Aquation of α-cis-$[CoCl_2(edda)]^-$ and of β-*cis*-$[CoCl_2(trien)]^+$ in cationic and anionic reverse micelles

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The aquation of α-*cis*-$[CoCl_2(edda)]^-$ and of β-*cis*-$[CoCl_2(trien)]^+$ has been studied in reverse micelles of water/AOT/*n*-heptane and water/CTAB/*n*-heptane+$CHCl_3$ for various concentrations of water and AOT at 298.1 K. The reaction rate depends on the molar ratio *W* as well as on the concentration of AOT. These results demonstrate the important effect of micelle size as well as of structure and state of confined water in the aquation rate.

Keywords: aquation, Co(III) complex ion, reverse micelle, AOT, CTAB, dynamic light scattering

Surfactants such as anionic sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and cationic cetyltrimethylammonium bromide (CTAB) can spontaneously form reverse micelles in nonpolar solvents. Reverse micelles may be a useful model for studying reactions in confined environments as they can solubilise relatively large amounts of water, other polar solvents and electrolyte solutions in the hydrophilic core. Numerous studies[1-4] have shown that the structure and dynamics of water in reverse micelles differ from that of bulk water. There are two or three distinct coexisting types of water in the interior of the micelle: bound water at the ionic layer, free water at the centre behaving as bulk water and trapped water within the ionic layer. The properties of encapsulated water strongly depend on the water-to-surfactant concentration ratio $W = [H_2O]/[AOT]$. The change of water state by solubilising in the reverse micelles should result in the aquation rate. In the present work we investigated the effect of micelle size and surfactant concentration on the aquation of α-*cis*-$[CoCl_2(edda)]^-$ (edda = ethylenediamine-N,N'-diacetic acid) and of β-*cis*-$[CoCl_2(trien)]^+$ (trien = triethylenetetraammine). In both cases, the aquation proceeds *via* an I_d mechanism with total retention[5] of configuration, accompanied by loss of the chloride ligand and giving as reaction products nonionic α-*cis*-$[CoCl(edda)(H_2O)]$ and β-*cis*-$[CoCl(trien)(H_2O)]^{2+}$, respectively. The reaction rate is independent of the acid concentration in the range $1.0 > [H^+] > 10^{-4}$ mol dm^{-3}.

The complex ions were found[6] to be preferentially solvated by water, so it can be assumed to occur in the water pools of reverse micelles and out of the hydrophobic chains of surfactant. They are easily soluble even in the very low amount of water solubilised in the micelle, forming solutions of appropriate concentration suitable for spectrophotometric measurements.

Results and discussion

The aquation of α-*cis*-$[CoCl_2(edda)]^-$ and of β-*cis*-$[CoCl_2(trien)]^+$ has been studied in reverse micelles of water/AOT/*n*-heptane for w varying from 1 to 40 or 50, respectively with AOT concentrations from 0.1 to 0.5 mol kg^{-1} as well as in reverse micelles of water/CTAB/*n*-heptane+$CHCl_3$ (50:50 vol.%) for w varying from 1 to 30 with 0.1 mol dm^{-3} CTAB at 298.1 K. In order to supress the base hydrolysis, the reactions of Co(III) complexes with the water are studied at $[H^+] \geq 10^{-3}$ mol dm^{-3}. In our case it was 10^{-3} mol dm^{-3} $HClO_4$, *i.e.* the lowest possible concentration, to be sure that in the whole concentration interval of surfactants and for all *W* there would be no problem with solubilisation in the micelles.

The corresponding rate constants, together with their mean deviations, are listed at Table 1. The concentration of complex refers to the entire micellar system while the concentration of $HClO_4$ refers to the aqueous phase in the core of the micelle and were the same in all experiments. The concentrations of AOT and CTAB refer to the organic phase not to the entire solution.

Figure 1 shows the effect of concentration of AOT and solubilised water on the reaction rate for α-*cis*-$[CoCl_2(edda)]^-$. For constant AOT concentration the rate constant goes through a maximum and decreases sharply at low *W*. On increasing the size of micelles with the amount of solubilised water the rate constants approached the value in bulk water. The inset of Fig. 1 shows the rate constants of aquation in 0.1 mol dm^{-3} CTAB as a function of *W*. The rate constants are lower than those in AOT reverse micelles. Similar behaviour was observed for the aquation of β-*cis*-$[CoCl_2(trien)]^+$ (Fig. 2). Evidently the charge of complex ions does not play a determining role in the studied systems. As found previously[6] both reactants are preferentially solvated by water so there is no reason to suppose that the aquation does not take place in the aqueous core of micelle.

