Intramolecular Processes of Cadmium Ethylenebis(oxyethylenenitrilo)tetraacetate: Effect of Solvents

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The influences of solvent mixtures, D_2O–$(CD_3)_2SO$, –CD_3OD and –dioxane, on the intramolecular processes of $[Cd(egta)]^{2-}$ [egta = ethylenebis(oxyethylenenitrilo)tetraacetate] were studied by dynamic nuclear magnetic resonance spectroscopy. It has been shown that the addition of the organic components can increase the rate of nitrogen inversion and decrease the activation energy for this process. Linear relations between the rate constants and the reciprocal of the solvent relative permittivity ε_r were obtained for all three mixed solvents, except at small ε_r values. A water displacement mechanism is proposed.

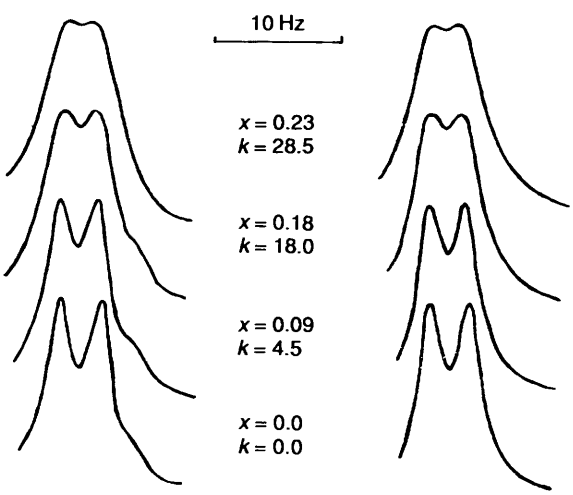
Nuclear magnetic resonance studies on the acetate intramolecular rearrangements of polyaminepolycarboxylate metal complexes at various temperatures in pure D_2O solution have been undertaken extensively.[1–9] However, the effects of solvents on the intramolecular scrambling processes of the complexes had not been investigated by dynamic nuclear magnetic resonance (DNMR) until 1984 when Mirti[10] found that for cadmium(II) ethylenediaminetetraacetate $[Cd(edta)]^{2-}$ in water–dioxane solvent the rate of nitrogen atom inversion increased with increasing amount of dioxane (and therefore with decreasing relative permittivity of the solvent).

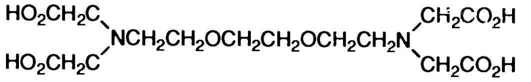
In the present work, in order to obtain more detailed information about the influence of solvents on the intramolecular exchange of polyaminepolycarboxylate metal complexes, the ^1H NMR spectra of $[Cd(egta)]^{2-}$ [egta = ethylenebis(oxyethylenenitrilo)tetraacetate] were measured in a variety of mixed solvents.

Experimental

The complex $[Cd(egta)]^{2-}$ was prepared by dissolving a 1:1 ratio of H_4egta and cadmium nitrate in an appropriate amount of dilute KOH solution and adjusting the pH to *ca.* 7, then concentrating and drying the solution. A *ca.* 0.2 mol dm^{-3} D_2O solution of the complex was prepared. Various amounts of $[^2H_6]$dimethyl sulfoxide, CD_3OD and dioxane solvents were added respectively to this D_2O solution which was placed in a 5 mm sample tube.

The ^1H NMR spectra were recorded on a Varian FT-80A spectrometer. The probe temperature was measured by a temperature-controller calibrated by a copper–constantan thermocouple. The theoretical spectra were obtained by the DNMR[11] computer program.





$$\begin{matrix} HO_2CH_2C \\ HO_2CH_2C \end{matrix} \!\!> NCH_2CH_2OCH_2CH_2OCH_2CH_2N <\!\! \begin{matrix} CH_2CO_2H \\ CH_2CO_2H \end{matrix}$$

H_4 egta

Fig. 1 The NMR spectra of the acetate methylenic protons of $[Cd(egta)]^{2-}$ (left) in D_2O–CD_3OD mixtures and the best-fit computer spectra (right). Only the inner peaks of the AB pattern are given; k in s^{-1}

