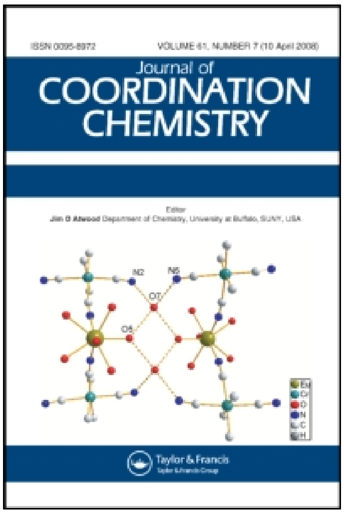

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

FORMATION AND DISSOCIATION KINETICS OF THE STRONTIUM(II) COMPLEX OF CRYPT AND C222 IN BINARY DIMETHYLSULFOXIDE-ACETONITRILE MIXTURES

Gholamhassan Azimi[a]; Mojtaba Shamsipur[a]
[a] Department of Chemistry, Razi University, Kermanshah, Iran

To cite this Article Azimi, Gholamhassan and Shamsipur, Mojtaba(1999) 'FORMATION AND DISSOCIATION KINETICS OF THE STRONTIUM(II) COMPLEX OF CRYPT AND C222 IN BINARY DIMETHYLSULFOXIDE-ACETONITRILE MIXTURES', Journal of Coordination Chemistry, 47: 4, 581 — 595

To link to this Article: DOI: 10.1080/00958979908024357

URL: http://dx.doi.org/10.1080/00958979908024357

J. Coord. Chem., 1999, Vol. 47, pp. 581–595
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

FORMATION AND DISSOCIATION KINETICS OF THE STRONTIUM(II) COMPLEX OF CRYPTAND C222 IN BINARY DIMETHYLSULFOXIDE–ACETONITRILE MIXTURES

GHOLAMHASSAN AZIMI and MOJTABA SHAMSIPUR*

Department of Chemistry, Razi University, Kermanshah, Iran

(Received 6 May 1998; In final form 1 July 1998)

The dissociation and the formation rates of the Sr^{2+}–C222 cryptate in different dimethylsulfoxide–acetonitrile mixtures have been studied spectrophotometrically using murexide as a metallochromic indicator. In all solvent mixtures used, the ratio of the rate constants for dissociation and formation of the cryptate was found to be in agreement with the formation constants obtained by an independent equilibrium spectrophotometric technique. The activation parameters E_a, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the formation and dissociation of the cryptate were determined from the temperature dependence of the corresponding rate constants, and found to be strongly solvent dependent. There is a linear relationship between the logarithm of the formation constant as well as the activation parameters and the mol fraction of acetonitrile in the mixed solvent.

Keywords: Kinetics and mechanism; Sr^{2+}–C222 complex; activation parameters; solvent effect

INTRODUCTION

Since the first synthesis of macrobicyclic cryptands by Lehn and co-workers,[1] extensive thermodynamic and kinetic data have been collected concerning interaction between these ligands and cations, especially alkali and alkaline earth metal ions.[2–4] This is partly due to the fact that the resulting

---

* Corresponding author.

complexes are considered as model systems for metal ion transportation in biological systems.[5] The stabilities of the selective metal cryptates are several orders of magnitude higher than those of natural or synthetic macrocyclic ligands;[2-4] the phenomenon is called the "cryptate effect".[6]

Understanding the interactions between cryptands and metal ions requires the study of structural and mechanistic aspects governing the complexation reactions; an important factor being the kinetic origin of the observed stabilities and selectivities. Although the thermodynamic considerations have dominated the subject of metal ion complexing of cryptands, increasing attention is being given to the kinetic aspects of cryptate formation in different solvent media.[3,4]

In the past decade, we have been involved in the study of the thermodynamics[7-11] and kinetics[12-14] of alkali and alkaline earth complexes with cryptands in nonaqueous and mixed solvents. In this paper we report the formation and dissociation kinetics of the Sr^{2+} ion complex with cryptand C222 in different dimethylsulfoxide–acetonitrile mixtures using murexide as a metallochromic indicator.[9,14,15] Strontium ion, with an ionic radius of 1.18 Å,[16] can be suitably located in the centre cryptand C222 (cavity radius = 1.4 Å),[17] and completely enclosed by the ligand in its *endo–endo* configuration.[18] In comparison with the extensive thermodynamic studies of the Sr^{2+}–C222 cryptate in different solvent,[6,7,9,10,19-27] corresponding kinetic reports are quite sparse.[21,23,24,26,28,29] The activation parameters for this cryptate have only been reported in aqueous solution.[26,28] To the best of our knowledge, this work is the first report on the formation and dissociation kinetics of the metal cryptates in binary aprotic solvent mixtures.

EXPERIMENTAL

Cryptand C222, murexide, strontium nitrate and potassium nitrate (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 for 72 h. Tetraethylammomium perchlorate (TEAP) was prepared from reagent grade aqueous tetraethylammonium hydroxide and perchloric acid (both from Merck). The resulting salt was recrystallized several times from distilled deionized water and used after vacuum drying. Dimethylsulfoxide (DMSO, Merck) and acetonitrile (AN, Merck) were purified and dried by previously reported methods.[38] Different DMSO–AN solvent mixtures were prepared by weight. Cryptand and murexide solutions were stored in the dark and used no more than five days after preparation.

