KINETIC STUDY OF THE DISSOCIATION OF Ba^{2+} -C222 CRYPTATE IN BINARY DIMETHYLSULFOXIDE-ACETONITRILE MIXTURES

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Abstract

The dissociation rates of the Ba^{2+} -C222 cryptate in different dimethylsulfoxide-acetonitrile mixtures have been studied spectrophotometrically using murexide as a suitable metallochromic indicator. The activation parameters E_a , $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the dissociation of the cryptate were determined from the temperature dependence of the dissociation rate constants (k_d). The correlation of the dissociation rate constant with the stability constant (K_s) of the barium cryptate was investigated. There is a linear relationship between $\log K_s$ and the activation parameters E_a , $\Delta H^\ddagger$ and $\Delta S^\ddagger$ and the mole fraction of acetonitrile in the mixed solvent.

Introduction

Macrobicyclic polyethers (cryptands), first synthesized by Lehn and co-workers,¹ in their endo-endo conformation contain an internal cavity of about spherical shape well suited for the recognition of alkali and alkaline earth ions.²⁻³ The stability and lability of metal cryptates are well known to be dependent on the structure of the cryptand, the type and number of its donor atoms, the nature of metal ion and the properties of solvents used.²⁻⁶ Among these factors, the ability of solvent molecules to solvate cations and thus to compete with the donating groups of the cryptands for the coordination sites of the central cation plays a fundamental role, both thermodynamically and kinetically. Thus, the thermodynamics of alkali and alkaline earth cryptates in various have been the subject of extensive research.^{4,6} However, information concerning complexation kinetics of these ligands with metal ions is comparatively low, despite the importance of such data for the elucidation of the mechanism of complexation reactions.^{4,5} Such kinetic studies not only result in important information on the rates and mechanism of complexation reactions, but also lead to a better understanding of the high stability and high selectivity of the cryptands toward different alkali and alkaline earth cations.

In the past decade, we have been involved in the study of the thermodynamics⁷⁻¹¹ and kinetics¹²⁻¹⁵ of complexation of alkali and alkaline earth cations with cryptands in some nonaqueous and mixed solvents. In this paper we report the dissociation kinetics of the Ba^{2+} ion complex with cryptand C222 in different dimethylsulfoxide (DMSO)-acetonitrile (AN) mixtures using murexide as a suitable metal ion indicator. Barium ion with an ionic size of 2.86 Å,¹⁶ can be suitably located in the spherical cavity of C222 (with a size of 2.8 Å)² and completely enclosed by the macrocyclic ligand in its endo-endo conformation.¹⁷ In comparison with the extensive thermodynamic studies of Ba^{2+} -C222 in different solvent systems,^{4,5,18-22} corresponding kinetic are quite sparse.^{22,23-27} The activation parameters for this cryptate have only been reported in aqueous media.^{23,26} To the best of our knowledge, this is the first report on the dissociation kinetics of Ba^{2+} -C222 cryptate in the binary aprotic solvent mixtures.

Experimental

Cryptand C222, murexide, barium 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. Tetraethylammonium 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 the previously reported methods.²⁸ Different DMSO-AN mixtures were prepared by weight. Cryptand and murexide solutions were stored in 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 personal computer using a 12 Bit A/D card (Bit Pardaz 1201) at various temperatures. At all temperatures, the cell was thermostated with a Haake D1 thermostat to ± 0.1 K.

In a typical run for the study of dissociation kinetics, a DMSO-AN solution (5 cm³) containing murexide (2.0 × 10⁻⁵ M), C222 (1.6 × 10⁻⁵ M), Ba²⁺ ion (8.0 × 10⁻⁵ M) and TEAP (0.02 M) was placed in the cell and thermostated to 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 above 1 × 10⁻⁴ M.

