Catalysis of Ionic Reactions by Micelles. Reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} in Sodium Alkyl Sulfate Solutions[1]

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Abstract: The Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ is strongly accelerated by micelles of sodium dodecyl, tetradecyl, and hexadecyl sulfate. The catalytic effect is observed below the critical micelle concentration as conventionally determined, probably due to micelle stabilization by the divalent reagent ions. Accelerations of the reaction rate by factors up to 140,000 were found. At high detergent concentrations the catalytic effect decreases since the reagent ions are distributed over a larger number of micelles. Added sodium perchlorate reduces the catalytic effect at low detergent concentration but is without effect if this concentration is high. Under optimum conditions, the catalytic efficiency of sodium alkyl sulfates for the reaction investigated increases on lengthening the alkyl chain and almost attains the catalytic power of poly(vinylsulfonate). When the detergent is in large excess over the reagent ions, it is a much less efficient catalyst than the polyion.

Reactions involving two ionic species may be accelerated or inhibited by very large factors in solutions containing charged micelles. Similar effects are observed in solutions of polyelectrolytes with polyions carrying a high density of ionized groups attached to the macromolecular chain backbone. Studies of such phenomena have been reviewed[2,3] but it seems that no attempt has been made to compare the efficiency of micelles and polyions in catalyzing the same chemical reaction.

Past work on catalytic effects in micellar solutions has concentrated on reactions of ionized organic reagents. In this case, the interpretation of the data is complicated since the interaction of the micelle with the reagents involves both Coulombic and hydrophobic forces. The importance of the latter may be illustrated by the observation that cationic micelles catalyze the reaction of cationic triphenylmethane dyes with hydroxyl ion,[4] implying that both reagents, although bearing charges of opposite sign, are being concentrated in the neighborhood of the micelles. To avoid this complication, we have chosen for the present investigation the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ since the interaction of these two compact ionic reagents with micelles may be assumed to involve mostly long-range electrostatic forces. The reaction was studied in micellar solutions of sodium alkyl sulfates, varying the length of the alkyl chain from C_{12} to C_{16} and the results were compared with those obtained previously for the same process in solutions of poly(vinylsulfonate).[5]

Results and Discussion

In the absence of micelle-forming additives, the second-order rate constant for the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ was found to be 0.13 ± 0.01 M^{-1} sec^{-1} at 25° at an ionic strength of 1.0 (*i.e.*, 1 M $NaClO_4$) in satisfactory agreement with the previously reported value of 0.116 ± 0.008 M^{-1} sec^{-1}.[6] Reduction of the ionic strength to 0.01 was found to decrease the rate constant to 0.024 ± 0.002 M^{-1} sec^{-1}. This decrease appears reasonable in the light of the Brønsted theory of the primary salt effect.[7] A quantitative comparison with theory would require, however, knowledge of the activity coefficient of the quadruply charged transition state complex at the two ionic strengths and this information is not available.

The effect of micelle-forming additives on the reaction rate was characterized most completely with sodium dodecyl sulfate (SDS). Figures 1 and 2 give doubly logarithmic plots of the factor by which the process was accelerated at the outset of the reaction as a function of the detergent concentration (compared to the detergent-free solution at the ionic strength of 0.01). The observations may be summarized as follows. Addition of 8×10^{-4} M SDS had little effect on the initial rate but an increase in the SDS concentration to 1.2×10^{-3} M led to a dramatic acceleration by about three orders of magnitude. (b) Further increase in the SDS concentration first led to a further acceleration of the reaction, but the reaction rate went eventually through a maximum and fell sharply at higher SDS concentrations. The SDS concentration corresponding to the largest catalytic effect was estimated as 2.5×10^{-3} and 4×10^{-3} M in solutions containing 10^{-5} and 2×10^{-5} M Hg^{2+}, respectively, and the largest acceleration factor observed was 42,000. (c) Addition of 0.01 and 0.03 M sodium perchlorate reduced substantially the reaction rate at SDS concentrations at which the catalytic effect was maximized. However, it had no effect on the threshold SDS concentration at which catalysis becomes significant and on the catalytic efficiency at high detergent concentrations. (d) The apparent second-order rate constant decreased with the progress of the reaction with SDS concentrations ranging from 1.2×10^{-4} to 4.8×10^{-4} M. This effect became less pronounced as the SDS concentration was raised (Figure 3); at higher detergent concentrations the reaction followed strictly second-order kinetics.

