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Note

Aquation of (Dimethyl sulphoxide)pentaamminecobalt(III) in Aqueous Cetyltrimethylammonium Bromide Solutions

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The rate of aquation of $[Co(NH_3)_5(DMSO)]Br_3$ was measured in solutions containing the surfactant cetyltrimethylammonium bromide (CTAB) over the concentration range 9.55×10^{-4} mol dm^{-3} to 0.450 mol dm^{-3}. This large change in CTAB concentration affected the rate very little and no significant amounts of $Co(NH_3)_5Br^{2+}$ were formed. It was concluded that, if Br^- counterions were concentrated in the microregions around the positively charged CTAB micelles, then there was no corresponding increase in the formation of $Co(NH_3)_5(DMSO)^{3+}$. Br^- ion-pairs in this region with subsequent $Co(NH_3)_5Br^{2+}$ formation.

For several years we have been interested in the effects of solvent composition on rates of inorganic substitution reactions. We have found[1] that the rate of aquation of $M(DMSO)^{3+}$ ($M = Co(NH_3)_5$ and DMSO = dimethyl sulphoxide) in ethanol-water-perchlorate media over a wide range of solvent compositions was independent of ionic strength and of the nature of the cation (H^+, Na^+, Mg^{2+}, Al^{3+}) in the perchlorate compound employed; it was dependent on the ClO_4^- concentration and on the ethanol: water ratio. Also, the activation enthalpy was independent of solvent composition within a small error of approximately 1 percent. This was interpreted to mean that increasing ClO_4^- and ethanol contents displaced water from the solvation shell of $M(DMSO)^{3+}$ increasing the extent of internal return of DMSO. Similar results were found in other mixed solvents[2]. Solvent interchange results for $M(OH_2)^{3+}$ and $M(DMF)^{3+}$, where DMF = dimethylformamide, were interpreted[3] in terms of a specific interaction between DMF molecules in coordinated and bulk phase sites. As an extension of these investigations it was of interest to study the aquation of $M(DMSO)^{3+}$ in solutions of a surfactant, cetyltrimethylammonium bromide (CTAB).

It has been found[4] that the rate of reaction (1) was dramatically increased

$$MCl^{2+} + Hg^{2+} + H_2O \rightarrow M(OH_2)^{3+} + HgCl^+ \qquad (1)$$

by the presence of 5×10^{-5} N polyvinylsulfonic (PVS) acid. The reason offered to explain this result was that the PVS concentrated the two cationic reactants

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in microregions surrounding the PVS polyions. To a significant degree micelles should function like polyions: the charged outer surface of a micelle (say, the positively charged outer surface of a CTAB micelle) should attract a high density of counterions (say, Br^- ions). Because[5] $M(DMSO)^{3+}$ forms ion-pairs with Br^- it is possible that in the microregions surrounding the micelles there would be increased ion-pair formation of $M(DMSO)^{3+}. Br^-$ with subsequent increased anation to form MBr^{2+}. Here we report the results of kinetic studies with $[M(DMSO)]Br_3$ in CTAB solutions.

RESULTS AND DISSCUSION

The rate of disappearance of $M(DMSO)^{3+}$ in these aqueous CTAB solutions was first—order for all solutions used. The observed first—order rate constants, k_{obs}, are listed in Table I as a function of surfactant concentration. The rate constants k_{obs} were independent of H^+ concentration so the latter was maintained constant at 0.010 mol dm^{-3}. It is seen that the k_{obs} show very little dependence on surfactant concentration although micelles are present[6]. The only reaction observed was the aquation of $M(DMSO)^{3+}$ as shown in reaction (2). There was, at most, only a small amount of MBr^{2+} formation. Had the ion-pairs concentrated in the micro-

TABLE I

Aquation Rate Constants for $[M(DMSO)]Br_3$ *in* CTAB *Solutions.* 1.00×10^{-3} mol dm^{-3} *Total* Co(III). 0.0100 mol dm^{-3} HBr.

CTAB/mol dm^{-3}	$t/^{0}C^{a}$	$10^4\ k_{obs}{}^{b}/s^{-1}$
	45.00	2.36
0.955×10^{-3}		2.36
2.52×10^{-3}		2.36
3.80×10^{-3}		2.40
4.94×10^{-3}		2.37
1.00×10^{-2c}		2.41^{c}
1.50×10^{-2}		2.40
3.00×10^{-2}		2.44
0.1000		2.44
0.2000		2.48
0.3000		2.50
0.4500		2.57
	35.00	0.609
3.797×10^{-3}		0.618
2.996×10^{-2}		0.620
0.2500		0.622
0.4000		0.626

[a] ± 0.05 °C

[b] All rate measurements performed in duplicate. Error in k_{obs} approximately 1 percent.