All spectra were recorded on a GBC 911 spectrophotometer and the absorbance measurements as a function of time, at fixed wavelengths, were made with a Metrohm 662 probe-type photometer interfaced to a 486 DX4 computer using a 12 Bit A/D card (Bit Pardaz 1201) at various temperatures. At all temperatures, the cell was thermostatted with a Haake D1 thermostat to ±0.1°C.

In a typical run for the study of the formation kinetics, a DMSO–AN mixture ($5\,cm^3$) containing murexide (3.0×10^{-5} M), Sr^{2+} (4.0×10^{-5} M) and TEAP (0.02 M) was placed in a jacketted glass cell and the photometer probe was immersed into the solution and fixed by using a suitable holder. The solution was thermostatted at the desired temperature for at least 20 min, while it was continuously stirred by a magnetic stirrer. Then a given amount of the cryptand (5.0×10^{-4} M) was injected instantaneously through a pre-calibrated microsyringe with the photometer on and the absorbance–time data were collected by the microprocessor. Reaction of Sr^{2+} ion with murexide was monitored at the λ_{max} of the resulting complex (505 nm). The rate was not susceptible to wavelength or indicator concentration range from 8.0×10^{-6} to 50×10^{-5} M. The resulting murexide solutions in different DMSO–AN mixtures are quite stable, so that at all temperatures studied no measurable time-dependent absorption changes were detected in the absence of the metal ion.

For the study of the dissociation kinetics of the strontium cryptate, a DMSO–AN solution ($5\,cm^3$) containing murexide (3.0×10^{-5} M), C222 (1.0×10^{-4} M), Sr^{2+} ion (4.0×10^{-5} M) and TEAP (0.02 M) was placed in the cell and thermostatted at the desired temperature. Then an excess amount of potassium ion as scavenger was instantaneously injected through a microsyringe to the cell and the absorbance–time data collected at 505 nm. The reaction rate was found to be independent of K^+ ion concentration in solution in the range 9.0×10^{-4}–4.0×10^{-3} M.

The stability constant of Sr^{2+}–C222 cryptate in different DMSO–AN mixtures was determined by means of a competitive spectrophotometric technique using murexide as indicator.[4,9,10] This was done by absorbance measurements, at λ_{max} of the Sr^{2+} murexide complex, of solutions in which constant concentrations of both ligands (2.75×10^{-5} M murexide and 1.97×10^{-4} M C222) and TEAP (0.02 M for maintaining ionic strength) were titrated with a concentrated Sr^{2+} ion solution in the same solvent mixture (1.0×10^{-2} M) using a pre-calibrated microsyringe. Attainment of equilibrium was checked by observation of no further change in spectra after several hours. The corresponding data handling is given in detail elsewhere.[10]

RESULTS

Since complex formation or dissociation reactions do not involve any easily observable absorption change in the UV and visible regions, spectrophotometric monitoring of the reaction rates of the strontium cryptate in DMSO–AN mixtures requires a suitable indicator. Such an indicator must fulfill some specific requirements as described before.[14,28] Based on the previously reported work on the reaction with strontium ion[15,31,32] murexide, was used as an excellent metallochromic indicator for the spectrophotometric monitoring of the kinetics of the Sr^{2+}–C222 system in binary DMSO–AN mixtures.

In the process of the kinetic investigations, the C222 concentration used was in excess over Sr^{2+} ion so that the reaction (1) will reduce to a *pseudo*-first-order reaction in the forward direction and a first-order reaction on the reverse side, and there will be a more sensitive murexide spectroscopic change with time. In order to evaluate the

$$\mathrm{Sr}^{2+} + \mathrm{C222} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{Sr}^{2+}\text{–C222} \tag{1}$$

observed rate constants, k_{obs}, for reaction (1) in different DMSO–AN mixtures, at various temperatures, solutions of Sr^{2+} (4.0×10^{-5} M) in the presence of murexide (3.0×10^{-5} M) were reacted with an excess of cryptand C222 (~ 10 fold) and the change in λ_{max} of the Sr^{2+}-murexide complex was monitored as a function of time. Some of the resulting absorbance time plots are shown in Figure 1. Under these conditions, the observed rate law was of the form shown in equation (2)

$$-\frac{1}{[\mathrm{Sr}^{2+}] - [\mathrm{Sr}^{2+}]_e} \frac{d[\mathrm{Sr}^{2+}]}{dt} = k_{obs} = k_f[\mathrm{C222}] + k_d. \tag{2}$$

Here, the observed first-order rate constant, k_{obs}, describes the approach to equilibrium, and is the sum of the first-order rate constants for the forward and reverse reactions.[33] All k_{obs} values, evaluated from the computer fitting of the absorbance–time data to equation (2), are summarized in Table I. Since, for the Sr^{2+}–C222 cryptate, especially in DMSO–AN mixtures of higher acetonitrile content, $k_f[\mathrm{C222}] \gg k_d$ over the concentration ranges employed, the direct evaluation of k_f and k_d values from equation (2) (*via* plots of k_{obs} *vs* [C222]) seems unreliable.[24] Thus, precise values of the dissociation rate constants, k_d, should be evaluated directly