Although the ionic strength of the water phase has changed by encapsulation in reverse micelles this need not play the determining role in increasing the reaction rate. Previous studies[7] on the primary kinetic salt effect showed that the aquation of Co(III)–amine complex ions had been influenced by ionic strength (up to 1.2 mol dm^{-3}) negligibly or to a much less extent than the reactions between ions. The observed specific effect of various anions has been explained by their action on the water structure. The comparison of rate

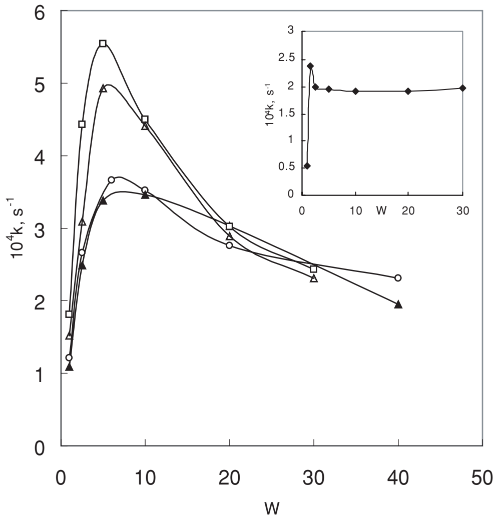

Fig. 1a Plots of rate constants *k* versus *W* for the aquation of α-*cis*-$[CoCl_2(edda)]^-$ in water/AOT/n-heptane at 298.1 K for various concentration of AOT: ○ – 0.1, ▲ – 0.3, □ – 0.4, △ – 0.5 mol kg^{-1}. Inset: Plot of rate constants versus *W* in water/0.1 M CTAB/*n*-heptane-chloroform

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Table 1 Rate constants of the aquation of (a) α-*cis*-$[CoCl_2(edda)]^-$ (b) β-*cis*-$[CoCl_2(trien)]^+$ in water/AOT/*n*-heptane and water/CTAB/*n*-heptane+$CHCl_3$ reverse micelles at 298.1 K: [complex a] = 9.25×10^{-5} mol dm^{-3}, [complex b] = 7.7×10^{-5} mol dm^{-3}, $[HClO_4]$ = 1×10^{-3} mol dm^{-3}

			10^4 k, s^{-1}			
			[AOT], mol kg^{-1}			[CTAB], mol dm^{-3}
W	0.1	0.2	0.3	0.4	0.5	0.1
(a) *k* (water) =(2.11 ± 0.07) × 10^{-4} s^{-1}						
1	1.21 ± 0.02		1.09 ± 0.02	1.81 ± 0.02	1.52 ± 0.02	0.545 ± 0.034
1.5					2.09 ± 0.01	2.39 ± 0.01
2.5	2.66 ± 0.05		2.49 ± 0.02	4.43 ± 0.05	3.09 ± 0.12	1.99 ± 0.05
5	3.66 ± 0.00		3.38 ± 0.01	5.54 ± 0.26	4.93 ± 0.02	1.95 ± 0.03
10	3.52 ± 0.05		3.46 ± 0.14	4.50 ± 0.14	4.41 ± 0.03	1.92 ± 0.05
20	2.76 ± 0.09		3.03 ± 0.02	3.02 ± 0.04	2.89 ± 0.01	1.91 ± 0.03
30				2.43 ± 0.05	2.31 ± 0.06	1.98 ± 0.04
40	2.31 ± 0.18		1.95 ± 0.01	1.97 ± 0.01	1.97 ± 0.01	
(b) *k* (water) = (0.713 ± 0.006) × 10^{-3} s^{-1}						
1	0.578 ± 0.028	0.535 ± 0.010	0.309 ± 0.010	0.499 ± 0.15	0.387 ± 0.012	0.271 ± 0.012**
2.5	1.26 ± 0.03	1.93 ± 0.04	1.06 ± 0.04	1.86 ± 0.04	1.03 ± 0.05	0.884 ± 0.048*
5	2.62 ± 0.12	3.41 ± 0.14	2.22 ± 0.07	4.40 ± 0.11	2.49 ± 0.05	1.38 ± 0.10
10	3.36 ± 0.11	3.57 ± 0.18	3.52 ± 0.16	5.35 ± 0.11	3.42 ± 0.15	1.02 ± 0.01
15						0.938 ± 0.039
20	2.50 ± 0.14	2.77 ± 0.13	2.08 ± 0.06	3.06 ± 0.11	2.24 ± 0.11	0.732 ± 0.011
30	1.83 ± 0.04	2.09 ± 0.05	1.50 ± 0.01	1.62 ± 0.05	1.51 ± 0.05	0.624 ± 0.034
40	1.09 ± 0.05	1.38 ± 0.05	0.967 ± 0.000	1.13 ± 0.02	1.03 ± 0.05	
50	0.743 ± 0.014	0.851 ± 0.019	0.726 ± 0.015	0.793 ± 0.034	0.792 ± 0.003	

