# Thermodynamic and Kinetic Studies on Calcium(II)–Cryptates in Acetonitrile and Water Mixtures

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## Abstract

Stability constants, $K_s$, of complexes between $Ca^{2+}$ and cryptands (2,1,1) and (2,2,2) have been determined in mixtures of acetonitrile (AN) and water. Additionally, the dissociation rates of the cryptate $Ca(2,1,1)^{2+}$ have been measured in this solvent system at 25 °C. There is a large variation of the stability constants with solvent composition but the increases of $\log K_s$ with mole fraction $x_{AN}$ of the two $Ca^{2+}$–cryptates are in an unexpected agreement among themselves and with results for $K(2,2,2)^+$. The dissociation rates, $k_d$, of $Ca(2,1,1)^{2+}$ are uncatalyzed by strong and weak acids and are almost constant up to $x_{AN} = 0.6$, while the increase in $K_s$ with $x_{AN}$ is determined directly by a parallel increase in the formation rate constant $k_f$. Only at higher mole fractions do changes in $k_f$ and in $k_d$ contribute similarly to the variation in $K_s$.

## Introduction

In water and in polar non-aqueous solvents, the equilibria between free metal ions, $M^{n+}$, neutral macrobicyclic diazapolyethers (cryptands [1], see Scheme 1), Cry, and the cryptate (inclusion) complexes, $MCry^{n+}$, depend strongly on the size of the cations in relation to number and spatial arrangement

$$M^{n+} + Cry \underset{\overrightarrow{\phantom{xx}}}{\overset{K_s}{\rightleftharpoons}} MCry^{n+} \qquad (1)$$

of the electronegative atoms within the cryptand's hydrophilic cavity [2]. In addition, the stability of cryptates is also quite sensitive to solvent variation, and the stability constant, $K_s$, increases as the interaction between $M^{n+}$ and the solvent molecules decreases [3–5].
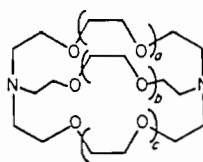


1, $a = 1$, $b = c = 0$ (2,1,1)
2, $a = b = 1$, $c = 0$ (2,2,1)
3, $a = b = c = 1$ (2,2,2)

Scheme 1.

In mixed solvents, equilibrium (1) also depends upon the preferential solvation of the ligand (Cry) and of the free and complexed cations by one or other of the solvent components. In previous papers [6–8] it was shown that in mixtures of acetonitrile (AN) and water the stability constants of the $Ag^+$ complexes with the three cryptands in Scheme 1 show a similar but only slight decrease with increasing mole fraction $x_{AN}$, while the stability constant for $K(2,2,2)^+$ increases by three orders of magnitude over the same range. Qualitatively, the sign of the variation of $K_s$ with $x_{AN}$ is in agreement with preferential solvation of $Ag^+$ by acetonitrile and of $K^+$ by water. Quantitatively, however, the situation is not so simple, as the magnitude of the preferential solvation of the former is larger than that of the latter, whereas the magnitude of the change in $K_s$ is the reverse. Therefore, a complete description of the system also has to take into account the selective solvation of the cryptate and cryptand. Earlier measurements have shown that cryptands show no strong preference for water or acetonitrile but that the cryptates are preferentially solvated by acetonitrile [6–9].

In this paper we report the stability constants of $Ca^{2+}$ complexes with (2,1,1) and (2,2,2) and the dissociation ($k_d$) and formation ($k_f$) rate constants of $Ca(2,1,1)^{2+}$ in acetonitrile and water mixtures.

The increase in $K_s$ with $x_{AN}$ is very similar for the two $Ca^{2+}$–cryptates and for $K(2,2,2)^+$. Thus it follows that for all three systems the difference in the free energies of transfer between the free and complexed cations, $[\Delta G_{tr}(MCry^{n+}) - \Delta G_{tr}(M^{n+})]$ are almost identical. This similarity in behaviour, however, does not extend to the complexation rates, as for the $Ca^{2+}$ systems variations in $K_s = k_f/k_d$ are determined mainly by variations in the formation rate constant, $k_f$, whereas for $K(2,2,2)^+$, $k_f$ and $k_d$ contribute almost equally to variations in $K_s$ [10].

## Experimental

### Materials

Cryptand $(2,1,1)$, $AgNO_3$, $CHCl_2COOH$, $CH_3$-$SO_3H$, $CF_3SO_3H$, HCl, $HClO_4$ were commercial samples of high purity and were used without further purification. $Ca(ClO_4)_2$ (Ventron) and $AgClO_4$ (Fluka, monohydrate) were dried under vacuum for more than 15 h at 200 and 100 °C, respectively. Tetraethylammonium perchlorate (Fluka) was recrystallized from ethanol and dried under vacuum. Acetonitrile (Merck, Uvasol) was used as purchased and had a water content of less than 100 ppm.

