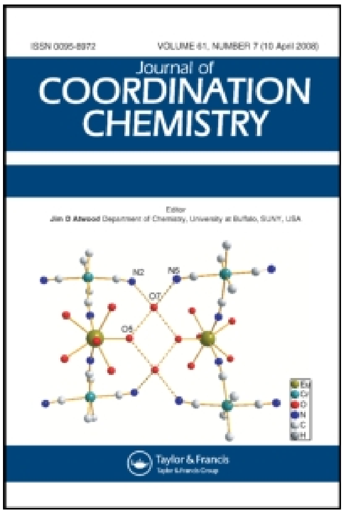

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Solution thermodynamics of Lanthanide-Cryptand 222 complexation processes

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SOLUTION THERMODYNAMICS OF LANTHANIDE–CRYPTAND 222 COMPLEXATION PROCESSES

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The thermodynamics of trivalent cations (Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+}) and cryptand 222 in acetonitrile at 298.15 K is discussed. Recent reports regarding the behavior of lanthanide(III) trifluoromethane sulfonate salts in acetonitrile are considered. Thus, the experimental work was carried out under conditions in which ions (M^{3+}) are predominantly in solution. Therefore, conductiometric titrations were carried out to establish the composition of the cation–cryptand 222 complexes and their ionic behavior in solution. Stability constants and derived standard Gibbs energies, enthalpies and entropies were determined by competitive titration microcalorimetry. Previously reported thermodynamic data for the complexation of cryptand 222 and a few lanthanide cations (La^{3+}, Pr^{3+} and Nd^{3+}) in acetonitrile are revisited. The medium effect on the stability of complex formation in acetonitrile relative to *N*,*N*-dimethylformamide is demonstrated. Thus, a drop in stability by a factor of 8×10^{10} is observed for the latter relative to the former solvent. The selectivity of cryptand 222 for these cations relative to La^{3+} in acetonitrile is discussed.

Keywords: Cryptand; Lanthanides; Thermodynamics of complexation

INTRODUCTION

The chemistry of lanthanide complexation has been extensively discussed in several articles [1–4]. A large number of neutral macrocycles are able to complex lanthanide cations, mainly through ion–dipole interactions between the donor atoms of the ligand and the charge of the cation. Solution studies involving trivalent cations and macrocyclic ligands, however, have been mostly confined to stability constant measurements. Publications with data on enthalpies of complexation and significant insight into the role of the reaction media in the binding process are indeed very rare.

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Cryptands are azamacrocycles synthesized by Lehn in 1969 [5]. These compounds contain a three-dimensional cavity lined with oxygen and nitrogen atoms. They have been shown to form strong complexes with metal cations, including the lanthanides. The thermodynamics of cryptands with univalent and bivalent cations in water and non-aqueous media has been extensively discussed [6–12]. Some lanthanide complexes of cryptands have been isolated and their solid-state structure has been investigated by X-ray crystallography [13,14]. These studies have shown that the cation lies inside the cavity of the ligand in the 'endo–endo' conformation. Because of their high coordination, the lanthanide cations were found to coordinate to solvent molecules as well as the counter-ion besides the ligand donor atoms. Stability constants of 1:1 lanthanide(III) cryptates determined by electrochemical or spectrophotometric methods have been reported in water [15], methanol [16], propylene carbonate [17,18], dimethylsulfoxide [19], *N*, *N*-dimethylformamide (DMF) [20] and acetonitrile [20] at 298.15 K. In some cases, data on enthalpies and entropies of complexation have been reported on the basis of the temperature variation of stability constant data (van't Hoff equation [21]). The accuracy of these data, however, should be regarded with caution owing to limitations of the van't Hoff equation in the derivation of enthalpy data. The thermodynamics of a few lanthanide cations (La^{3+}, Pr^{3+} and Nd^{3+}) and cryptands 222 and 221 in two dipolar aprotic solvents (acetonitrile and propylene carbonate) at 298.15 K has been reported [22]. Titration calorimetry was used to derive enthalpy data. Lanthanide trifluoromethane sulfonates were used as the metal cation sources for various authors to carry out the experimental work. The selection of these salts was based on the work of Seminara and Rizzarelli [23]. These authors claimed that coordination of the trifluoromethane sulfonate anion and the lanthanides does not occur in anhydrous acetonitrile. Later Di Bernardo *et al.* [24] concluded that this is not the case since the anion participates in the inner coordination sphere of the cation.