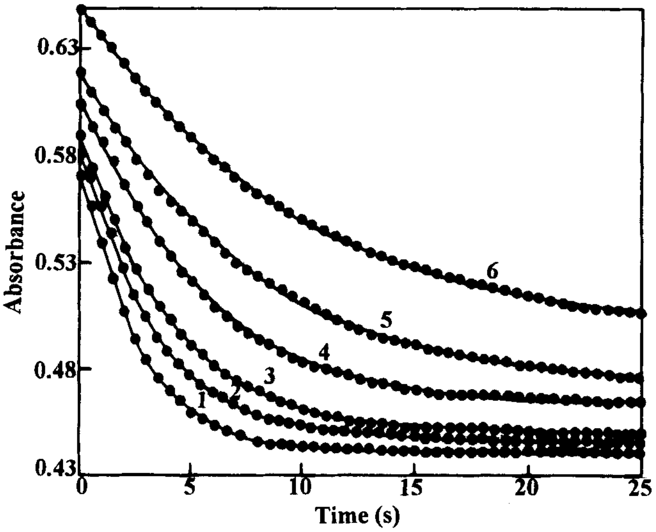

FIGURE 1 Absorption–time plots for the reaction of the Sr^{2+} ion (4.0×10^{-5} M) with cryptand C222 (2.0×10^{-4} M) in the presence of murexide (3.0×10^{-5} M) in a DMSO–AN mixture with $X_{AN} = 0.37$ at various temperatures (K): (1) 308, (2) 303, (3) 298, (4) 293, (5) 288, (6) 283.

from separate experiments, in order to calculate the corresponding k_f values from Equation (2).

The dissociation rates were measured by reacting the cryptate Sr^{2+}–C222 with K^+ ion as an appropriate scavenger for the free cryptand. In this case,

$$Sr^{2+}\text{–C222} \underset{k_f}{\overset{k_d}{\rightleftharpoons}} Sr^{2+} + \text{C222} \qquad (3)$$

$$K^+ + \text{C222} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} K^+\text{–C222} \qquad (4)$$

$$Sr^{2+} + \text{murexide} \overset{\text{fast}}{\rightleftharpoons} Sr^{2+}(\text{murexide}) \qquad (5)$$

the scavenger ion was chosen so that $k_1[K^+][\text{C222}] \gg k_f[Sr^{2+}][\text{C222}]$ and the stability of the K^+–C222 cryptate was greater than that of Sr^{2+}–C222; thus reaction (4) is irreversible (k_{-1} could be ignored). Under these conditions, (6) holds,

$$-\text{d}\ \ln[Sr^{2+}\text{–C222}]/\text{d}t = k'_{obs} = k_d. \qquad (6)$$

TABLE I Rate constants for the formation and dissociation of Sr^{2+}–C222 cryptate in different DMSO–AN mixtures at various temperatures

T (K)	*AN mol fraction*[a]														
	0.0			0.13			0.25			0.37			0.47		
	k_{obs} $\times 10^2 s^{-1}$	k_d $\times 10^3 s^{-1}$	k_f $M^{-1} s^{-1}$	k_{obs} $\times 10^2 s^{-1}$	k_d $\times 10^3 s^{-1}$	k_f $M^{-1} s^{-1}$	k_{obs} $\times 10^2 s^{-1}$	k_d $\times 10^3 s^{-1}$	k_f $M^{-1} s^{-1}$	k_{obs} $\times 10^2 s^{-1}$	k_d $\times 10^3 s^{-1}$	k_f $M^{-1} s^{-1}$	k_{obs} $\times 10^2 s^{-1}$	k_d $\times 10^3 s^{-1}$	k_f $M^{-1} s^{-1}$
283				6.0	4.1	279	7.4	2.6	356	10.4	2.1	511	14.8	1.3	735
288				8.0	5.0	377	9.9	3.9	474	12.7	3.2	619	16.9	2.4	834
293	8.4	8.5	378	10.6	7.2	493	12.9	6.3	613	16.5	4.5	803	22.1	3.8	1084
298	12.1	12.2	542	14.0	10.2	651	16.9	9.0	802	22.1	8.0	1084	28.2	5.9	1382
303	15.8	17.5	703	18.8	16.3	861	22.6	13.8	1060	22.4	11.7	1411	37.0	8.4	1806
308	22.1	25.4	978	24.8	23.8	1122	30.8	21.2	1434	40.5	16.6	1943	52.0	11.8	2540

[a] The corresponding solvent composition (wt% AN in DMSO) are: 0.00, 0.00%; 0.13, 7.0%; 0.25, 15.0%; 0.37, 23.5%; 0.47, 32.0%.

All k_d values, calculated from the computer fitting of the absorbance–time data to equation (6), are given in Table I. The corresponding k_f values were also evaluated from the k_d and k_{obs}, values by using equation (2). The resulting k_f values are also included in Table I.

In all solvent mixtures studied, the Arrhenius plots of ln k *vs* $1/T$ (for both the cryptate formation and dissociation) resulted in fairly straight lines (Figure 2), from the slopes of which the activation energies for the cryptate formation and dissociation processes were evaluated. Resulting E_a values are summarized in Table II. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by using the Eyring transition state theory.[34] The results of these calculations are also included in Table II.