### Stability Constant Measurements

The stability constants of $Ca(2,1,1)^{2+}$ in mixtures of acetonitrile and water up to a mole fraction $x_{AN} = 0.60$ were determined by pH-potentiometric titrations using a glass electrode. At higher mole fractions, an $Ag/Ag^+$ electrode was employed to monitor the competition between $Ca^{2+}$ and $Ag^+$ for $(2,1,1)$.

The pH-potentiometric titrations were carried out at 298 K in a thermostated glass cell. All solutions, including those in the salt bridge, were at a constant ionic strength of 0.1 M $(Et_4NClO_4)$. The potential readings were referred to an aqueous 1.0 M NaCl calomel electrode. The glass electrode was calibrated against standard buffers in water (Merck).

In mixtures of acetonitrile and water the observed pH values, $(pH)_{obs}$, are related to the true pH for hydrogen ion activity referred to the standard state in a given mixture by eqn. (2).

$$pH = (pH)_{obs} + \delta \qquad (2)$$

The factor $\delta$ corrects for changes in hydrogen ion activity and the liquid junction potential. During an experiment, a 0.01 M HCl solution was added successively to a solution of $Ca(ClO_4)_2 \sim 5 \times 10^{-3}$ M and $(2,1,1) \sim 2 \times 10^{-3}$ M. The $\delta$ values were taken from measurements at large excess of acid over $(2,1,1)$, and the true pH values were transformed to hydrogen ion concentrations using activity coefficients calculated from the Davies equation [11]. The stability constant $K_s$ of $Ca(2,1,1)^{2+}$ was calculated using the known protonation constants $K_1$ and $K_2$ for $(2,1,1)$-

TABLE 1. Stability Constants (log $K_s$) of $Ca^{2+}$ with the Cryptands $(2,1,1)$ and $(2,2,2)$ and Related Free Energies of Transfer, at 25 °C

| $x_{AN} = 1 - x_{H_2O}$ | log $K_s$($Ca^{2+}$–$(2,1,1)$) | log $K_s$($Ca^{2+}$–$(2,2,2)$) | $\Delta G_{tr}(Ca(2,1,1)^{2+}) - \Delta G_{tr}(Ca^{2+})$ (kJ/mol) | $\Delta G_{tr}(Ca(2,2,2)^{2+}) - \Delta G_{tr}(Ca^{2+})$ (kJ/mol) |
|---|---|---|---|---|
| 0.0 | 2.7[a], 2.5[c] | 4.91[d], 4.57[e] | 0.0 | 0.0 |
| 0.05 | | 5.43[d] | | −5.1 |
| 0.1 | 3.5[a] | 5.77[d] | −5.5 | −7.7 |
| 0.2 | 4.4[a] | 6.11[d] | −10.3 | −10.2 |
| 0.3 | 4.8[a] | 6.67[d] | −12.9 | −12.9 |
| 0.4 | 5.0[a] | 7.01[d] | −14.2 | −14.2 |
| 0.5 | 5.5[a] | 7.60[d] | −16.7 | −16.5 |
| 0.6 | 6.3[b] | 8.12[d] | −20.2 | −18.8 |
| 0.7 | 6.7[b] | | −22.1 | |
| 0.9 | 7.7[b] | | −26.5 | |
| 1.0 | 8.5 ± 0.2 | 10.5 ± 0.4 | −30.0 | −27.0 |

[a]pH-titration, experimental error ±0.1.   [b]pAg-titration, experimental error ±0.2.   [c]See ref. 2.   [d]pAg-titration, experimental error ±0.05.   [e]See ref. 5.

$H^+$ and $(2,1,1)H_2^{2+}$ respectively [3, 12, 13], the autoprotolysis constants $K_w$ of water [13], and the measured $\delta$ values. The results are listed in Table I.

The stability constant of $Ag(2,1,1)^+$ in acetonitrile and water mixtures varies only slightly between $\log K_s = 7.0$ (pure water) and 8.5 (pure acetontrile) [9], and the disproportionation reaction (eqn. (3)) has been measured in mixtures with $x_{AN} \geqslant 0.5$ by