On the basis of these investigations, Danil de Namor and Jafou [25] established through conductance measurements the concentration range at which lanthanide(III) cations are the predominant species in acetonitrile. Since the previous work [22] was carried out at much higher concentrations at which other species besides La(III) cations are present in acetonitrile, we decided (i) to revisit the thermodynamics of La^{3+}, Pr^{3+} and Nd^{3+} and cryptand 222 in acetonitrile and (ii) to extend these investigations to other lanthanide(III) cations as well as Sc^{3+} and Y^{3+}. In addition, the medium effect on the complexation process is assessed. For this purpose, DMF, a protophilic solvent, was selected, unlike acetonitrile (protophobic dipolar aprotic solvent).

EXPERIMENTAL

Chemicals

Scandium (99%), yttrium (98%), lanthanum (99.9%), praseodymium (99%), neodymium (99%), europium (99%), gadolinium (99%), terbium (99%), holmium (99%), erbium (99%), ytterbium (99.9%) trifluoromethanesulfonate (triflate) salts and potassium perchlorate anhydride (99%) were all purchased from Aldrich Chemical Co. The lanthanide triflate salts were further dried by a chemical reaction using triethylorthoformate [26]. All the salts were stored over phosphorus pentoxide (P_4O_{10}) under vacuum for several days before use. Cryptand 222; (Fluka) was used without further purification. It was kept over P_4O_{10} under vacuum for several days before use.

Acetonitrile (MeCN), HPLC grade (Fisher), was refluxed in a nitrogen atmosphere and distilled from calcium hydride [26]. Only the middle fraction of the solvent was collected. DMF, HPLC grade from Fisher, was dried over 4 Å molecular sieves and subsequently distilled under reduced pressure. The middle fraction of the solvent was used.

Conductiometric Measurements

A Wayne–Kerr Autobalance Universal Bridge (type B642) was used for the conductance measurements. Fresh dry solutions of the metal-cation salt and the ligand were prepared for every experiment. Solutions of the ligand and the metal-cation salts were weighed accurately using a Mettler AE 240 balance. The cell was subsequently filled with the lanthanide salt solution ($25\,\mathrm{cm}^3$), sealed and then left for an hour in a thermostatted bath at 298.15 K to reach thermal equilibrium before each experiment. Then, stepwise addition of the ligand solution was performed using a hypodermic syringe. A steady nitrogen flow to the reaction vessel was maintained throughout the whole experiment and was stopped prior to each measurement.

Generally, the concentration of cryptand 222 ranged from 4.0×10^{-4} to $5.8 \times 10^{-4}\,\mathrm{M}$, while the concentrations of the salts in the appropriate solvent were around $1 \times 10^{-5}\,\mathrm{M}$.

Calorimetric Titrations

Competitive microcalorimetric titrations were carried out using a four-channel heat conduction microcalorimeter (ThermoMetric, 2277 Thermal Activity Monitor) [27].

To check the reliability of the equipment, chemical calibration was carried out using the method described by Briggner and Wadsö [28] for complexation of 18-crown-6 and barium chloride ($BaCl_2$), in aqueous medium at 298.15 K. The reaction vessel was charged with a solution of 18-crown-6 in water ($2.8\,\mathrm{cm}^3$) and about 14 injections were made with the aqueous solution of $BaCl_2$ in a Hamilton gas-tight syringe.

A separate dilution experiment was performed and the heat of complexation was corrected for this value. The values obtained ($\log K_s = 3.77 \pm 0.01$, $\Delta_c H^\circ = -31.42 \pm 0.02\,\mathrm{kJ\,mol^{-1}}$) were in good agreement with those published [28].