The stability constant of Ba²⁺-C222 cryptate in different DMSO-AN mixtures was determined by means of a competitive spectrophotometric technique using murexide as metal ion indicator.^{9,10} This was done by absorbance measurements, at λ_{max} of the Ba²⁺-murexide complex, of solutions in which constant concentration of both ligands (2.7 × 10⁻⁵ M murexide and 1.57 × 10⁻⁴ M C222 and 0.02 M TEAP for maintaining ionic strength) were titrated with a concentrated Ba²⁺ ion solution in the same solvent mixture (1 × 10⁻² M) using a calibrated microsyringe. Attainment of equilibrium was checked by observation of no further change in spectra after several minutes. The corresponding data handling is given in detail elsewhere.¹⁰

Results

The complex formation or dissociation reactions between Ba²⁺ ion and C222 do not involve any easily observable absorption in the ultraviolet and visible spectral regions. Thus, spectrophotometric monitoring of the reaction rates of the barium cryptate in the DMSO-AN mixtures requires a suitable indicator. Such an indicator must fulfill some specific requirements described before.^{12,15,23} Based on the previously reported work on its reaction with barium ion,²⁷⁻³¹ murexide was used as an excellent metallochromic indicator for the spectrophotometric monitoring of the dissociation kinetics and thermodynamics of the Ba²⁺-C222 system in various binary DMSO-AN mixtures.

The dissociation rates were measured by reacting the Ba²⁺-C222 cryptate with K⁺ ion as an appropriate scavenger for the free cryptand. In this case:

The scavenger ion was chosen so that $k_1[\text{K}^+][\text{C222}] \gg k_f[\text{Ba}^{2+}][\text{C222}]$ and the stability of K⁺-C222 cryptate was greater than that of Ba²⁺-C222. Thus, reaction (2) is irreversible (k_{-1} could be ignored). Some of the resulting absorbance time data plots are shown in Fig. 1. Under these conditions, equation (4) holds,

$$-\text{dln}[\text{Ba}^{2+}\text{-C222}]/\text{dt} = k_d \quad (4)$$

All k_d values, evaluated from the computer fitting of the absorbance-time data to equation (4), are given in Table I.

In all solvent mixtures studied, the Arrhenius plots of $\ln k_d$ vs $1/T$ resulted in fairly straight lines (Fig. 2) from the slopes of which the activation energies for the cryptate dissociation process were evaluated. The resulting E_a values are summarized in Table I. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated by using Eyring transition state theory.³² The results of these calculations are also included in Table I.

The stability constants of Ba²⁺-C222 and Ba²⁺-murexide complexes in different DMSO-AN mixtures at 298 K were evaluated by computer fitting of the absorbance vs $[\text{Ba}^{2+}]/[\text{C222}]$ mole ratio data in the presence of a fixed amount of murexide using a previously described competitive method.^{9,10}

Fig. 1. Absorption-time plots for the dissociation of Ba^{2+} -C222 cryptate in the presence of murexide and excess K^+ ion at 308 K in different DMSO-AN mixtures. X_{AN} : 1, 0.0; 2, 0.13; 3, 0.25; 4, 0.37; 5, 0.47.

Table I. Dissociation rate constants at various temperatures and activation parameters for Ba^{2+} -C222 cryptate in different DMSO-AN mixtures

T (K)	X_{AN}^a	0.0	0.13	0.25	0.3	0.47
293		1.02	0.80	0.68	0.54	0.43
298		1.66	1.34	1.04	0.88	0.68
303		3.05	2.31	1.90	1.49	1.18
308		5.22	3.99	3.21	2.51	1.96
313		9.80	7.45	5.83	4.51	3.39
$E_a(\text{kJ mol}^{-1})$		86.4	84.6	82.6	80.7	79.1
$\Delta H^\ddagger(\text{kJ mol}^{-1})$		83.9	82.1	80.1	78.1	76.5
$\Delta S^\ddagger(\text{J mol}^{-1}\text{K}^{-1})$		2.9	-5.1	-13.4	-21.9	-29.2

^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%.