$$Ca(2,1,1)^{2+} + Ag^+ \xrightarrow{K_e} Ca^{2+} + Ag(2,1,1)^+ \quad (3)$$
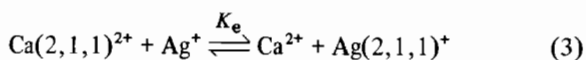
direct pAg-potentiometry, with a silver wire indicating electrode. The solutions in the 0.01 M $AgClO_4$/Ag-reference electrode and the salt bridge were of the same solvent composition as the reacting solutions. In all cases the concentration of metal ions was in excess over that of $(2,1,1)$, in order to ensure that the fraction of uncomplexed ligand was negligibly small. The stability constant $K_s$ of $Ca(2,1,1)^{2+}$ in Table I is the ratio of $K_s(Ag^+)$ and $K_e$ of eqn. (3). The stability of $Ca(2,2,2)^{2+}$ in water is larger than that of $Ca(2,1,1)^{2+}$, and so only the disproportionative reaction with $Ag^+$ using the $Ag^+/Ag$ electrode has been studied (Table I). The stability constants of both $Ca^{2+}$–cryptates in solvent mixtures with $x_{AN} \geqslant 0.8$ are equal to or larger than those of the corresponding $Ag^+$–cryptates, and therefore the accuracy of $K_s(Ca^{2+})$ in this mole fraction range is lower than in mixtures with lower $x_{AN}$ values.

*Measurement of Dissociation Rate Constants*

All kinetic experiments were initiated by rapid mixing of an equilibrated solution of $Ca^{2+}$ and $(2,1,1)$ with an acid scavenger, using a home-built, all-glass stopped-flow apparatus. Excess acid was used in order to observe a pseudo-first-order reaction. The concentration of $Ca^{2+}$ ($9 \times 10^{-4}$–$6 \times 10^{-3}$ M)

was always sufficiently large relative to that of $(2,1,1)$ to ensure that prior to mixing with the acid almost all of the ligand molecules were complexed by $Ca^{2+}$. The change in conductance occurring during the reaction (eqn. (4)) was used to calculate the rate constant $k_e$. The measured rate constants are

$$Ca(2,1,1)^{2+} + 2H^+ \xrightarrow{k_e} Ca^{2+} + (2,1,1)H_2^{2+} \quad (4)$$
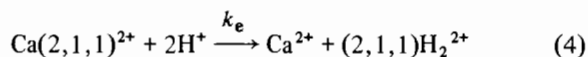
listed in Table II, and each represents an average of at least eight measurements.

In highly aqueous media, when strong acids such as $CH_3SO_3H$, $CF_3SO_3H$, $HClO_4$, and $HCl$ are used, the reactions are accompanied by a significant decrease in conductance (due to consumption of the highly mobile $H^+$). However, as the mole fraction of acetonitrile increases, the overall change in conductance decreases, because the proton loses its extraordinary mobility and becomes similar to the other ionic species. Also a weak acid, $CHCl_2CO_2H$ ($pK_a = 1.35$ in $H_2O$, $pK_a = 15.8$ in acetonitrile) [14] was used as a scavenger, as in this case there was an increase in conductance during the reaction (eqn. (5)), because of the generation of additional ionic

$$Ca(2,1,1)^{2+} + 2CHCl_2CO_2H \xrightarrow{k_e}$$
$$Ca^{2+} + (2,1,1)H_2^{2+} + 2CHCl_2CO_2^- \quad (5)$$
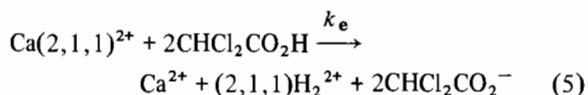
species. However, in mixtures with $x_{AN} > 0.85$, possibly because of ion-pair formation or reversibility of the reactions, the conductance changes were too small to enable reliable determination of $k_e$ values.

## Results and Discussion

*Stability Constants and Free Energies*

The stability constants of $Ca(2,1,1)^{2+}$ and $Ca(2,2,2)^{2+}$ in Table I increase with the concentration

TABLE II. Rate Constants of Dissociation of $Ca(2,1,1)^{2+}$ for Various Acids (Scavenger) in Acetonitrile + Water Mixtures at 25 °C

| $x_{AN} = 1 - x_{H_2O}$ | $k_e$ (s$^{-1}$) (scavenger) | $k_e^a$ (s$^{-1}$) |
|---|---|---|
| 0.0 | $0.820 \pm 0.013$ (CF$_3$SO$_3$H) | $0.826 \pm 0.007$ |
| | $0.840 \pm 0.007$ (CH$_3$SO$_3$H) | $0.82^b$ |
| | $0.820 \pm 0.034$ (HClO$_4$) | |
| | $0.840 \pm 0.014$ (HCl) | |
| 0.20 | $0.685 \pm 0.005$ (CF$_3$SO$_3$H) | $0.676 \pm 0.005$ |
| 0.40 | $0.667 \pm 0.009$ (CF$_3$SO$_3$H) | $0.574 \pm 0.013$ |
| 0.60 | $0.546 \pm 0.003$ (CF$_3$SO$_3$H) | $0.355 \pm 0.008$ |
| | $0.524 \pm 0.008$ (CH$_3$SO$_3$H) | |
| | $0.546 \pm 0.003$ (HClO$_4$) | |
| 0.70 | $0.395 \pm 0.006$ (CF$_3$SO$_3$H) | $0.187 \pm 0.003$ |
| 0.80 | $0.119 \pm 1.4 \times 10^{-3}$ (CH$_3$SO$_3$H) | $0.0618 \pm 9.2 \times 10^{-4}$ |
| | $0.217 \pm 4.7 \times 10^{-3}$ (HClO$_4$) | |
| 0.85 | | $0.0261 \pm 2.0 \times 10^{-4}$ |
| 0.90 | | $6.10 \times 10^{-3} \pm 9 \times 10^{-4}$ |