For competitive titration experiments, the reaction vessel was charged with a solution of the silver cryptate complex in the appropriate solvent ($2.8\,\mathrm{cm}^3$, 1.0×10^{-4}–$3.0 \times 10^{-4}\,\mathrm{M}$, $n^{+}_{\mathrm{Ag}} = 3n_{1\,\mathrm{or}\,2}$, where n^{+}_{Ag}, and $n_{1\,\mathrm{or}\,2}$ are the number of moles of the metal cation in the vessel and the ligand respectively). The metal-ion salt (6.0×10^{-3}–$9.0 \times 10^{-3}\,\mathrm{M}$) was injected incrementally using a $0.5\,\mathrm{cm}^3$ gas-tight motor-driven Hamilton syringe. In each titration experiment about 20 injections were made at time intervals of 35–50 min for single injection. Corrections for the enthalpy of dilution of the titrant in the solvent were carried out in all cases.

RESULTS AND DISCUSSION

Conductiometric Titrations

Although it is well established that cryptands form mostly 1:1 complexes with metal cations [29], conductiometric titrations were performed in an attempt to corroborate

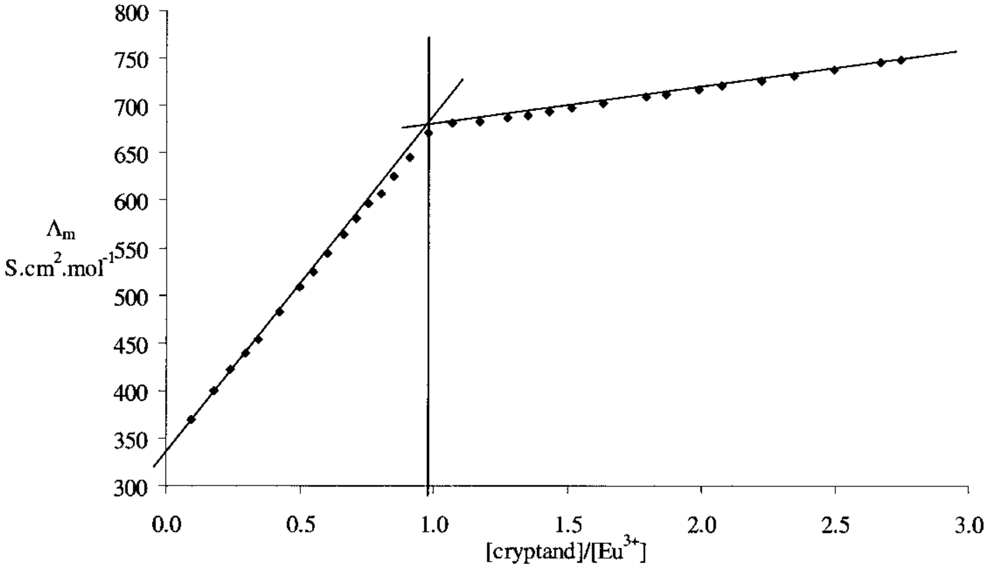

FIGURE 1 Conductimetric titration curve for the complexation of cryptand 222 with Eu^{3+} (as trifluoromethane sulfonate) in acetonitrile at 298.15 K.

that interaction of cryptand 222 with lanthanide cations leads to the formation of 1:1 complexes in acetonitrile. A representative conductiometric curve for the titration of Eu^{3+} with cryptand 222 in acetonitrile at 298.15 K is shown in Fig. 1. In this figure, the molar conductance (Λ_m in $S\,cm^2\,mol^{-1}$) is plotted against the ligand : metal cation concentration ratio.

While the break observed at the 1:1 ratio confirmed the composition of the complex, the slope of the conductimetric titration curve suggests the formation of a rather stable complex. In addition, there are three important aspects to emphasize.

(i) Λ_m in the absence of the ligand (ratio of 0) is close to the expected value for solutions containing predominantly the trivalent lanthanide cations (concentration of the metal-ion salt was lower than 5×10^{-5} M) [30].

(ii) The increase in conductance on complex formation must be attributed to a decrease in the solvation of the complex relative to the free cation in acetonitrile. Similar findings were previously reported [31] for lithium salts complexed with crown ethers in this solvent.

(iii) The complexation process is kinetically very slow as previously observed [32]. This was attributed to the slow removal (partial or total) of the solvation shell of the highly charged lanthanide cations.

Another important aspect to emphasize is that, in complexationes processes involving lanthanide salts and cryptands, the dryness of the salt and the solvent are of crucial importance. Indeed, very small amounts of water lead to ligand protonation. This statement is corroborated in the conductiometric titration curve shown in Fig. 2 where an additional break at a ligand : metal ratio of 0.5 was found. This was confirmed by performing the conductiometric titration of $HClO_4$ with cryptand 222 in acetonitrile (Fig. 3), which shows a break at 0.5 resulting from formation of the diprotonated cryptand 222.