Stability constants of Sr^{2+}-murexide and Sr^{2+}–C222 complexes in different DMSO–AN mixtures at 25°C were evaluated by computer fitting of the absorbance *vs* $[Sr^{2+}]/[C222]$ mol ratio data in the presence of a fixed amount

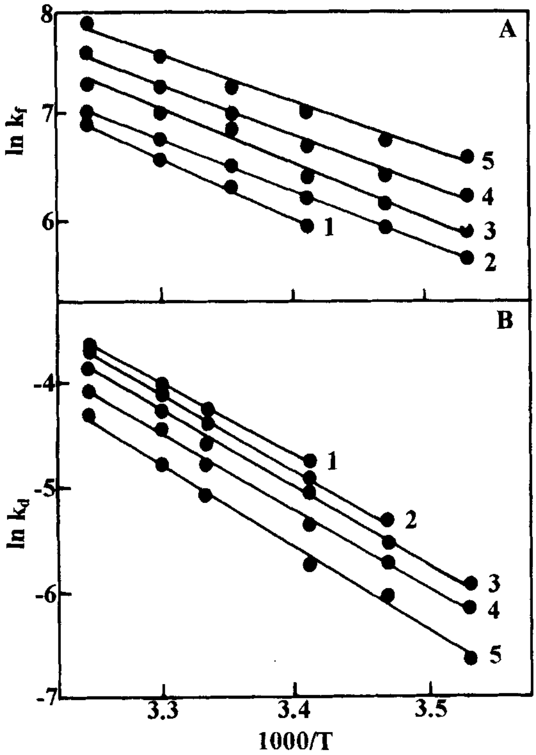

FIGURE 2 Arrhenius plots for the formation (A) and dissociation (B) of the Sr^{2+}–C222 cryptate in different DMSO–AN mixtures. The mol fraction of acetonitrile (X_{AN}) in the solvent mixture is: (1) 0.00, (2) 0.13, (3) 0.25, (4) 0.37, (5) 0.47.

TABLE II Activation parameters for the formation and dissociation of Sr^{2+}–C222 cryptate in different DMSO–AN mixtures

AN mol fraction	0.0	0.13	0.25	0.37	0.47
$E_a^f/kJ\,mol^{-1}$	47 ± 1	40.0 ± 0.2	38.6 ± 0.4	37 ± 1	33 ± 2
$\Delta H_f^\ddagger/kJ\,mol^{-1}$	44 ± 1	37.5 ± 0.3	36.2 ± 0.4	34 ± 1	30 ± 2
$\Delta S_f^\ddagger/J\,mol^{-1}\,K^{-1}$	−44 ± 4	−65 ± 1	−68 ± 1	−71 ± 4	−83 ± 6
$E_a^d/kJ\,mol^{-1}$	54.6 ± 0.6	58 ± 1	60.4 ± 0.7	61 ± 1	63 ± 2
$\Delta H_d^\ddagger/kJ\,mol^{-1}$	52.1 ± 0.6	55 ± 1	58.0 ± 0.7	59 ± 1	61 ± 2
$\Delta S_d^\ddagger/J\,mol^{-1}\,K^{-1}$	−106 ± 2	−96 ± 5	−89 ± 2	−88 ± 5	−84 ± 7
$\Delta H^0/kJ\,mol^{-1a}$	−7.6	−18	−21.8	−25	−31
$\Delta S^0/J\,mol^{-1}\,K^{-1b}$	62	31	21	17	1

[a] $\Delta H^0 = \Delta H_f^\ddagger - \Delta H_d^\ddagger$.
[b] $\Delta H^0 = \Delta S_f^\ddagger - \Delta S_d^\ddagger$.

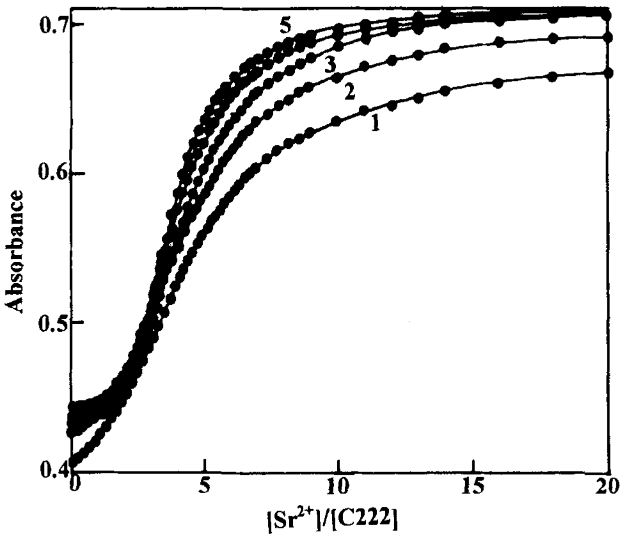

FIGURE 3 Absorbance *vs* $[Sr^{2+}]/[C222]$ mol ratio data in the presence of murexide as a metal ion indicator in different DMSO–AN mixtures at 298 K; $[C222] = 1.97 \times 10^{-4}$ M and $[murexide] = 2.75 \times 10^{-5}$ M. The mol fraction of acetonitrile in the solvent mixture is: (1) 0.00, (2) 0.13, (3) 0.23, (4) 0.37, (5) 0.47.

of murexide using the previously described competitive method.[9,10] Resulting absorbance–mol ratio plots in different solvent mixtures are shown in Figure 3, and a sample computer fit of these data is given in Figure 4. A fair agreement between the observed and calculated absorbances support the formation of 1 : 1 Sr^{2+} complexes with both murexide and C222 in solution, as shown by equations (1), (3) and (5). All the calculated stability constants