$^a$Scavenger: dichloroacetic acid.    $^b$Ref. 5.
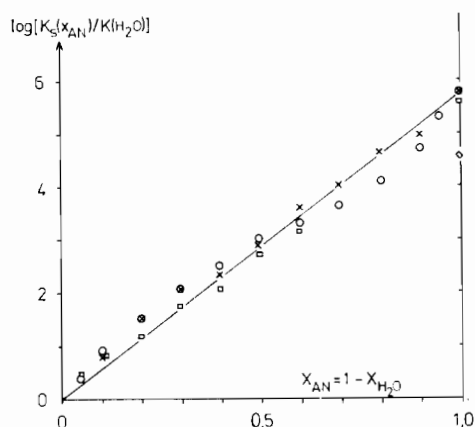
Fig. 1. Stability constants of $Ca(2,1,1)^{2+}$ ($\times$), $Ca(2,2,1)^{2+}$ ($\diamond$), $Ca(2,2,2)^{2+}$ ($\square$) and $K(2,2,2)^{2+}$ ($\circ$) in acetonitrile + water mixtures at 25 °C.
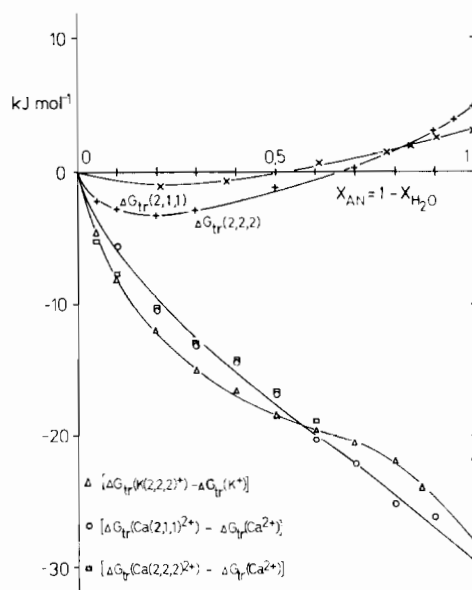


Fig. 2. Free energies of transfer of (2,1,1), (2,2,2) and of cryptates minus metal ion in acetonitrile + water mixtures at 25 °C. ($\diamond$, $\Delta G_{tr}(Ca(2,2,1)^{2+}) - \Delta G_{tr}(Ca^{2+})$).

of acetonitrile, and $\log K_s$ changes almost linearly with the mole fraction $x_{AN}$. In addition, the overall variations for the two systems are very similar, as demonstrated in Fig. 1 where $\log[K_s(x_{AN})/K_s(H_2O)]$ is plotted against $x_{AN}$. $K_s(H_2O) \equiv K_s(x_{AN} = 0)$ is the stability constant in water. Somewhat more surprising is the observation that when the stability constants of $K(2,2,2)^+$ in acetonitrile and water mixtures [7] are included the relative $\log K_s$ values agree within ±0.5 units with those of the $Ca^{2+}$–cryptates.

This unexpected behaviour is best discussed in terms of the free energies of transfer, $\Delta G_{tr}$ – with water as reference solvent – of the species involved in the complexation equilibria: the metal ion, the cryptand, and the cryptate ion. The stability constants are related to the free energies of transfer by eqn. (6).

$$-2.303RT \log[K_s(x_{AN})/K_s(H_2O)] = \qquad (6)$$
$$\Delta G_{tr}(MCry^{n+}) - \Delta G_{tr}(M^{n+}) - \Delta G_{tr}(Cry)$$

The free energies of transfer of the cryptands (2,1,1) [9] and (2,2,2) [6] are small and show no evidence of striking selectivity in solvation (Fig. 2). Thus the overall variations in $\log K_s$ with solvent composition are dominated by differences in the behaviour of the free and complexed cations ($\Delta G_{tr}(M^{n+}) - \Delta G_{tr}(MCry^{n+})$ Fig. 2).

$K^+$ and $Ca^{2+}$ are preferentially hydrated in the mixtures, having positive $\Delta G_{tr}$ values which should be of appreciable magnitude only at higher mole fractions $x_{AN}$, when water is rare. In the case of $K^+$, earlier work has shown that the left-hand side of eqn. (6) is much larger in magnitude than $\Delta G_{tr}(K^+)$ [7], so that $\Delta G_{tr}(K(2,2,2)^+)$ is strongly negative, i.e. $K(2,2,2)^+$ is preferentially solvated by acetonitrile. The degree of preferential solvation of K-$(2,2,2)^+$ is even larger than that of $Ag(2,2,2)^+$, and similar to that of $Ag^+$ [7].