[c] An average of $k_{obs} = (2.30 \pm 0.20) \times 10^{-4}\ s^{-1}$ was obtained from 8 separate kinetic experiments employing a Beckman DU spectrophotometer with a cell compartment thermostated at (45 .0 ± 0.1) °C and a wavelength of 518 nm. These k_{obs} values have a larger error because of the much smaller absorbance change at 518 nm as compared to 290 nm.

$$M(DMSO)^{3+} + H_2O \rightarrow M(OH_2)^{3+} + DMSO \qquad (2)$$

regions around micelles there should have been a significant amount of MBr^{2+} formed. The reasons for this statement are: (1) MBr^{2+} undergoes solvolysis more slowly than $M(DMSO)^{3+}$ undergoes anation by Br^- [5] so that MBr^{2+} would accumulate in solution to some extent. (2) About 75 percent of the ion-pairs $M(DMSO)^{3+} \cdot Br^-$ in DMSO undergo anation by Br^- rather than solvent exchange[5]. In purely aqueous solutions about 20 percent of the ion-pairs $M(OH_2)^{3+} \cdot Br^-$ undergo anation since anation occurs at approximately one-fifth the rate of solvent exchange[7]. Therefore a minimum of approximately 20 percent of all ion-pairs formed in the microregions around CTAB micelles should be undergoing anation reactions and forming MBr^{2+} as product. Since we did not observe any singnificant MBr^{2+} formation throughout the reaction we must conclude that there was not a marked increase of ion-pairs in the microregions surrounding the CTAB micelles even if there was a high concentration of Br^- ions in these regions.

In aqueous solutions at 25 °C the formation constants[8] for the bromo-complex given by equation (3) is not markedly temperature-dependent and con-

$$K_f = \frac{[MBr^{2+}]}{[MOH_2^{3+}]\,[Br^-]} = 0.3 \qquad (3)$$

sequently would be expected to have approximately the same value at 35 and 45 °C. Since total bromide ion concentration was 0.013 mol dm^{-3}, only about 0.4 percent of MBr^{2+} at most would be expected to form unless kinetic control via ion-pair formation in regions of high Br^- concentration produced larger amounts of MBr^{2+}. This is substantially less than the approximately 1 percent of MBr^{2+} that could have been detected and explains the absence of MBr^{2+} in the reaction mixtures.

We were unable to study this reaction in reversed micelles since addition of benzene or toluene to the solutions produced precipitation.

EXPERIMENTAL

Materials. The $Co(NH_3)_5(DMSO)^{3+}$ complex in DMSO was prepared by the method of Mac-Coll and Beyer[9]. The bromide salt was prepared by addition of a saturated NaBr solution in methanol to the solution containing the freshly prepared $Co(NH_3)_5(DMSO)^{3+}$ ion. The purple crystals were washed with cold water, ethanol and ether and dried over silica gel. Analysis: Calculated for $[Co(NH_3)_5(DMSO)]Br_3$: Co, 12.75; Br, 51.90. Found: Co, 12.52 Br, 51.63. From thermogravimetric analysis: Calculated Co_3O_4, 17.4; Found, 18.2. All the rest of the chemicals were reagent grade.

Procedures. Most of the kinetic data were taken in aqueous media with a Unicam SP 500 spectrophotometer at a wavelength of 290 nm. The temperature of a reaction mixture was maintained within ±0.05 °C by a water bath. Plots of log $(A_t - A_\infty)$, where the A's are the absorbances at time t and infinite time, respectively, against time were linear for several half-lives. Kinetic measurements made at wavelength of 518 nm with a Beckman DU spectrophotometer having a thermostated cell compartment were not significantly different from the measurements made at 290 nm.

Analyses were made for $Co(NH_3)_5Br^{2+}$ formation by passing various reaction mixtures containing the surfactant, CTAB, at various stages of completion of the reaction through a Dowex 50W-X4, 100—200 mesh, column in hydrogen form which adsorbed the complex cations. The bromo-complex was readily eluted by 2 mol dm^{-3} $HClO_4$ but the aquo- and dmso-complexes were not. About 1% of bromo-complex could have been readily detected.

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SAŽETAK

Akvacija (dimetilsulfoksid)pentaaminkobalta(III) u rastvorima cetiltrimetilamonium bromida

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Mjerena je brzina akvacije [Co $(NH_3)_5$ (DMSO)] Br_3 u rastvorima koji su sadržavali površinski aktivnu supstancu cetiltrimetilamonium-bromida (CTAB) u području koncentracija od 9.55×10^{-4} mol dm^{-3} do 0.450 mol dm^{-3}. Ta velika promjena u koncentraciji CTAB vrlo malo je utjecala na brzinu i nisu bile stvorene znatnije koilčine $Co(NH_3)_5Br^{2+}$. Zaključeno je da, ako su se Br^- protujoni koncentrisali u mikropodručjima oko pozitivno nabijenih micela CTAB, onda nije bilo odgovarajućeg povećanja stvaranja jonskih parova $Co(NH_3)_5(DMSO)^{3+} \cdot Br^-$ u tom području uz naknadno stvaranje $Co(NH_3)_5Br^{2+}$.

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