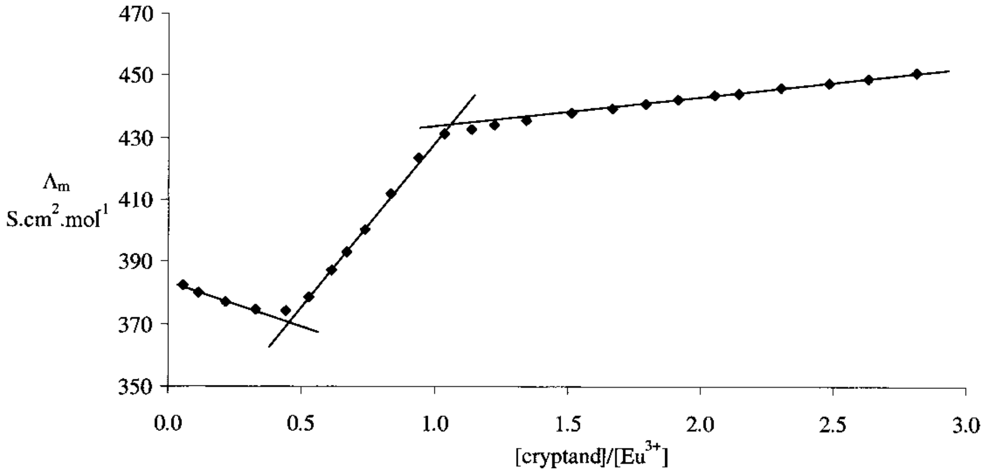

FIGURE 2 Conductimetric titration curve for the complexation of protonated cryptand 222 with Eu^{3+} (as trifluoromethane sulfonate) in acetonitrile at 298.15 K.

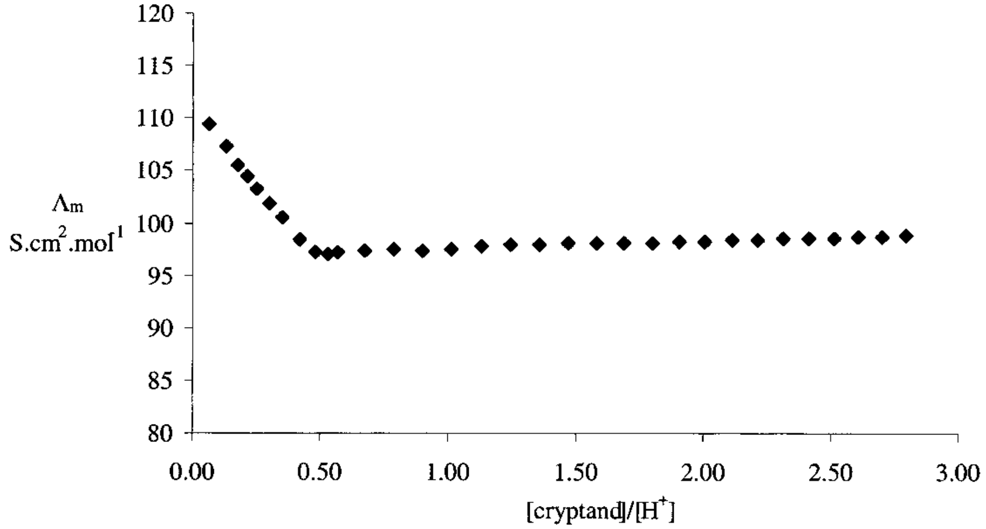

FIGURE 3 Conductimetric titration curve of cryptand 222 with perchloric acid in acetonitrile at 298.15 K.

Having established the composition of the metal-ion complex and the optimum experimental conditions for the formation of the 1:1 complexes, we proceeded with an investigation of the thermodynamics associated with these processes. Considering that (i) the kinetics of the complexation process is very slow in accordance with previous reports [32] and (ii) the system is very sensitive to moisture, we carried out microcalorimetric titration measurements using the thermal activity monitor designed by Wadsö and Suurkussk [29] to follow the course of kinetically slow processes. Because of the high stability of the lanthanide complexes, competitive titration microcalorimetry was used as reported in the following section, where the thermodynamics of complexation of tervalent cations and cryptand 222 in dipolar aprotic media is discussed.