The resulting absorbance-mole ratio plots in different solvent mixtures are shown in Fig. 3 and a sample computer fitting of the mole ratio data is given in Fig. 4. The fair agreement between the observed and calculated absorbances support the formation 1:1 Ba^{2+} complexes with both murexide and C222 in solution, as shown by equations (2) and (3). All the calculated stability constants are listed in Table II. The stability constants previously reported in the literature for the Ba^{2+} -C222 cryptate and Ba^{2+} -murexide in DMSO are also included in Table II for comparison.

Discussion

It is well established that, similar to the complexation of many other ligands with metal ions, the cryptate formation and dissociation are straightforward second order and first order processes, respectively.^{2,4,5,12,15} Meanwhile, despite the increased stability of alkaline earth metal cryptates such as Ba^{2+} -C222, the rate of formation of these complexes in solution is always several orders of magnitude lower than that for the complexation of different cations with simple ligands,³² crown ethers and naturally occurring ionophores,^{4,5,33} which are in many cases close to the diffusion controlled limits. Consequently, the

dissociation rates of the relatively stable metal cryptates can be followed by conventional techniques, as in this work.

Fig. 2. Arrhenius plots for the dissociation of Ba^{2+} -C222 cryptate in different DMSO-AN mixtures. X_{AN} : 1, 0.0; 2, 0.13; 3, 0.25; 4, 0.37; 5, 0.47.

Table II. Stability constants for Ba^{2+} complexes with murexide and C222 in different DMSO-AN mixtures at 298 K

	$\log K_s (\text{Ba}^{2+}\text{-murexide})$	$\log K_s (\text{Ba}^{2+}\text{-C222})$
0.00	3.71 ± 0.02 3.89^a	5.62 ± 0.05 5.44^b
0.13	3.77 ± 0.02	5.92 ± 0.04
0.25	3.87 ± 0.02	6.06 ± 0.03
0.37	3.99 ± 0.03	6.17 ± 0.09
0.47	4.13 ± 0.03	6.27 ± 0.06

^a Data taken from R. Pizer and R. Selzer, *Inorg. Chem.*, **22**, 1359 (1983).

^b Date taken from M. K. Chantooni and I. M. Kolthoff, *J. Solution Chem.*, **14**, 1 (1985).

Several possible reasons for such pronounced decrease in the rate of cryptate formation, in comparison with that of the two-dimensional macrocyclic ligand complexes, are proposed in the literature.^{17,23,27,34-40} Among these, two important factors are frequently pointed out. First, the cryptate formation is rather strongly sterically controlled so that the first bond formation of the cation with the cryptand as a rigid molecule is not very effective. Second, there is an incomplete compensation for the loss of solvation of the metal ion in the course of cryptate formation which may effectively contribute to the decreased cryptate formation rates.

The data given in Table I indicate that the addition of acetonitrile as a solvent of intermediate solvating ability ($\text{DN} = 14.1$)⁴¹ to DMSO as a strongly solvating medium ($\text{DN} = 29.8$)⁴¹ will decrease the rate of dissociation of the Ba^{2+} -C222 cryptate at all temperatures studied. X-ray crystallographic analysis of alkaline earth cryptates revealed that the Ba^{2+} ion is in the midst of the C222 cavity, formed by an endo-endo conformation of the cryptand.¹⁷ Thus, in the process of cryptate dissociation, the cryptand cage has to be opened to release the cation trapped inside the molecular cavity. Molecular modeling shows that the oxygen atoms in the C222 bridges can rotate outward from the cavity,⁴² so that the initial interaction of the cation in the cavity with the solvent molecules can be provided. It has been shown that the dissociation of metal cryptates could happen via such a direct solvent attack.⁴³ The solvent effect observed in Table I is in support of the occurrence of Ba^{2+} -C222 dissociation via the above mentioned pathway; thus, decreasing solvating ability of the medium resulted in diminished dissociation rate constant.