Results and Discussion

It is known that the resonances of the acetate methylenic protons in the NMR spectrum of $[Cd(egta)]^{2-}$ in D_2O at room temperature consist of an AB quartet superimposed on the AB part of an ABX pattern, and that the Δ, Λ conversion occurs rapidly on the NMR time-scale, whereas the nitrogen inversion is regarded as a slow process under these conditions.[12] When an appropriate amount of $(CD_3)_2SO$, CD_3OD or dioxane solvent was added respectively to D_2O solutions of $[Cd(egta)]^{2-}$ the AB quartet coalesced. The rate of coalescence increased, with increasing mole fraction x of the organic component in the solvent, which indicates that the rate of nitrogen inversion increases. Typical acetate resonance spectra of $[Cd(egta)]^{2-}$ in D_2O–CD_3OD solvent mixtures are shown in Fig. 1. The low-frequency shoulder arises from the AB part of the ABX pattern which is due to the cadmium-111 and -113 complexes; these isotopes have a nuclear spin quantum number of $\frac{1}{2}$ and are present at 25% natural abundance. The rate constants k were obtained by fitting of the computer-simulated spectra with the experimental spectra. For simplicity, only the AB pattern resulting from the acetate groups bound to the cadmium isotope with zero nuclear spin was considered in the simulation of the spectra. Fig. 2 illustrates the variation of the rate constant k with the mole fraction x of the organic components in the solvent mixtures. An increase in x will lead to a decrease in the relative permittivity ε_r of the solvent. Thus, the results also show that the rate constant k for nitrogen inversion increases with ε_r in our case.

The addition of the organic components also affects the activation energy E_a and the activation entropy $\Delta S^\ddagger$ of the nitrogen inversion process as shown in Table 1. Both E_a and $\Delta S^\ddagger$ decrease with increasing x (or with decreasing ε_r). This

Table 1 Effects of the mole fraction x of the solvent on the activation energy, enthalpy, entropy and free energy in the mixed solvents

Solvent	x	E_a/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
D_2O	0.0	53.4 ± 1.0	50.9 ± 1.0	72.5 ± 1.7	−72.6 ± 2.5
D_2O–$(CD_3)_2SO$	0.063	49.5 ± 0.9	47.0 ± 0.9	71.9 ± 1.6	−83.4 ± 2.5
	0.105	37.6 ± 0.1	35.1 ± 0.1	70.0 ± 0.2	−117.0 ± 0.3
D_2O–dioxane	0.03	48.8 ± 3.0	46.3 ± 3.0	71.5 ± 5.5	−85.3 ± 8.4
	0.06	43.7 ± 1.2	41.2 ± 1.2	70.9 ± 2.1	−99.7 ± 3.3
	0.09	40.4 ± 0.4	37.9 ± 0.4	70.0 ± 0.8	−107.0 ± 1.3

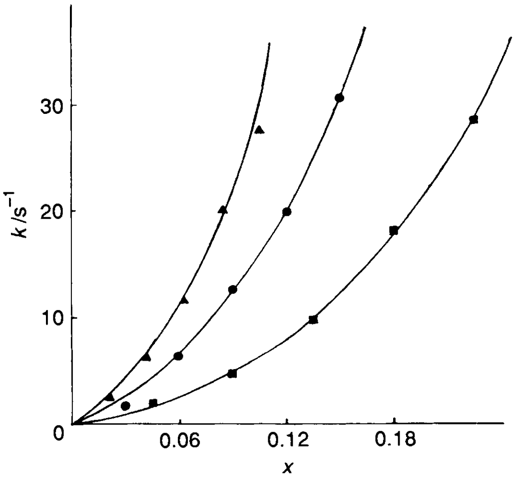
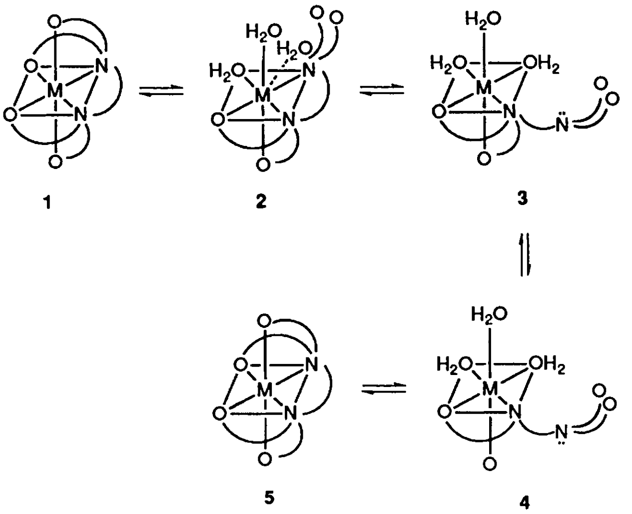


Fig. 2 Plots of k against x for the solvents D_2O–$(CD_3)_2SO$ (▲), –dioxane (●) and –CD_3OD (■)