Unfortunately, the solvation energies of $Ca^{2+}$ in mixtures of acetonitrile and water are not available, although the general trend expected can be ascertained from published work on other $M^{2+}$ systems including $Mn^{2+}$ [15], $Cu^{2+}$ [16] and $Fe^{2+}$ [16]. In all cases up to $x_{AN} \sim 0.6$, $\Delta G_{tr}$ values are small (slightly negative for $Mn^{2+}$) but increase sharply over the range $x_{AN} = 0.6$–1.0 to large positive values ($+22$ kJ mol$^{-1}$ ($Mn^{2+}$) to $+100$ kJ mol$^{-1}$ ($Fe^{2+}$)). Even in the absence of $\Delta G_{tr}(Ca^{2+})$ data, however, the differences $[\Delta G_{tr}(CaCry^{2+}) - \Delta G_{tr}(Ca^{2+})]$ can be calculated via eqn. (6). These are compared with the corresponding values for the $K^+/(2,2,2)$ system in Fig. 2, and it may be seen that there is a striking agreement between the three sets of values, to within ±3 kJ mol$^{-1}$. This value corresponds to only ±0.5 in $\delta \log K_s$, and is within the combined experimental errors for the determination of the two stability constants and distribution coefficients [6, 9] (required for $\Delta G_{tr}(Cry)$ values). There remains then the question of whether this agreement is fortuitous and of whether or not the solvation of $MCry^{n+}$ is determined mainly by the organic character of the complex, but this may be answered at least in pure acetonitrile where the solvation energy of $Ca^{2+}$ is available for comparison with that in water.

Case and Parsons [17] have determined the real free energy of transfer of $Ca^{2+}$ between water, $\Delta \alpha = \Delta G_{tr} + 2F\Delta\chi = 50$ kJ mol$^{-1}$ where $\Delta\chi$ is the contribution due to the electrical double layers at the free surfaces of water and acetonitrile. This value, when combined with an estimate of $2F\Delta\chi = -58$ kJ mol$^{-1}$ [18], gives a value of $\Delta G_{tr}(Ca^{2+}) = 108$ kJ

mol⁻¹. In an independent study, Constantinescu [19, 20] obtained the solvation energy of $Ca^{2+}$ in acetonitrile ($-1464$ kJ mol⁻¹), which when combined with the hydration energy of $-1593$ kJ mol⁻¹ [21], leads to $\Delta G_{tr}(Ca^{2+}) = 129$ kJ mol⁻¹. Both values are as expected positive, and the agreement between the two is satisfactory for the present purpose. The important point is that the values are considerably larger than the corresponding value for $K^+$ of $\Delta G_{tr}(K^+) = 8$ kJ mol⁻¹ [22]. This in turn means that $\Delta G_{tr}(CaCry^{2+}) = 90$ kJ mol⁻¹ (calculated via eqn. (6)) differs both in sign and magnitude from that of $K(2,2,2)^+$, for which $\Delta G_{tr} = -14.4$ kJ mol⁻¹ [8]. Similar results are also found for $Ca(2,2,1)^{2+}$, with $\log K_s = 11.5$ and $6.95$ in acetonitrile and water [3] respectively, although the points in Figs. 1 and 2 are somewhat lower for this cryptate. These large positive values of $\Delta G_{tr}(CaCry^{2+})$ relative to $\Delta G_{tr}(K(2,2,2)^+)$ suggest strongly that $Ca^{2+}$ is not shielded effectively from the solvent by the ligand. Thus even when complexed, $Ca^{2+}$ is able to interact more effectively with water than with acetonitrile. This is consistent with X-ray diffraction studies of alkaline earth metal cryptates [23] which show that the metal ions are coordinated not only with the electronegative atoms of the cryptand, but also by a water molecule. It is important to note that these large differences between $\Delta G_{tr}(MCry^+)$ and $\Delta G_{tr}(MCry^{2+})$ are not restricted to transfers involving water as one of the solvents, as similar behaviour is observed for transfer between two aprotic solvents [4], e.g. acetonitrile and dimethylformamide.

The general behaviour of the calcium cryptates in the acetonitrile and water system is, however, by no means extraordinary, either in comparison with that in other solvents or of other alkali metal/ alkaline earth metal cryptates. Thus in water the stability constant of $Ca(2,2,1)^{2+}$ is larger than those of $Ca(2,2,2)^{2+}$ and $Ca(2,1,1)^{2+}$ because of optimal agreement between the sizes of the ligand cavity and $Ca^{2+}$. This remains true in the mixtures and in pure acetonitrile. In addition the three stability constants in pure acetonitrile agree closely (within 0.3 in $\log K_s$) with those in propylene carbonate [5] (Fig. 3), a solvent known to have similar solvating properties towards cations.

