Aquation of β-*cis*-[CoCl₂(trien)]⁺ in water/AOT/ n-heptane reverse micelles†

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The aquation of β-*cis*-[CoCl₂(trien)]⁺ has been studied in reverse micelles of water/AOT/*n*-heptane for various concentrations of water and AOT at 298.1 K. The results are discussed in terms of a two-state model of confined water.

Keywords: aquation, Co(III) complex ion, reverse micelle, dynamic light scatttering

Previous studies[1] of aquation of coordination compounds in binary aqueous mixtures have proved the importance of cosolvent effects on the water structure. The change of structure results in preferential solvation of the complex ions and finally in the reaction rate.

The structure of water and the mobility of its molecule can be changed by solubilisation in reverse micelles. Of all the surfactants, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) has been the most widely used, as the reverse micelles formed by AOT can solubilise large amounts of water, other polar solvents and electrolyte solutions. Numerous studies[2-5] have shown that the structure and state of water in reverse micelles are different from that of bulk water. There are two or three distinct coexisting types of a water in the core of a micelle: bound water at the ionic layer, free water at the centre of the micelle that behaves like bulk water, and trapped water within the ionic layer. The properties of confined water strongly depend on the water-to-surfactant concentration ratio: $w = [H_2O]/[AOT]$.

The change of water state by encapsulating in the core of the micelles should be apparent in the aquation rate. To test this assumption we decided to investigate the aquation of β-*cis*-[CoCl₂(trien)]⁺ (trien = triethylenetetraammine) in water/AOT/*n*-heptane reverse micelles with varying concentration of AOT and water. The kinetics of aquation of the complex have been studied previously[6]. The complex ion aquates with full retention of the *cis*-configuration. It is easily soluble even in a very low amount of water solubilised in the micelle, forming a solution of appropriate concentration suitable for spectrophotometric measurements.

Results and discussion

The aquation of β-*cis*-[CoCl₂(trien)]⁺ has been studied in reverse micelles of water/-AOT/*n*-heptane for *w* varying from 10 to 50 with AOT concentrations from 0.1 to 0.4 m at 298.1 K. The corresponding rate constants, together with their mean deviations, are listed in Table 1. The concentration of complex and HClO₄ referred to the aqueous phase in the core of the micelle was the same in all experiments.

Table 1 shows the effect of the concentration of AOT and solubilised water. For constant AOT concentration the reaction rate increases with decreasing the ratio w, *i.e.* with decreasing the amount of water solubilised in the reverse micelle. Unfortunately it was not possible to investigate the reaction at *w* < 10. Although the complex was soluble enough, the micellar system was not stable due to the presence of 0.001 mol/dm³ HClO₄.

Table 1 Rate constants of the aquation of β-*cis*-[CoCl₂(trien)]⁺ in water/AOT/n-heptane reverse micelles at 298.1 K; [complex] = 1.44 x 10⁻³ mol/dm³, [HClO₄] = 1x10⁻³ mol/dm³

| | 10³ *k*/s [AOT], mol/kg | | | |
w	0.1	0.2	0.3	0.4
10	2.72 ± 0.05	1.77 ± 0.06	2.98 ± 0.06	2.67 ± 0.06
20	1.95 ± 0.06	1.41 ± 0.03	2.02 ± 0.05	1.69 ± 0.01
30	1.49 ± 0.02	1.32 ± 0.03	1.49 ± 0.08	1.42 ± 0.01
40	1.16 ± 0.02	1.07 ± 0.05	1.04 ± 0.02	1.14 ± 0.02
50	1.06 ± 0.02	0.99 ± 0.07	0.98 ± 0.02	0.98 ± 0.02

k (pure water) = (0.96 ± 0.02) x 10⁻³ s⁻¹ for [complex] = 5.78 x 10⁻⁵ mol/dm³.

The reaction rate also changed with the AOT concentration at constant *w*. There is an appreciable difference between the rate constant at 0.1 mol/kg AOT and the rate constants at 0.2, 0.3 and 0.4 mol/kg AOT.

The structure of the encapsulated water seems to be reflected in the rate constants of aquation of β-*cis*-[CoCl₂(trien)]⁺ in reverse micelles. The IR spectra[2-5] of water confined within AOT/*n*-heptane micelles agree well with a two-stage model based on the existence of bound and free water. The motion of water molecules is strongly affected on decreasing the size of the micelles. The size of micelle depends on the molar ratio *w*. At low *w* < 10 the confined water exists mainly as bound at the ionic layer of the micelles. With increasing *w* additional water occupies the core of the micelles. In larger micelles with *w* ≥ 40 the state of water is essentially identical to that in bulk water.

The hydrodynamic diameters of micelles containing the water, determined by dynamic laser light scattering (Table 2), are in good accordance with those published previously[7] and are not affected by the reactant. The increase in aquation rate may be indeed the response to the change of water state though opposite to that in aqueous mixtures of cosolvents. Numerous studies[8,9] provided information on the microscopic structures of binary aqueous mixtures. The addition of *e.g.* alcohol to the water has a strengthening effect on the structure of water and at mole fraction x_2^* – typical for the alcohol – the clusters of alcohol begin to form due to hydrophobic interaction. These microheterogeneities control the solvation of the reactants and thus also the decrease in aquation rate of complex ions.

Experimental

β-*cis*-[CoCl₂(trien)]Cl was prepared by the method published previously[6] and its purity was checked by elemental analysis and electronic spectra.[6] The surfactant AOT (Fluka) and n-heptane (Fluka) were used without further purification.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Table 2 Hydrodynamic diameters, d(nm) of water/AOT/n-heptane reverse micelles for various water/AOT concentrations

w	d [AOT], mol/kg			
	0.1	0.2	0.3	0.4
10	7	8	9	9
20	10	11	10	13
50	27	–	29	–

The kinetics of aquation were followed spectrophotometrically (SPECORD M40, Zeiss Jena) by measuring the absorbance changes at $\lambda = 260$ nm. To be sure that the kinetics of aquation do not differ from those in normal aqueous solutions the spectra were recorded throughout the reaction. The rate constants were evaluated by the time lag method[10] not requiring the knowledge of the absorbance at the end of the reaction:

$$k = \ln |S| / \tau$$

where S denotes slope of the straight line $A_{t+\tau}$ vs A_t. The rate constants are from at least three independent experiments.

A typical experiment was done as follows. A stock solution of AOT in n-heptane (1 mol/kg) was prepared by weight. Less concentrated AOT solutions were obtained by diluting this stock solution. The complex β-cis-[CoCl$_2$(trien)]Cl (0.45 mg) was dissolved in 10^{-3} mol/dm^3 HClO$_4$ (1 ml) and 200 μl of this solution was immediately injected by microsyringe into the thermostatted micellar solution. After short sonication (10 – 30 s) in the ultrasonic generator TESLA UC 005 AJ 1 with output of 30 W at 50 kHz frequency, the turbid solution had changed to a perfectly clear solution and the measurements could start.

Dynamic light scattering experiments were performed with a Brookhaven Instruments light scattering goniometer BI-200SM using a BI-2030 AT correlator and 514.5 nm radiation from an Ar ion laser. The autocorrelation functions were analyzed by the cumulant method[11] and the CONTI software. The size of reverse micelles (the hydrodynamic diameter) has been evaluated from the Stokes-Einstein equation. The measurements were recorded at room temperature. The samples for the scattering measurements were centrifuged at 1000 rpm for about 1 h.

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