Fig. 3. Absorbance vs $[Ba^{2+}]/[C222]$ mole ratio plots in the presence of murexide in different DMSO-AN mixtures at 298 K: $[C222] = 1.60 \times 10^{-4}$ M and $[murexide] = 2.76 \times 10^{-5}$ M. X_{AN} : 1, 0.0; 2, 0.13; 3, 0.25; 4, 0.37; 5, 0.47.

Fig. 4. Computer fit of the plot of absorbance vs mole ratio data in a mixture with $X_{AN} = 0.47$ at 298 K: (x) experimental point; (o) calculated point; (≡) experimental and calculated points are the same within the resolution of the plot.

From Table I, it is immediately obvious that the activation parameters E_a , $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the release of Ba^{2+} ion from its C222 cryptate are strongly depend on the composition of solvent mixture. As can be seen, the activation energy for the release of Ba^{2+} ion from its C222 cryptate decreases with increasing mole fraction of AN in the solvent mixture (i.e. with decreasing solvating ability of the medium). This observation, which is opposite from the overall energy change of the complexation, emphasizes the necessity of a substantial ionic solvation in the transition state.^{28,44,45} This is also confirmed by the calculated $\Delta H^\ddagger$ and

$\Delta S^\ddagger$ values. Positive enthalpy of activation reflects a weaker transition state, a poorer overlap of the ligand and cation and a sloppy geometry. While the negative activation entropy shows a higher degree of solvent organization in the transition state than in the initial complex. 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.

Fig. 5. Plot of $\log K_s$, E_a , $\Delta H^\ddagger$ and $\Delta S^\ddagger$ vs acetonitrile mole fraction for Ba^{2+} -C222 cryptate in different DMSO-AN mixtures.

Previous literature reports show that the stability of alkali⁴⁶ and alkaline earth cryptates²⁵ correlate well with their dissociation rate constants. In order to investigate the existence of such correlation in this study, stability constants of the Ba^{2+} -C222 cryptate in different AN-DMSO mixtures at 298 K were evaluated from the competitive spectrophotometric method^{10,11} described in the Experimental Section. The results, together with the stability constants of the Ba^{2+} -murexide complex the same solvent mixtures, are given in Table II. A comparison between the stability constants (Table II) and the dissociation rate constants (Table I) of the Ba^{2+} -C222 cryptate in all AN-DMSO mixtures studied at 298 K revealed the existence of a nice correlation; the k_d values decreased with increasing K_f values of the barium cryptate.

Moreover, data given in Table II clearly illustrate the important role of the solvent properties in the thermodynamics of complexation reaction. The stability of the Ba^{2+} -C222 cryptate (and that of the Ba^{2+} -murexide complex) increases rapidly with increasing mole fraction of AN in the mixed solvent. It has been shown that the solvating ability of the solvent, as expressed by the Gutmann donor number,⁴¹ plays a key

role in the complexation reactions^{7-11,15,28,29,46} DMSO is a solvent of high solvating ability ($DN = 29.8$)⁴¹ which can compete strongly with the ligand for the cation. Thus, it is reasonable to expect that the addition of AN as a solvent of intermediate donicity solvent ($DN = 14.1$)⁴¹ to DMSO will increase the extent of interaction between the Ba^{2+} ion and C222.

There is actually a linear relationship between $\log K_s$ of the barium cryptate and mole fraction of acetonitrile (X_{AN}) in the solvent mixture (Fig. 5). The same kind of relationship is also reported between the data obtained from the study of complexation in a number of metal-ligand systems in different binary solvent mixtures.^{8,11,47,48} 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 solvent composition

It is interesting to note not only the Ba^{2+} -C222 cryptate stability constant, but also its dissociation rate constants and the activation parameters reveal a nice linear correlation with the solvent composition (see Fig. 5). Similar correlations has been previously for some metal cryptates^{15,45,49} and crown ether complexes.⁴⁸

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