Thermodynamics of Complexation

Stability constant data (expressed as $\log K_s$) and derived standard Gibbs energies, enthalpies and entropies of complexation at 298.15 K in acetonitrile are listed in Table I. The standard deviation values of the data are also included in Table I. These data were derived from competitive titration microcalorimetry against the silver cation. The processes taking place are in Eq. (1).

$$\mathrm{Ag^{+}222\quad(MeCN) + M^{3+}\quad(MeCN) \rightarrow M^{3+}222\quad(MeCN) + Ag^{+}\quad(MeCN)} \qquad (1)$$

Thermodynamic data for the complexation of silver and cryptand 222 in acetonitrile at 298.15 K, i.e., are well established [33]. Combination of Eqs. (1) and (2) leads to the derivation of

$$\mathrm{Ag^{+}\quad(MeCN) + 222\quad(MeCN) \rightarrow Ag^{+}222\quad(MeCN)} \qquad (2)$$

$\log K_s$ and $\Delta_c H^\circ$ values for the complexation of trivalent cations and cryptand 222 in acetonitrile at 298.15 K:

$$\mathrm{M^{3+}\quad(MeCN) + 222\quad(MeCN) \rightarrow M^{3+}222\quad(MeCN)} \qquad (3)$$

Enthalpy data obtained from competitive microcalorimetric titrations were compared with those obtained from direct microcalorimetric titrations for Gd^{3+} and Tb^{3+}. The latter are reported in Table I. $\Delta_c H^\circ$ values from competitive titrations for

TABLE I Thermodynamic parameters of lanthanide(III) cations and cryptand 222 in acetonitrile and *N*,*N*–dimethylformamide at 298.15 K

Cations	*Log K_s*	$\Delta_c G^\circ$/kJ mol^{-1}	$\Delta_c H^\circ$/kJ mol^{-1}	$\Delta_c S^\circ$/J K^{-1} mol^{-1}
		Acetonitrile		
Y^{3+}	11.16 ± 0.01^a	-63.69 ± 0.50^a	-198.3 ± 0.9^a	-451^a
La^{3+}	15.06 ± 0.01^a	-85.96 ± 0.50^a	-132.8 ± 1.2^a	-157^a
	10.81^c	-61.71^c	-78.2^c	-56^c
Pr^{3+}	15.35 ± 0.01^a	-87.61 ± 0.52^a	-119.5 ± 0.8^a	-107^a
	11.01^c	-62.8^c	-92.8^c	-100^c
Nd^{3+}	14.74 ± 0.02^a	-84.13 ± 0.53^a	-117.2 ± 0.8^a	-111^a
	11.06^c	-63.14^c	-104.2^c	-138^c
Eu^{3+}	14.12 ± 0.01^a	-80.60 ± 0.67^a	-136.8 ± 0.9^a	-189^a
Gd^{3+}	14.44 ± 0.04^a	-82.42 ± 0.50^a	-113.6 ± 1.2^a	-105^a
Tb^{3+}	13.70 ± 0.01^a	-78.20 ± 0.92^a	-148.6 ± 1.5^a	-236^a
			-144.1 ± 0.9^b	
Ho^{3+}	15.00 ± 0.03^a	-85.62 ± 0.50^a	-99.2 ± 1.7^a	-46^a
Er^{3+}	13.88 ± 0.02^a	-79.22 ± 0.67^a	-133.6 ± 1.8^a	-182^a
Yb^{3+}	14.12 ± 0.02^a	-80.67 ± 0.70^a	-93.3 ± 1.5^a	-43^a
			-95.6 ± 0.6^b	
		N,*N*–dimethylformamide[b]		
Eu^{3+}	3.28 ± 0.10	-18.72 ± 0.57	-29.57 ± 0.82	-36
Gd^{3+}	3.29 ± 0.08	-18.78 ± 0.45	-23.47 ± 0.42	-16
Tb^{3+}	3.08 ± 0.05	-17.58 ± 0.29	-18.08 ± 0.67	-2
Yb^{3+}	3.15 ± 0.11	-17.98 ± 0.63	-15.49 ± 0.69	-8.4

[a] Competitive microcalorimetry; [b] Direct microcalorimetry; [c] Ref. [22].

