] = 1.0 M

[K22]	pH 6.0	pH 7.0	pH 8.0	pH 9.0[b]
Nil	2.64[a]	12.38[a]	18.59[a]	5.49[a]
1×10^{-5} M	—	—	—	26.59
1×10^{-4} M	—	17.39	145	73.1
1×10^{-3} M	2.21	36.45	305	72.0
1×10^{-2} M	10.4	14.42	73.5	6.53

[a] The high value in the absence of ligand compared with those determined at pH 2.0 is due to hydrolysis of the metal ion.[15]

[b] There was lack of material balance (up to 30%) in some data points.

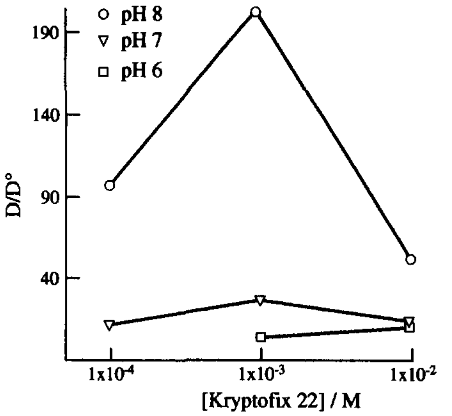

Fig. 3. Plots of D/D_0 at varying ligand concentration values at different pH values, (□) pH = 6.9; (△) pH = 7.0; (○) pH = 8.0.

increases beyond 1×10^{-3} M probably due to the presence of ligand in comparable proportion to DNNS. It causes the concentration of the latter to be insufficient for extracting synergistic species of americium(III). Similarly the D/D_0 values decrease spectacularly at pH 9.0 probably due to the formation of hydrolysed species.[15] It appears that due to the slow kinetics of complexation, as reported for lanthanides,[16] side reactions involving the hydrolysis of the metal ions play a significant role at this pH.[15]

Evaluation of complex formation constant

An attempt has been made in the present work to compute the complexation constant of americium(III) with K22 employing the distribution data obtained at pH 7.0 as well as at pH 8.0 (Table 1). There was lack of material balance (up to −10% in the experiments at pH 7–8 and −30% at pH 9.0) in the experiments carried out in the absence of K22. It is for this reason the distribution data at pH 9.0 was not used for the computation of complexation constant. ^{241}Am activity appears to get adsorbed on the glass surface of the extraction tube and as expected, it is related to pH and ligand concentration.

Table 2 lists the complex formation constant data obtained during the present work along with the relevant data from the literature. Individual $\log\beta^{L}$ values at pH 7.0 and 8.0 were 6.29 and 5.81, respectively. These values are significantly larger compared with those observed earlier with crown ethers. This is suggestive of the stronger complexation of diaza-crown ethers with trivalent actinide ions compared with that of crown ethers. The variation in these values is attributed to the varying degree of (i) interaction of the protonated form of K22 with DNNS, (ii) the hydrolysis of the metal ion and (iii)

Table 2. The aqueous phase complex formation constants for trivalent actinide and lanthanide ions, temp. = 25°C; ionic strength = 1.0 M

Metal ion	18-crown-6	K22	K222	$A_6$18C6
La^{III}	3.29 ± 0.03[a]	6.18[c]	9.4[c] 6.45 ± 0.03[d]	9.1[e]
Eu^{III}	1.84 ± 0.14[a]	—	5.90 ± 0.09[d]	10.2[e]
Am^{III}	0.55 ± 0.06[b]	6.05 ± 0.3[f]	—	—

[a] Data obtained in MeOH medium; ref. 20.

[b] Data taken from ref. 9.

[c] Data obtained in 95% MeOH medium; ref. 13.

[d] Data taken from ref. 5.

[e] Data taken from ref. 16.

[f] Present work; this is the mean value of $\log\beta^{L}$ values obtained at pH 7.0 and 8.0.

varying $[NaDNNS]_{n,org}$ concentration in eq. (6) as a consequence of (i). A mean log K value of 6.05 ± 0.3 observed in the present study is comparable with that of lanthanum(III) with K22 in 95% methanol/5% water medium.[13]

As there is no data available in the literature on the complexation of trivalent actinide ions with nitrogen substituted crown compounds, those for some of the trivalent lanthanide ions are included for comparison. It is significant to note that the enhancement in the log K values on going from 18-crown-6 to K22 is much larger for americium(III) ion than for the lanthanide ions. This could be attributed to the better availability of the *f*-orbitals for partial covalent interaction in case of the former. It is only logical to propose that more favourable complex formation will be observed with the hexa-aza derivative of 18-crown-6 ($A_6$18C6) and the cryptand K222. Incorporation of ionisable pendant groups on K22 has been found to suppress the hydrolysis and holds a better promise for studying the size selective complexation behaviour of trivalent lanthanides[17] and actinides.[18]

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REFERENCES

1. C. J. Pedersen, *J. Am. Chem. Soc.* 1967, **89**, 7017.
2. R. M. Izatt and J. J. Christensen (Eds), *Synthetic Multidentate Macrocyclic Ligands*, Academic Press, New York (1978).
3. G. W. Gokel, *Crown Ethers and Cryptands*, Royal Society of Chemistry, London (1992).
4. A. Bianchi, M. Micheloni and P. Paoletti, *Coord. Chem. Rev.* 1991, **110**, 17.
5. J. C. G. Bünzli, in *Handbook on the Physics and Chemistry of Rare Earths* (Edited by K. A. Gschneidner Jr and L. Eyring), Vol. 9, Chap. 60. Elsevier, Amsterdam (1987).
6. E. L. Loufouilou, Ph.D. Thesis, University Louis Pasteur, Strassbourg (1986).
7. R. D. Rogers and L. K. Kurihara, *Inorg. Chim. Acta* 1986, **116**, 171.
8. K. Nakagawa, S. Okada, Y. Inoue, A. Tai and T. Hakushi, *Anal. Chem.* 1988, **60**, 2527.
9. P. K. Mohapatra and V. K. Manchanda, *Radiochim. Acta* 1991, **55**, 193.
10. V. K. Manchanda and P. K. Mohapatra, *Polyhedron* 1990, **9**, 2455.
11. P. K. Mohapatra, Ph.D. Thesis, University of Bombay, Bombay (1993).
12. M. Y. Markovits and G. R. Choppin, in *Ion Exchange and Solvent Extraction* (Edited by J. A. Marinsky and Y. Marcus), Vol. 3, p. 51. Marcel Decker, New York (1973).
13. G. Anderegg, *Helv. Chim. Acta* 1981, **64**, 1790.
14. D. D. Ensor, G. R. McDonald and C. G. Pippin, *Anal. Chem.* 1986, **58**, 1814.
15. P. K. Mohapatra and V. K. Manchanda, *J. Radioanal. Nucl. Chem., Articles* 1992, **156**, 215.
16. W. Sczepaniak, B. Juskowiak and W. Ciszewska, *Inorg. Chim. Acta* 1988, **147**, 261.
17. V. K. Manchanda, P. K. Mohapatra, C. Zhu and R. M. Izatt, *J. Chem. Soc., Dalton Trans.*, 1995 (in press).
18. V. K. Manchanda and P. K. Mohapatra, *Inorg. Chim. Acta* 1990, **170**, 141.
19. R. D. Shannon, *Acta Cryst.* 1976, **32A**, 751.
20. R. M. Izatt, J. D. Lamb, J. J. Christensen and B. L. Haymore, *J. Am. Chem. Soc.* 1977, **99**, 8344.