## Reaction Rates at 25 °C

The dissociation rate of $Ca(2,1,1)^{2+}$ was monitored by the reaction with several different acids as scavengers to give protonated $(2,1,1)$ and $Ca^{2+}$. In an extensive series of experiments at 25 °C, it was shown (Table II) that the observed rate constants, $k_e$, are independent of the concentrations of $Ca^{2+}$, $(2,1,1)$ and the excess acid whether it is strong or weak. The range of acid concentrations investigated can be taken from Fig. 4.



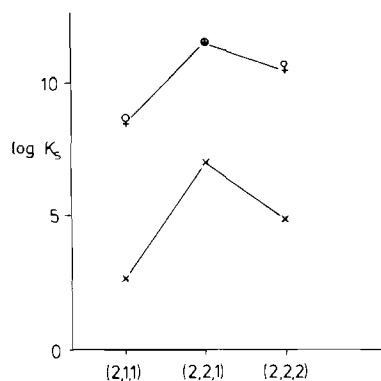Fig. 3. Stability constants of $Ca^{2+}$–cryptates in water (X), acetonitrile (+) and propylene carbonate (o) at 25 °C.
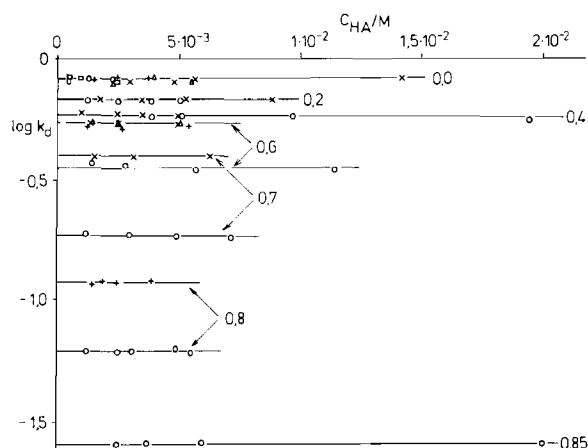


Fig. 4. Dissociation rate constants for $Ca(2,1,1)^{2+}$ in acetonitrile + water mixtures at 25 °C. (Scavenging acids are $CHCl_2COOH$ (o), $CF_3SO_3H$ (X), $CH_3SO_3H$ (+), $HClO_4$ (△), and HCl (□)).

In mixtures with $x_{AN} \leqslant 0.4$, the dissociation rate constant is also independent of the nature of the acid used. Thus the complex dissociates in a rate determining step $(k_e = k_d)$ into $Ca^{2+}$ and $(2,1,1)$ which is then protonated in a subsequent rapid step:

$$Ca(2,1,1)^{2+} \xrightarrow{k_d} Ca^{2+} + (2,1,1) \qquad (7)$$

$$(2,1,1) + 2H^+ \longrightarrow (2,1,1)H_2^{2+} \qquad (8)$$
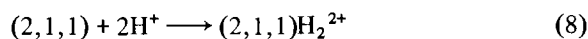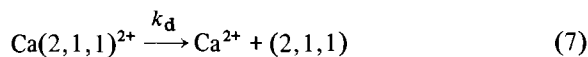
where $k_d$ is the rate constant for the uncatalysed dissociation. Additional experiments in these mixtures have confirmed that in more aqueous solutions the rate of protonation of $(2,1,1)$ is much faster than the dissociation of the cryptate.
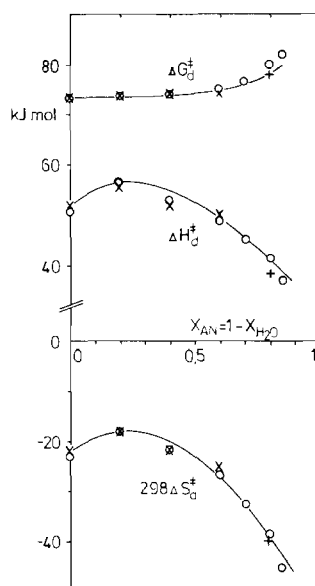
For mole fractions $\geqslant 0.6$, the observed dissociation rate constant, $k_e$, is still independent of the acid concentration, but is dependent upon the particular acid used. The rate constant decreases as the strength of the acid decreases from strong acids ($HClO_4$, $CF_3SO_3H$) to dichloroacetic acid (Fig. 4) and still