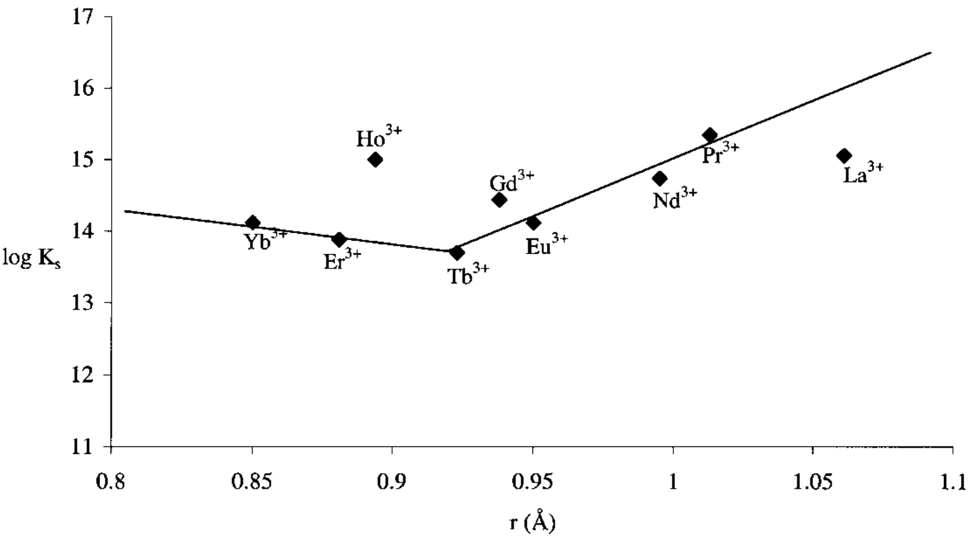

FIGURE 4 Stability constant (log K_s) of cryptand 222–lanthanide complexes against cation radii in acetonitrile at 298.15 K.

Gd^{3+} and Tb^{3+} are -123.5 ± 0.6 and -144.1 ± 0.9, whereas those from direct titrations are -120.5 ± 0.7 and -148.6 ± 0.5 respectively. Good agreement is found between the two sets of data. Also included in Table I are the data previously reported for La^{3+}, Pr^{3+} and Nd^{3+} with cryptand 222 complexes in acetonitrile at 298.15 K derived from potentiometry (log K_s) and classical calorimetry ($\Delta_c H^\circ$) [22]. The large discrepancies observed are therefore attributed to (i) the high concentration of the metal-ion salts used for these measurements in acetonitrile and (ii) the relatively slow kinetics of the process which introduces uncertainty in the determination of log K_s by potentiometry. The same limitations apply to the determination of the enthalpy associated with these processes by classical calorimetry. An interesting aspect of these data is that, in the complexation of cryptand 222 and these cations in acetonitrile, the stability constants (which are essentially the parameters which determine the affinity of the ligand for one cation relative to another) can be differentiated. This is illustrated in Fig. 4 where log K_s values are plotted against the cation size [34]. In fact the affinity of cryptand 222 for one trivalent cation relative to another can be quantitatively assessed through the calculation of the selectivity factor S, ($S = K(\mathrm{La}^{3+})/K_{s(\mathrm{M}^{3+})}$). Thus the selectivity of the ligand for La^{3+} is greater by factors of 4, 28, 71, 34, 186, 93, 123 and 71 relative to Pr^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+} and Yb^{3+} respectively.

The pattern observed in Fig. 4 shows that, as one goes across the series from La^{3+} to Eu^{3+}, the stability decreases with decreasing ionic radius. A discontinuity is observed at Tb^{3+} at which point a slight increase in stability is observed. Burgess [35] has extensively investigated the varied and complicated patterns of solvation number for lanthanide cations in solution. He suggested that the molar volumes, activity coefficient, transfer number, conductance and thermochemical studies have all provided evidence which can be interpreted in terms of a change in coordination number around the middle of the series of lanthanide(III) cations. A break somewhere in the middle of the lanthanide series (often referred to as 'gadolinium' break when