*W = 4; **W = 3.

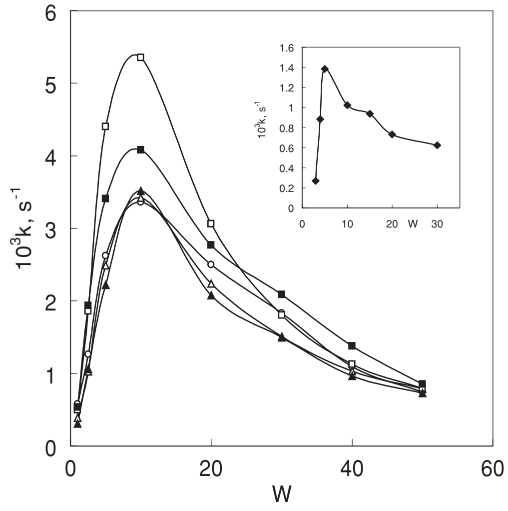

Fig. 2 Plots of rate constants *k* versus *W* for the aquation of β-*cis*-$[CoCl_2(trien)]^+$ in water/AOT/*n*-heptane at 298.1 K for various concentration of AOT: ○ – 0.1, ■ – 0.2, s – 0.3, □ – 0.4, △ – 0.5 mol kg^{-1}. Plot of rate constants versus *W* in water/0.1 M CTAB/*n*-heptane-chloroform.

constants for aquation in aqueous bulk and in reverse micelles might confirm this opinion: Rate constants of the aquation of α-*cis*-$[CoCl_2(edda)]^-$ and of β-*cis*-$[CoCl_2(trien)]^+$ at the foot of Table 1 are for $I = 0.0011$. If the ionic strength I^* calculated according to the equation given in ref. 8 can be taken as the ionic strength for the aqueous core of AOT reverse micelle, the rate constants $k_a = 2.31 \times 10^{-4}$ s^{-1} and $k_b = 0.743 \times 10^{-3}$s^{-1} at $W = 50$ correspond to $I^* = 1.11$, *i.e.* the rate constants at the two different ionic strengths do not practically differ.

The plots of rate constants *vs W* seem to reflect the effect of micelle size and of the state of water confined in the core of the reverse micelles. The size of reverse micelles in water/AOT/*n*-heptane and in H_2O/CTAB/*n*-heptane+chloroform increases with the molar ratio *W*. The hydrodynamic diameters of 0.1 M CTAB micelles in *n*-heptane+chloroform (50:50 vol.%) for various *W* are listed in Table 2. The data are described by the linear equation:

$$\text{hydrodynamic diameter/nm} = (3.18 \pm 0.09) + (0.89 \pm 0.01)\,W$$

Table 2 Hydrodynamic diameters, *d*(nm) of water/CTAB/*n*-heptane+chloroform reverse micelles for 0.1 M CTAB and for various *W*

W	0	1	2.5	5	10	20	30
d, nm	3.0	4.0	5.5	8.0	12.0	21.0	30.0

The size of reverse micelles in H_2O/AOT/*n*-heptane determined previously[9] are in good accordance with published ones.[10] The hydrodynamic diameters did not change linearly with *W* and were nearly half of those of CTAB at $W \geq 5$. The size of cationic as well as anionic micelles has not been changed by the solubilised reactant.