Scheme 1

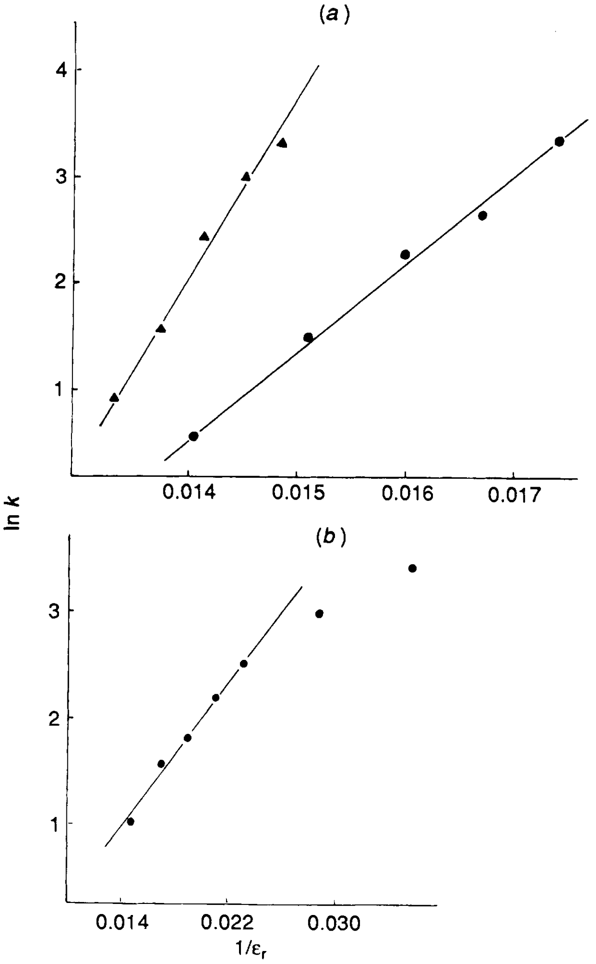


Fig. 3 Plots of ln k vs. $1/\varepsilon_r$ for $(CD_3)_2SO$–D_2O (▲) and CD_3OD–D_2O (●) mixed solvents (*a*) and for dioxane–D_2O (*b*)

may suggest that in solvents with lower ε_r the solvation of the activated complex is easier than that of the reactant complex, *i.e.* the polarity of the former is less than that of the latter. So the process is favoured in solvents with lower polarity. These results are in agreement with those for k, and would be helpful in understanding the mechanism of the intramolecular process.

In order to explain the isomerization of octahedral metal complexes, several mechanisms have been proposed,[13,14] including the twisting mechanism through a trigonal-prismatic intermediate, pathways proceeding through trigonal-bipyramidal and square-pyramidal five-co-ordinate intermediates, and the water displacement octahedral mechanism. In the first mechanism, the conversion of the reactant complex into the trigonal-prismatic intermediate (activated complex) through the twist is rate-determining. From consideration of the ionic solvation, the solvation of the activated complexes is almost the same as that of the reactant complexes because of their similar polarity. So, the relative permittivity of the solvents would not have an obvious influence on the rate constant for the nitrogen inversion process. However, it can be seen clearly from Fig. 2 that k increases with increasing x, *i.e.* decreasing ε_r. This demonstrates that the twist mechanism may not apply to the nitrogen inversion of $[Cd(egta)]^{2-}$. The second and the third mechanisms may be also impossible owing to the larger negative value of the activation entropy for nitrogen inversion[3] (see Table 1). The negative activation entropy, however, indicates that the water displacement octahedral mechanism, as shown in Scheme 1, is possible. Here the breaking of metal–nitrogen bonds is the rate-determining step (from **1** to **3** in Scheme 1). This step corresponds to a reaction between the complex ion and water molecules in our case.

According to the kinetics of the reaction in solution, the rate constant between the complex ion and water molecules can be expressed as[15] in equation (1) where the symbols have their

$$\ln k = \ln k_o + \frac{LZ^2e^2}{8\pi\varepsilon_o\varepsilon_rRT}\left(\frac{1}{r} - \frac{1}{r_\ddagger}\right) \qquad (1)$$

usual meanings. Since the radius $r_\ddagger$ of the activated complex is larger than that (r) of the reactant ion, the rate should be somewhat greater in a medium of lower relative permittivity. The equation predicts a linear plot of ln k against $1/\varepsilon_r$ with a positive slope. This seems to be true in most cases.[16,17] In Fig. 3 the plots of ln k *vs.* $1/\varepsilon_r$ are linear for all the three solvents (there are some deviations for the small ε_r in the D_2O–dioxane solvent mixture). The similarity of the effect of the solvent on the intramolecular process to that on reactions between ions and molecules may further support the participation of water molecules in the nitrogen inversion process of $[Cd(egta)]^{2-}$ in the mixed solvents. Attack of organic molecules on the metal in the reactant complex **1** may not be easy due to their larger volume and lower polarity than those of water.

Moreover, from the water displacement mechanism (see Scheme 1) it is concluded that the solvation of the activated complex is easier than that of the reactant complex. Since in the activated complex, water replaces two co-ordinated acetate groups, the former has a smaller volume and lower polarity than the latter, then organic components with lower polarity interact more easily with the metal ion in the activated complex. The interaction between the organic solvents and Cd^{II} decreases the effective charge on the metal, and therefore facilitates breaking of the Cd–N bond.

Acknowledgements

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