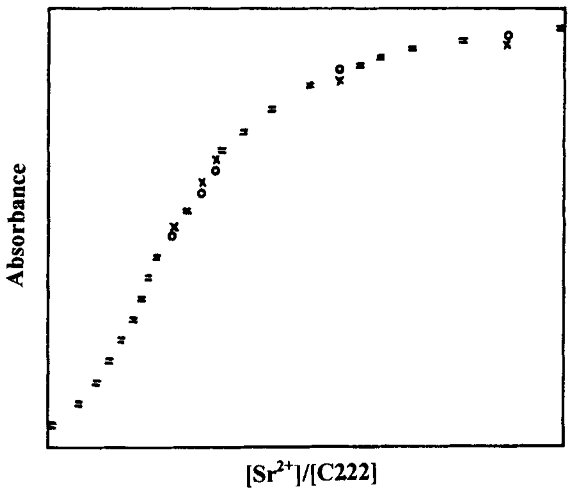

FIGURE 4 Computer fit of the plot of absorbance *vs* mol ratio data obtained in pure DMSO solution at 298 K; (×) experimental points; (○) calculated points; (=) experimental and calculated points are the same within the resolution of the plot.

TABLE III Stability constants for Sr^{2+} complexes with murexide and C222 in different DMSO–AN mixtures at 298 K

AN mol fraction	$\log K_s$	$\log(k_f/k_d)$	$\log K_s(Sr^{2+}\text{-murexide})$
0.00	4.69 ± 0.03	4.65 ± 0.04	3.83 ± 0.02
0.13	4.90 ± 0.02	4.81 ± 0.04	3.92 ± 001
0.25	5.10 ± 0.02	4.95 ± 0.06	4.02 ± 0.03
0.37	5.30 ± 0.03	5.13 ± 0.06	4.17 ± 0.02
0.47	5.46 ± 0.05	5.37 ± 0.07	4.31 ± 0.02

are listed in Table III. The stability constants of the Sr^{2+}–C222 cryptate calculated from the formation and dissociation rate constants (*i.e.*, $K_s = k_f/k_d$) are also included for comparison.

DISCUSSION

It is well known that, similar to the complexation of many other ligands with metal ions, cryptate formation and dissociation are straightforward second-order and first-order processes, respectively.[2–4] However, despite the increased stability of alkaline earth metal cryptates such as Sr^{2+}–C222, the rate of formation of these complexes in solution is always several orders of magnitude lower than that for the complexation of the cations with simple ligands,[32] crown ethers and naturally occurring ionophores,[3,4,35] which are in many cases close to the diffusion controlled limits. This means that the dissociation rates of the relatively stable metal cryptates can be followed by conventional techniques, as in this work.

Such pronounced decrease in k_f of the metal cryptates supposedly is due to a very low concentration of the reactive *endo–endo* form (in which lone pairs of the bridgehead nitrogens are directed inside the cavity) of the cryptand in solution.[28,36] However, this possibility has recently been rejected by ultrasonic absorption studies of the kinetics of conformational changes of different cryptands in nonaqueous aprotic solvents,[37,38] where only one relaxation process was observed for the cryptands. It has been pointed out that the process in aprotic solvents is attributed to the conformational equilibrium *endo–exo* $\rightleftharpoons$ *endo–endo*. Moreover, the conformational analysis of cryptands of various sizes has been carried out by different spectroscopic techniques.[1,18,39–42] As a result, it has been found that *endo–endo* would be the dominant conformation of the cryptand in nonaqueous solutions.

Alternatively, since cryptate formation could be rather strongly sterically controlled,[43] the first bond formation of the action with C222 as a rigid ligand is not very effective. Incomplete compensation for the loss of solvation of the metal ion in the course of the cryptate formation may also contribute to decreased cryptate formation rates.[24,43] This is because the rigid cryptand will have serious difficulties in adopting optimal conformations at various stages of cryptate formation.

Moreover, in a comparison of k_f values for alkali metal complexes with monocyclic and bicyclic ligands, Grell and Oberbaumer[44] have suggested that, in the multistep process of cryptate formation, there is a rate determining step in which two or more remaining solvent molecules of a partially complexed cation must be removed prior to the entry of the action into the cryptand cavity. However, it seems difficult to distinguish experimentally between this possibility and that of a simple stepwise process with incomplete compensation for loss of solvation, as discussed earlier. Thus, desolvation of the metal ion is very important before or at the rate determining stage of the cryptate formation.

The data given in Table I reveal that the rate of formation of the Sr^{2+}–C222 cryptate increases with increasing amount of acetonitrile in the solvent mixture, which is in agreement with the above conclusion. As expected, addition of acetonitrile as a solvent of intermediate solvating ability (DN = 14.1)[45] to a strongly solvating media such as DMSO (DN = 29.8)[45] will increase the k_f values at all temperature studied.