TABLE III. Rate Constant, $k_d$, and Activation Parameters for the Dissociation of $Ca(2,1,1)^{2+}$ in Acetontrile + Water Mixtures at 25 °C

| $x_{AN} = 1 - x_{H_2O}$ | Scavenger | $k_d$ (s$^{-1}$) | $\Delta G_d^{\ddagger}$ (kJ mol$^{-1}$) | $\Delta H_d^{\ddagger}$ (kJ mol$^{-1}$) | 298 $\Delta S_d^{\ddagger}$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.0 | CH$_3$COOH | 0.82 | 73.5 | 50.4 ± 0.3 | −23.1 |
| 0.0 | CF$_3$SO$_3$H | 0.82 | 73.5 | 52.1 ± 0.2 | −21.5 |
| 0.2 | CHCl$_2$COOH | 0.68 | 74.0 | 56.3 ± 0.1 | −17.7 |
| 0.2 | CF$_3$SO$_3$H | 0.68 | 74.0 | 55.9 ± 1.0 | −18.0 |
| 0.4 | CHCl$_2$COOH | 0.57 | 74.4 | 53.2 ± 0.3 | −21.2 |
| 0.4 | CF$_3$SO$_3$H | 0.67 | 74.0 | 52.3 ± 0.4 | −21.8 |
| 0.6 | CHCl$_2$COOH | 0.35 | 75.5 | 49.0 ± 0.1 | −26.5 |
| 0.6 | CF$_3$SO$_3$H | 0.55 | 74.5 | 50.2 ± 0.5 | −24.4 |
| 0.7 | CHCl$_2$COOH | 0.18$_7$ | 77.1 | 44.9 ± 0.3 | −32.2 |
| 0.8 | CHCl$_2$COOH | 0.061$_7$ | 80.0 | 41.5 ± 0.3 | −38.5 |
| 0.8 | CH$_3$SO$_3$H | 0.11$_9$ | 78.3 | 38.9 ± 0.1 | −39.4 |
| 0.8 | HClO$_4$ | 0.21$_9$ | 76.9 | 45.5 ± 1.2 | −31.4 |
| 0.85 | CHCl$_2$COOH | 0.025$_7$ | 82.1 | 36.9 ± 0.3 | −45.2 |
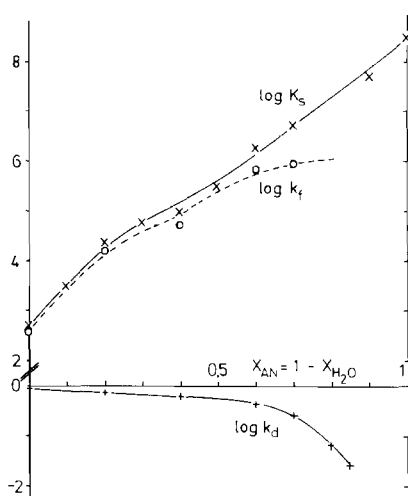


Fig. 5. Variation of stability constants (log $K_s$) and the rate constants of dissociation (log $k_d$) and of formation (log $k_f$) of $Ca(2,1,1)^{2+}$ in acetonitrile + water mixtures at 25 °C.



Fig. 6. Activation free energies ($\Delta G^{\ddagger}_d$), enthalpies ($\Delta H^{\ddagger}_d$) and entropies (298 $\Delta S^{\ddagger}_d$) in acetonitrile + water mixtures at 25 °C. (CHCl$_2$COOH (o), CF$_3$SO$_3$H (X), CH$_3$SO$_3$H (+)).

more for monochloroacetic acid as scavenger. It is difficult to interpret these results quantitatively, but for the weaker acids the rate of the second protonation step $((2,1,1)H^+ + HA \rightarrow (2,1,1)H_2^{2+} + A^-)$ becomes comparable to the overall rate constant, and so may be interfering the observed conductance change during reaction. For the strong acids, the protonation steps are very rapid and therefore we use values measured in strong acid solutions for the dissociation rate constants in the high $x_{AN}$ region. An alternative explanation of the results is that the faster reactions in strong acid solution result from the formation of the protonated intermediate Ca-$(2,1,1)H^{3+}$. However, the concentration of such

a species would depend upon the acid concentration, unless $Ca(2,1,1)^{2+}$ were sufficiently basic to be protonated quantitatively in the mixtures, even in very dilute acid solution ($10^{-3}$ M). This seems very unlikely, and in particular it would require a dramatic change in basicity in the region $0.4 \leqslant x_{AN} \leqslant 0.6$.

Figure 5 shows a comparison between the variation with $x_{AN}$ in stability constant, $K_s$, and the rate constants for dissociation, $k_d$, and of cryptate formation, $k_f = K_s \times k_d$. The almost linear increase in log $K_s$ with $x_{AN}$ is determined directly by parallel

increases in $\log k_f$ up to $x_{AN} \sim 0.6$, whereas $\log k_d$ values decrease only very slightly over this region. Only at higher $x_{AN}$ (>0.6) do changes in $k_f$ and $k_d$ make comparable contributions to the increase in $\log K_s$, as observed previously for the $K^+$—(2,2,2) system in acetontrile and water mixtures [10].