The motion of water molecules is strongly affected on decreasing the size of the micelles. The IR spectra[1-4] of water within AOT/*n*-heptane micelles agree well with a two-stage model based on the existence of bound and free water. At low *W* the solubilsed water exists mainly as bound molecules at the ionic layer of the micelles with static and dynamic properties determined by local interactions with Na^+ counterions and strong dipoles of polar headgroups of AOT. With increasing *W* excess water occupies the core of micelles. In larger micelles the state of water is almost identical to that in bulk. Although this qualitative picture has been generally accepted, there is not perfect accordance in quantitative determination. The critical value W_c – the value at which the water with the properties of bulk appears in the micelles – has been determined from the estimation of relative amounts of free and bound water in the micelles as a function of *W*. This value changes from 2 to 8 depending on the method used. Molecular dynamics simulation of the core of aqueous AOT reverse micelles indicated[11] the existence of three structural regions of water. At $W = 4$ the aqueous pool of the micelle is composed of almost equal fractions of free, bound and trapped water. At $W < 4$ the bound water prevails.

The close similarity of the chemical shift of the water proton in CTAB[12] and AOT[4] reverse micelles indicates that the extent of bound water, rather than the nature of the surfactant, may determine the physical properties of confined water. The value of the molar ratio *W* at which the water with the properties of bulk begins to prevail in the AOT reverse micelles falls on two-fold size of CTAB micelles. Therefore the comparison of aquation rate of α-*cis*-$[CoCl_2(edda)]^-$ in reverse micelles formed with cationic or anionic surfactant reveals that the rate constants in CTAB reverse micelles are closer to that in bulk water at lower *W* than to those in AOT.

In the aquation of α-*cis*-$[CoCl_2(edda)]^-$ and of β-*cis*-$[CoCl_2(trien)]^+$ the reaction rate depends not only on *W* but also on the AOT concentration. The distinctive change in rate constants with the [AOT] has been observed at the maxima on the plots *k vs W*. The explanation of this effect is not simple. It may be related to the aggregation number, as the size of micelles changes slightly with increasing [AOT] at constant *W* but the aggregation number increases[10]: slightly from 68 for 0.1 M AOT to 71 for 0.2 M AOT and significantly to 486 for 0.5 M AOT. The aggregation numbers of CTAB[12] are much higher than that of AOT at the same W. Micellar interfacial structure – the surfactant polar headgroups and counterions – plays an important role[13] in immobilising water so the changes in the concentration of polar surfactant groups and counterions at the interface may result in the reaction rate.

Surprisingly the concentration of complex ion affected in some way the reaction rate. By comparing the rate constants from reference 9 with those in Table 1 and realising the difference given to the concentration, we see that the distribution of various amounts of complex ion between the micelles led to the different reaction rates. At the constant amount of complex ion equally distributed between all the micelles the reaction rate increases with decrease of the micelle size. The values of rate constants were higher than that obtained previously at constant concentration of complex ion in the aqueous phase when not only the size of micelles has changed but simultaneously also the amount of complex ion. In the redox reaction $S_2O_8^{2-} + I^-$ the authors[14] found that at constant concentration of the reactants referring to the total system and at constant molar ratio *W* there was a linear correlation between ln *k* and ln [AOT]. They explained it with the diminution of the concentration in the aqueous cores of the micelles and thus of the reaction rate. For the same reaction at constant aqueous phase concentration the reaction rate did not depend on AOT concentration. Although the aquation seems to be much more simple, the effect of [AOT] on rate constants was observed in both cases, but never such a linear correlation. At present an unambiguous explanation on the effect of the concentration of surfactant as well as of reactant does not exist.

The investigation of aquation of complex anion and cation in water pools of anionic AOT and cationic CTAB reverse micelles supported the idea that the change of water state by encapsulating in the core of the micelles may result in the aquation rate. For constant surfactant concentration the reaction rate increases with the decreasing radius of curvature, and goes through a maximum at the value W_c corresponding to almost equal amounts of free and bound water in the micelles. At $W < 5$ the water exists as completely bound and this immobilisation of water results in a sudden decrease of the aquation rate.

Comparison of the reaction rates in AOT and CTAB reverse micelles indicated the determining role of the size of these micelles and consequently of the amount of bound water and not the nature of surfactant.

Experimental

α-*cis*-$Na[CoCl_2(edda)]$ and β-*cis*-$[CoCl_2(trien)]Cl$ were synthesised by the literature method[5] and their purity checked by elemental analysis and electronic spectra[5]. Surfactant CTAB (Fluka) was recrystalised from acetone and dried at 60^0C. Surfactant AOT (Fluka), *n*-heptane (Fluka) and chloroform (Lachema, Brno – reagent grade) were used without further purification. Both surfactants were kept over P_2O_5 in a vacuum desiccator before use. The kinetics of aquation were followed spectrophotometrically (SPECORD M40, Zeiss Jena) by measuring the absorbance at 285 nm for α-*cis*-$[CoCl_2(edda)]^-$ and at 260 nm for β-*cis*-$[CoCl_2(trien)]^+$. 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 rates were calculated by the time lag method, which does not require 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. Even at *W*=1 there is a sufficient excess of water molecules in the micelle for the pseudo-first-order conditions of the reaction.