According to X-ray crystallographic analysis of Sr^{2+}–C222 cryptate,[18] the Sr^{2+} ion is in the midst of the cavity of C222, formed by an *endo–endo* conformation of the cryptand. In the process of Sr^{2+}–C222 cryptate dissociation, the cryptand cage has to be opened to release the metal ion trapped inside the molecular cavity. Molecular modelling reveals that the oxygen atoms in the bridges can rotate outward from the cavity,[46] so that the initial interaction of the cation in the cavity with the solvent molecules can be provided. It has been shown that dissociation of metal cryptates could happen *via* an acid-assisted path and/or by direct solvent attack.[47] Thus, in comparison with cryptate formation, a reverse solvent effect is expected in the process of the Sr^{2+}–C222 cryptate dissociation; as seen from Table I, an increase in the acetonitrile content of the solvent mixture results in diminished dissociation rates, at all temperatures studied.

Since the transition state for Sr^{2+}–C222 cryptate formation and dissociation should be the same, it follows that the reaction might occur solely through the dominant *endo–endo* conformation.[38] Meanwhile, it has been reasonably suggested that the transition state for the complexation of metal ions by cryptands more resembles the reactants rather than the resulting cryptate, in which some solvent molecules bound to the cation have been lost.[12,13] The activation parameters listed in Table II are in support of this idea. The positive enthalpy of activation (more positive in the dissociation step) reflects a weaker transition state (weaker than either the initial solvated cation or the final rigid cryptate), a poorer overlap and a sloppy geometry. On the other hand, the entropies of activation for both cryptate formation and dissociation are much more negative than the thermodynamic ΔS^0 value. In the process of cryptate formation, some solvent molecules may be lost on going from the initial reactants to the transition state, which could be balanced by a considerable decrease in cryptand internal entropy resulting in $\Delta S_f^\ddagger$ being very negative. The remaining solvent molecules are then stripped off during the rapid encapsulation of the Sr^{2+} ion inside the C222 cavity. In the dissociation process, some solvent molecules are again coordinated to the cation in the transition state, resulting in a large negative $\Delta S_d^\ddagger$. It should be noted, however, that there is no direct evidence for the possible contribution of the cryptand conformational change to the negative entropies of activation.

The data given in Table II reveal that the activation parameters E_a, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for both the formation and dissociation processes strongly depend on the nature of the solvent. It is seen that, in the case of the Sr^{2+}–C222 dissociation, the activation energy for the release of Sr^{2+} from its C222 cryptate increases with the mol fraction of acetonitrile in the mixed solvent.

As mentioned earlier, since DMSO has greater solvating ability than acetonitrile, an increase in the amount of acetonitrile results in its decreased solvating power. Thus, this observation emphasizes that the charge density in the transition state is greater than that in the resulting strontium cryptate, as was also deduced from the observed trend in the $\Delta H_d^{\ddagger}$ and $\Delta S_d^{\ddagger}$ values. Obviously, the data given in Table II show an opposite solvent effect on the activation energy for the cryptate formation; E_a^f decreases with increasing amounts of acetonitrile in the solvent mixture.

It is interesting to note that the influences of solvent properties on $\Delta S_f^{\ddagger}$ and $\Delta S_d^{\ddagger}$ of the Sr^{2+}–C222 cryptate are also opposite to each other. A decrease in the solvating power of the mixed solvent will result in a more negative $\Delta S_f^{\ddagger}$, but more positive $\Delta S_d^{\ddagger}$ values. This is mainly due to the higher charge density of the initial Sr^{2+} ion, but lower charge density of the final Sr^{2+}–C222 cryptate, when they are compared with the transition state of the complexation reaction. Of course, the influence of a change in rigidity of the cryptand, brought about by the partial release of the cation from its C222 cryptate in the transition state, on the overall entropy change of the system cannot be neglected.

Stability constants of the Sr^{2+}–C222 cryptate in different solvent mixtures at 298 K, obtained from the competitive spectrophotometric method described in the Experimental Section, K_s, are compared with the corresponding values calculated from the rate constants (i.e. $K_s = k_f/k_d$) in Table III. As seen, the two series of K_s values are in satisfactory agreement. In addition, the data given in Table III clearly illustrate the important role of the solvent properties in the thermodynamics of the complexation reaction. The stability of the Sr^{2+}–C222 cryptate increases rapidly with increasing weight percent of acetonitrile in the mixed solvent. It has been shown that the solvating ability of the solvent, as expressed by the Gutmann donor number,[45] plays a fundamental role in the complexation reactions.[7,15,48–50] DMSO is a solvent of high solvating ability (DN = 29.8)[45] which can compete strongly with the ligand for the cation. Thus, it is reasonable to expect that the addition of acetonitrile as an intermediate donicity solvent (DN = 14.1)[45] to DMSO will increase the extent of interaction between the Sr^{2+} ion and C222. Meanwhile, DMSO is well known as a highly structured solvent, the structure of which can be destroyed by adding more weakly structured solvents such as acetonitrile.[51–53] Such a pronounced change in the solvent structure of the binary DMSO–AN mixtures is expected to result in a significant increase in the formation constant of the Sr^{2+}–C222 cryptate.[51–53]

It is further interesting to note that there is a linear relationship between log K_s and mol fraction of acetonitrile (X_{AN}) in the solvent mixture

(Figure 5). The same kind of relationship is also reported between data obtained from the study of complexation in a number of metal–ligand systems in methanol–water,[54] ethanol–water,[55] acetonitrile–water,[56,57] and dimethylsulfoxide–acetonitrile[11] mixed solvents. It has been reasonably assumed that the preferential solvation of the cation by one of the solvent components is mainly responsible for the monotonic dependence of the stability constants and the solvent composition.