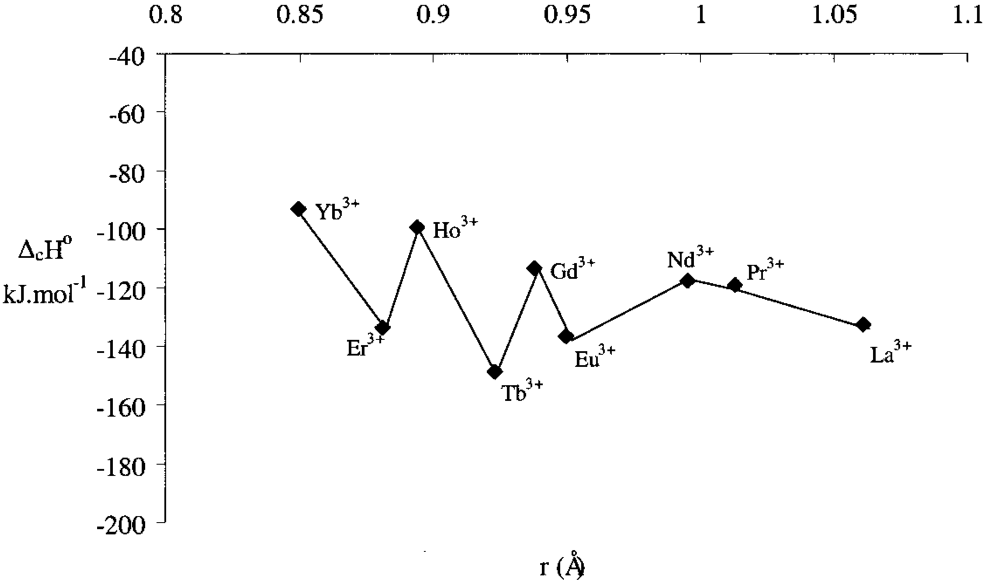

FIGURE 5 Standard enthalpy of complexation, Δ_cH°, for cryptand 222–lanthanide complexes against ionic radii in acetonitrile at 298.15 K.

plotting thermodynamic data as a function of radius) indicating a change in the coordination number has also been reported by Choppin and Bertha [36] as well as by Spedding and Atkinson [37]. Lastly, Habenschuss and Spedding [38] have clearly demonstrated using X-ray crystallography that a change in coordination number occurs in the rate-earth series in aqueous chloride solution. It was concluded that, bearing in mind that the radius of these cations decreases across the series, the larger lanthanide ions (La^{3+}–Nd^{3+}) could accommodate one more water molecule than the smaller ones (Tb^{3+}–Lu^{3+}) with the transition occurring between Nd^{3+} and Tb^{3+}. Although there is no evidence to substantiate the idea that the findings in water could be extrapolated to acetonitrile, it is worth noting these observations.

The most striking feature of these results is shown in the enthalpy data where the most favorable complexation enthalpy is observed for the complex of lowest stability (Fig. 5). As shown in Fig. 6 it is the entropy term (unfavorable) which plays a predominant role in determining the pattern found in the stability constants of these systems in acetonitrile.

In an attempt to assess the medium effect on the complexation process, a few representative data in DMF have been obtained and these are now discussed.

The Medium Effect

For cryptands, competition between ligand and solvent for the cation plays a crucial role on the stability of complex formation. On this basis, DMF, known as a protophilic aprotic solvent, was selected to assess the medium effect on the binding process. Thus $\log K_s$ (hence Δ_cG°), Δ_cH° and Δ_cS° for a few trivalent cations and cryptand 222 in DMF are listed in Table I. These data were derived from titration microcalorimetry. The substantial drop in stability observed in DMF relative to acetonitrile led us to