Micellar solutions were prepared on mixing and short sonication of a weighed amount of AOT and *n*-heptane or CTAB and mixture of *n*-heptane and chloroform (50:50 vol.%) . While the micellar solutions of AOT can be prepared in various concentrations and can solubilise large amounts of water, the cationic CTAB reverse micelles in *n*-heptane + chloroform (50:50 vol.%) are stable at $T = 298.1$ K only for 0.1 mol dm^{-3} concentration.

The reaction mixture was prepared by adding weighed amount of α-*cis*-$Na[CoCl_2(edda)]$ or β-*cis*-$[CoCl_2(trien)]Cl$ to an appropriate volume of the aqueous solution of $HClO_4$ and was immediately injected into the thermostatted micelar solution. After short sonication (10–30 s) in the ultrasonic generator TESLA UC 005 AJ 1 with an output of 30 *W* at 50kHz frequency, the turbid solution changed to a clear solution.

The size of water/CTAB/n-heptane+$CHCl_3$ reverse micelles were determined by the dynamic light scattering technique. The experiments were performed with Brookhaven Instruments light scattering goniometer BI-200SM utilising 136-channel BI-2030 AT correlator (fy Brookhaven Instruments Inc. – Holtsville, USA) and 514.5 nm radiation from an Ar ion laser (Lexel 95). The autocorrelation functions were analysed by the cumulant method[15] and the CONTIN software. The size of reverse micelles (the hydrodynamic diameter) has been evaluated from the Stokes–Einstein equation. The measurements were recorded at room temperature. All samples for the scattering measurements were centrifuged at 1000 rpm for about 30 minutes and filtered through filter (Anotop 10, Whatman) of 220 nm pores.

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References

1 G. Onori and A. Santucci, *J. Phys. Chem.*, 1993, **97**, 5430.
2 Q. Li, S. Weng, J. Wu and N. Zhou, *J. Phys. Chem.*, 1998, **102**, 3168.
3 D.S. Venables, K. Huang and C.A. Schmuttenmaer, *J. Phys. Chem. B,* 2001, **105,** 9132.
4 J.E. Boyd, A. Briskman, C.M. Sayes, D. Mittleman and V. Colvin, *J. Phys. Chem. B*, 2002, **106**, 6346.
5 (a) P.J. Garnett and D.W. Watts, *Inorg. Chim. Acta,* 1974, **8**, 293, 307; (b) A.M. Sargeson and G.H. Searle, *Inorg. Chem.*, 1967, **6**, 787, 2172.
6 O. Grančičová, *Transition Met. Chem.*, 1999, **24**, 115.
7 (a) V. Holba and O. Grančičová, *Collection Czech. Chem. Commun.* 1977, **42**, 819; (b) W.F. Cain and J.A. McLean, Jr., *Inorg. Chem.* 1965, **4**, 1416.
8 J. Casado, C. Izquierdo, S. Fuentes and M. L. Moyá, *J. Chem. Educ.* 1994, **71**, 446.
9 F. Fusek, O. Grančičová and D. Lath, *J. Chem. Res., (S)* 2003, 364.
10 H.B. Bohidar and M. Behboudnia, *Colloid Surf. A*, 2001, **178**, 313.
11 J. Faeder and B.M. Ladanyi, *J. Phys. Chem. B*, 2000, **104**, 1033.
12 (a) J. Lang, G. Mascolo, R. Zana and P. L. Luisi, *J. Phys. Chem.*, 1990, **94**, 3069; (b) P. DiProfio, R. Germani, G. Onori, A. Santucci, G. Savelli and C. A. Bunton, *Langmuir,* 1998, **14**, 768.
13 D. Pant, R.E. Riter and N.E. Levinger, *J. Chem. Phys.*, 1998, **109**, 9995.
14 (a) M.L. Moyá, C. Izquierdo and J. Casado, *J. Phys. Chem.* 1991, **95**, 6001; (b) P. Lopez, A. Rodriguez, C. Gomez-Herrera, F. Sanchez and M.L. Moyá, *J. Chem. Soc. Faraday Trans.* 1992, **88**, 2701.
15 D. Koppel, *J. Chem. Phys.*,1972, **57**, 4814.