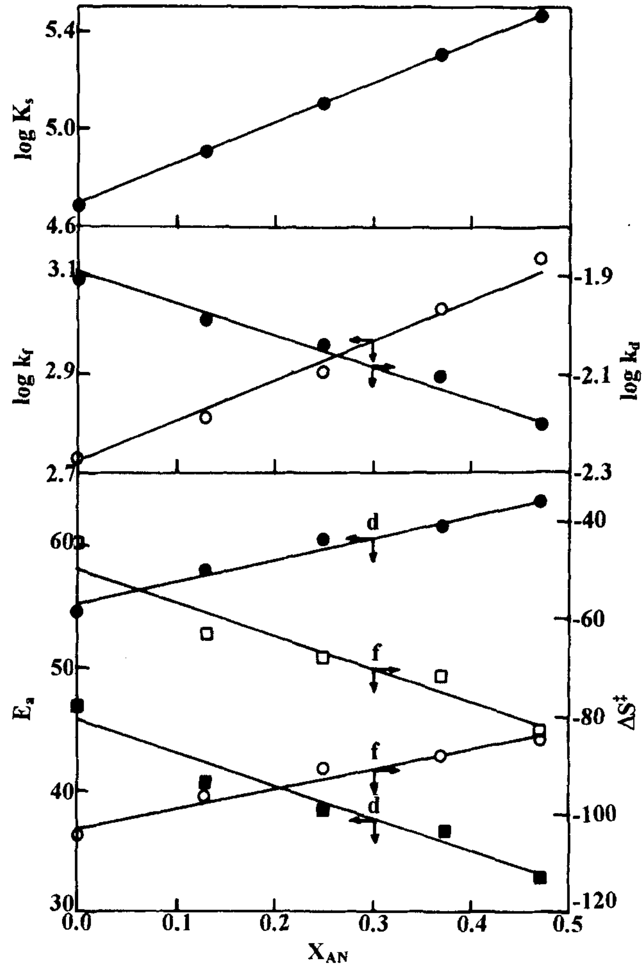

FIGURE 5 Plots of logK_s, logk_f, logk_d, E_a and $\Delta S^\ddagger$ vs acetonitrile mol fraction for Sr^{2+}–C222 cryptate in different DMSO–AN mixtures; f = formation and d = dissociation.

It should be noted that not only the cryptate stability constant, but also the rate constants and the activation parameters for both the formation and dissociation processes (Tables I and II), reveal a nice linear correlation with the solvent composition (see Figure 5). The same kind of correlation has been previously reported for some metal cryptates[12,13,58] and crown ether complexes.[57,59] Since the Gutmann donicity scale[45] is known to be a good measure of primary solvation energy, we would expect the net energy required for either the release of Sr^{2+} ion from the C222 cryptate into the solvent medium or its transfer from the solution inside the cryptand cavity to correlate well with the solvent donicity, or with the solvent composition of binary mixed solvents of different donicities.

References

[1] B. Dietrich, J.M. Lehn and J.P. Sauvage, *Tetrahedron Lett.*, 2885 and 2889 (1969).
[2] J.M. Lehn, *Struct. Bonding* (*Berlin*) **16**, 1 (1973).
[3] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.* **85**, 271 (1985).
[4] R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening, *Chem. Rev.* **91**, 1721 (1991).
[5] Yu.A. Ovchinnikov, V.T. Ivanov and A.M. Shkrob, *Membrane-Active Complexones* (Elsevier, New York, 1974).
[6] J.M. Lehn and J.P. Sauvage, *J. Am. Chem. Soc.* **97**, 6700 (1975).
[7] S. Kashanian, A. Nikrahi and M. Shamsipur, *Iranian J. Sci. Technol.* **12**, 105 (1988).
[8] H. Parham and M. Shamsipur, *J. Electroanal. Chem.* **314**, 71 (1991).
[9] H. Parham and M. Shamsipur, *Polyhedron* **11**, 987 (1992).
[10] J. Ghasemi and M. Shamsipur, *J. Coord. Chem.* **31**, 265 (1994).
[11] M. Shamsipur and J. Ghasemi, *J. Incl. Phenom.* **20**, 157 (1995).
[12] M. Shamsipur and A.I. Popov, *J. Phys. Chem.* **90**, 5997 (1986).
[13] M. Shamsipur and A.I. Popov, *J. Phys. Chem.* **91**, 447 (1987).
[14] J. Ghasemi and M. Shamsipur, *Polyhedron* **15**, 923 (1996).
[15] S. Kashanian, M.B. Gholivand, S. Madaeni, A. Nikrahi and M. Shamsipur, *Polyhedron* **7**, 1227 (1988).
[16] R.D. Shannon, *Acta Crystallogr.* **A32**, 751 (1976).
[17] B. Dietrich, *J. Chem. Educ.* **62**, 954 (1985).
[18] B. Metz, D. Moras and R. Weiss, *Acta Crystallogr.* **B29**, 388 (1973).
[19] G. Anderegg, *Helv. Chim. Acta* **58**, 1218 (1975).
[20] E. Kauffmann, J.M. Lehn and J.P. Sauvage, *Helv. Chim. Acta* **59**, 1099 (1976).
[21] B.G. Cox, P. Firman and H. Schneider, *Inorg. Chim. Acta* **64**, L263 (1982).
[22] R. Pizer and R. Selzer, *Inorg. Chem.* **22**, 1359 (1983).
[23] B.G. Cox, Ng. Van Troung, J. Garcia-Rosas and H. Schneider, *J. Phys. Chem.* **88**, 996 (1984).
[24] B.G. Cox, Ng. Van Troung and H. Schneider, *J. Am. Chem. Soc.* **106**, 1273 (1984).
[25] H. Buschmann, *J. Solution Chem.* **15**, 453 (1986).
[26] H. Kitano, J. Hasegawa, S. Iwai and T. Okubo, *J. Phys. Chem.* **90**, 6281 (1986).
[27] D. Blanco-Gomis, E. Fuente-Alonso and P. Arias-Abrodo, *Polyhedron* **8**, 2797 (1989).
[28] V.M. Loyola, R. Pizer and R.G. Wilkins, *J. Am. Chem. Soc.* **99**, 7185 (1977).
[29] B.G. Cox and H. Schneider, *J. Am. Chem. Soc.* **99**, 2809 (1977).
[30] M.S. Greenberg and A.I. Popov, *Spectrochim. Acta* **31A**, 697 (1975).
[31] G. Geier, *Helv. Chim. Acta* **51**, 94 (1968).
[32] H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass and R. Winkler, *Pure Appl. Chem.* **20**, 93 (1969).