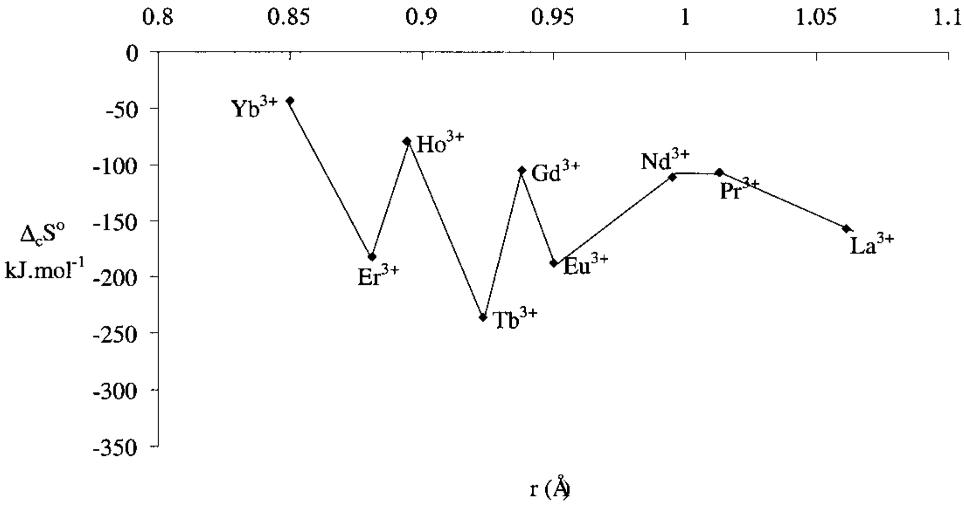

FIGURE 6 Standard entropy of complexation, $\Delta_c S^\circ$, for cryptand 222–lanthanide complexes against ionic radii in acetonitrile at 298.15 K.

analyse the factors that contribute to it in terms of the transfer enthalpy of the reactants and the product [39]. A representative example is given for Eu^{3+}. The $\Delta_t H^\circ$ value for the single cation is based on the Ph_4AsPh_4B convention [40]. Data for Eu^{3+}–222 have been calculated *via* the cycle, while $\Delta_t H^\circ$ for cryptand 222 from acetonitrile to DMF is that from the literature [39].

$$\begin{tikzcd}
\mathrm{Eu}^{3+}\ (\mathrm{MeCN}) \arrow[d, "\Delta_t H^\circ" above, "-253.8\,\mathrm{kJ\,mol^{-1}}" below] & + & 222\ (\mathrm{MeCN}) \arrow[d, "\Delta_t H^\circ" above, "1.6\,\mathrm{kJ\,mol^{-1}}" below] \arrow[r, "\Delta_c H^\circ", "-136.8\,\mathrm{kJ\,mol^{-1}}"'] & \mathrm{Eu}^{3+}-222\ (\mathrm{MeCN}) \arrow[d, "\Delta_t H^\circ" above, "-144.6\,\mathrm{kJ\,mol^{-1}}" below] \\
\mathrm{Eu}^{3+}\ (\mathrm{DMF}) & + & 222\ (\mathrm{DMF}) \arrow[r, "\Delta_c H^\circ", "-29.7\,\mathrm{kJ\,mol^{-1}}"'] & \mathrm{Eu}^{3+}-222\ (\mathrm{DMF})
\end{tikzcd}$$

The results show that the higher $\Delta_c H^\circ$ value of Eu^{3+} and cryptand 222 in acetonitrile relative to DMF is entirely attributed to the contribution of the free cation. Although $\Delta_t H^\circ$ of the lanthanide complex favors complexation in the latter solvent, this is overcome by the higher enthalpic stability of the cation in DMF relative to acetonitrile. The same conclusions apply to the other cations considered (Sc^{3+}, Y^{3+}, Gd^{3+}, Tb^{3+} and Yb^{3+}).

CONCLUSIONS

From the above discussion the following conclusions can be drawn.

(i) Great experimental care is required in the thermodynamic characterization of neutral macrocycles and lanthanide cations regarding the dryness of the salt and purity of the solvent as well as the range of concentrations used to ensure that the tervalent cation in its ionic form is the predominant species in solution.

(ii) Cryptand 222 is able to discriminate among lanthanide cations in acetonitrile as assessed from the calculated selectivity factors.

(iii) The medium effect on the complexation process involving the lanthanide cations is remarkable $S = (K_s(\text{MeCN})/K_s(\text{DMF})) \cong 8.6 \times 10^{10}$ (average of S values for four cations) and it is mainly controlled by the extent of cation–solvent interactions.

(iv) A lot remains to be revisited for thermodynamics of complex formation of neutral macrocycles and lanthanide cations as well as for the solution thermodynamics of the free and the complex lanthanide salts.

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