*Activation Enthalpies and Entropies of Dissociation*

The dissociation rate of $Ca(2,1,1)^{2+}$ was also measured as a function of temperature in mixtures with $x_{AN} \leqslant 0.85$. Again in all cases $k_e$ was independent of the concentrations of $Ca^{2+}$, (2,1,1) and the acid in excess. The activation enthalpies, $\Delta H^{\ddagger}{}_d$, and entropies, $\Delta S^{\ddagger}{}_d$, in Table III have been determined by linear regression analysis using the Eyring equation in the form

$$\ln \frac{k_d h}{k_B T} = \frac{\Delta S^{\ddagger}{}_d}{R} - \frac{\Delta H^{\ddagger}{}_d}{RT} \qquad (13)$$

where $k_B$ is Boltzmann's constant and $h$ Planck's constant. The errors quoted for a given quantity, which is the mean value over all $n$ experimental runs, is the largest deviation calculated using only $n - 1$ of the runs. As is frequently observed in mixed solvent systems, simple monotonic variations in $\Delta G^{\ddagger}{}_d$ (and $\log k_d$) result from partial compensation of $\Delta H^{\ddagger}{}_d$ and $\Delta S^{\ddagger}{}_d$ values which individually pass through maxima at $x_{AN} \simeq 0.2$ (Fig. 6). Beyond $x_{AN} \simeq 0.2$, both $\Delta H^{\ddagger}{}_d$ and $\Delta S^{\ddagger}{}_d$ decrease steeply with increasing $x_{AN}$. This behaviour of $\Delta H^{\ddagger}{}_d$ and $\Delta S^{\ddagger}{}_d$ almost certainly results from the properties of the solvent system itself. Several studies have shown that extrema in thermodynamic properties occur at $x_{AN} \simeq 0.3$ [9, 24], resulting from destruction of the water structure. Beyond this region the mixtures behave as typical non-aqueous, unassociated solvents.

## References

1 B. Dietrich, J. M. Lehn and J. P. Sauvage, *Tetrahedron Lett.*, *2885*, 2889 (1969).
2 J. M. Lehn, *Struct. Bonding (Berlin)*, *16*, 1 (1973).
3 J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, *97*, 6700 (1975).
4 B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.*, *103*, 1384 (1981).
5 B. G. Cox, Ng. van Truong and H. Schneider, *J. Am. Chem. Soc.*, *106*, 1273 (1984).
6 B. G. Cox, C. Gumiński and H. Schneider, *J. Am. Chem. Soc.*, *104*, 3789 (1982).
7 B. G. Cox, P. Firman, D. Gudlin and H. Schneider, *J. Phys. Chem.*, *86*, 4988 (1982).
8 B. G. Cox, J. Stroka, P. Firman, I. Schneider and H. Schneider, *Aust. J. Chem.*, *36*, 2133 (1983).
9 B. G. Cox, J. Stroka, P. Firman, I. Schneider and H. Schneider, *Z. Phys. Chem. N.F.*, *139*, 175 (1984).
10 B. G. Cox, C. Gumiński, P. Firman and H. Schneider, *J. Phys. Chem.*, *87*, 1357 (1983).
11 C. W. Davis, 'Ion Association', Butterworths, London, 1962, eqn. 3.1.
12 B. G. Cox, D. Knop and H. Schneider, *J. Am. Chem. Soc.*, *100*. 6002 (1978).
13 B. G. Cox, C. Gumiński and H. Schneider, in preparation.
14 I. M. Kolthoff and M. K. Chantooni, *J. Am. Chem. Soc.*, *98*, 5063 (1976).
15 J. Broda and Z. Galus, *J. Electroanal. Chem.*, *145*, 147 (1983).
16 B. G. Cox, A. J. Parker and W. E. Waghorne, *J. Phys. Chem.*, *78*, 173 (1974).
17 B. Case and R. Parsons, *Trans. Faraday Soc.*, *63*, 1224 (1967).
18 B. Case, N. S. Hush, R. Parsons and M. E. Peover, *J. Electroanal. Chem.*, *10*, 360 (1965).
19 E. Constantinescu, *Rev. Roumaine Chim.*, *17*, 1819 (1972).
20 J. Burgess, 'Metal Ions in Solution', Ellis Horwood, Chichester, 1978, Chap. 7.
21 R. M. Noyes, *J. Am. Chem. Soc.*, *84*, 513 (1962).
22 B. G. Cox, *Annu. Rep. Prog. Chem.*, *Sect. A*, *70*, 249 (1973).
23 B. Metz, D. Moras and R. Weiss, *Acta Crystallogr.*, *Sect. B*, *29*, 1377, 1382 (1973).
24 D. F. Grant-Taylor and D. D. Macdonald, *Can. J. Chem.*, *54*, 2813 (1976).