[33] C. Capellos and B.H. Bielski, *Kinetic Systems*, (Interscience, New York, 1972), p. 30.
[34] S.H. Lin, K.P. Li and H. Eyring, in *Physical Chemistry, an Advanced Treatise*, Vol. VII, H. Eyring, D. Handerson and W. Yost (Eds.) (Academic Press, New York, 1977).
[35] R. Winkler, *Struct. Bonding (Berlin)* **10**, 1 (1972).
[36] V.M. Loyola, R.G. Wilkins and R. Pizer, *J. Am. Chem. Soc.* **97**, 7382 (1975).
[37] F. Eggers, T. Funck, K.H. Richmann, H. Schneider, E.M. Eyring and S. Petrucci, *J. Phys. Chem.* **91**, 1961 (1987).
[38] T. Tanaka, T. Hida, S. Funahashi and M. Tanaka, *J. Am. Chem. Soc.* **113**, 1259 (1991).
[39] B. Metz, O. Moras and R. Weiss, *J. Chem. Soc., Perkin Trans.* **2**, 423 (1976).
[40] P.B. Smith, J.L. Dye, J. Cheney and J.M. Lehn, *J. Am. Chem. Soc.* **103**, 6044 (1981).
[41] E. Schmidt, J.M. Tremillon, J.P. Kintzinger and A.I. Popov, *J. Am. Chem. Soc.* **105**, 7563 (1983).
[42] H.J. Brugge, D. Carboo, K. van Deuten, A. Knochel, W. Kopf and W. Dreissig, *J. Am. Chem. Soc.* **108**, 107 (1986).
[43] K. Kustin, R.F. Pasternack and M. Weinstock, *J. Am. Chem. Soc.* **88**, 4610 (1966).
[44] E. Grell and I. Oberbaumer, in *Chemical Relaxation in Molecular Biology*, I. Pecht and R. Rigler (Eds.) (Springer-Verlag, Berlin, 1977).
[45] V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions*, (Plenum, New York, 1978).
[46] B.G. Cox, H. Schneider and J. Stroka, *J. Am. Chem. Soc.* **100**, 4746 (1978).
[47] K. Ishihara, H. Miura, S. Funahashi and M. Tanaka, *Inorg. Chem.* **27**, 1706 (1988).
[48] M. Shamsipur and A.I. Popov, *J. Am. Chem. Soc.* **101**, 4051 (1979).
[49] M.K. Amini and M. Shamsipur, *Inorg. Chim. Acta* **183**, 65 (1991).
[50] T. Madrakian, A. Afkhami, J. Ghasemi and M. Shamsipur, *Polyhedron* **15**, 3647 (1996).
[51] S.-I. Ishiguro, H. Suzuki, B.G. Jeliazkova and H. Ohtaki, *Bull. Chem. Soc. Jpn.* **62**, 39 (1989).
[52] H. Suzuki, S.-I. Ishiguro and H. Ohtaki, *J. Chem. Soc., Faraday Trans. 1* **85**, 2587 (1989).
[53] H. Suzuki, S.-I. Ishiguro and H. Ohtaki, *J. Chem. Soc., Faraday Trans. 1* **86**, 2179 (1990).
[54] R.M. Izatt, R.E. Terry, D.P. Nelson, Y. Chan, D.J. Eatough, J.S. Bradshaw, L.D. Hansen and J.J. Christensen, *J. Am. Chem. Soc.* **98**, 7626 (1976).
[55] M. Saeidi and M. Shamsipur, *J. Coord. Chem.* **22**, 131 (1990).
[56] M.B. Gholivand and M. Shamsipur, *Inorg. Chim. Acta* **121**, 53 (1986).
[57] A. Rouhollahi, M.K. Amini and M. Shamsipur, *J. Solution Chem.* **23**, 63 (1994).
[58] B.C. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.* **103**, 1054 (1981).
[59] B.O. Strasser and A.I. Popov, *J. Am. Chem. Soc.* **107**, 7921 (1985).