The sudden appearance of the catalytic effect at SDS concentrations above 8×10^{-4} M may be assumed to

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[2] (a) E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969); (b) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).

[3] H. Morawetz, *Advan. Catal.*, 20, 341 (1969).

[4] E. F. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, **81**, 4540 (1959).

[5] H. Morawetz and B. Vogel, *ibid.*, **91**, 563 (1969).

[6] C. Bifano, *Inorg. Chem.*, **7**, 908 (1968).

[7] J. N. Brønsted, *Z. Phys. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

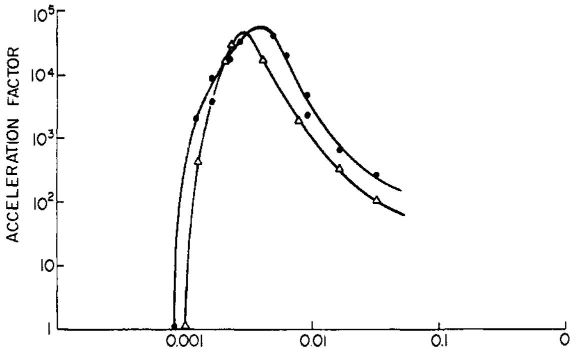

Figure 1. Catalytic effect of SDS: (△) 10^{-5} *M* Hg^{2+}; (●) 2 × 10^{-5} *M* Hg^{2+}.

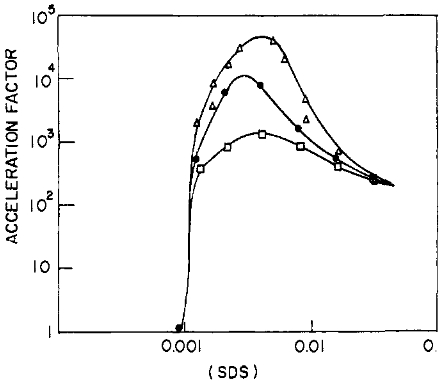

Figure 2. Catalytic effect of SDS: (△) no added salt; (●) 0.01 *M* $NaClO_4$; (□) 0.03 *M* $NaClO_4$.

be the result of micelle formation. Although the critical micelle concentration (cmc) of SDS has been reported to be 8.65 × 10^{-3} *M*,[8] *i.e.*, about an order of magnitude higher than the concentration producing the catalytic effect, it is reasonable to assume that the discrepancy can be accounted for by the stabilization of micelles in the presence of the reagent ions with a double positive charge.

The deviation from second-order kinetics observed in systems containing relatively low concentrations of the detergent can be thought of as a consequence of a competition between the doubly charged reagent ions and the triply charged $Co(NH_3)_5H_2O^{3+}$ reaction product for the counterion sites near the micellar surface. However, it must be noted that with an initial concentration of 5 × 10^{-6} *M* $Co(NH_3)_5Cl^{2+}$ the system contains, when the aquation has gone to completion, only 1.5 × 10^{-5} *N* reaction product. We must then explain why the inhibitory effect of this product should still be pronounced at SDS concentrations up to 4.8 × 10^{-3} *M*. The data seem to indicate that in this concentration range (lying below the normal cmc of SDS) the fraction of the dodecyl sulfate anions which can associate to micelle is limited by the requirement that a high proportion of the micellar charge be compensated by multivalent counterions. Thus, the concentration of micelles might be two orders of magnitude below the stoichiometric concentration of SDS, even in the concentration range where the catalytic effect of the micelles is pronounced.

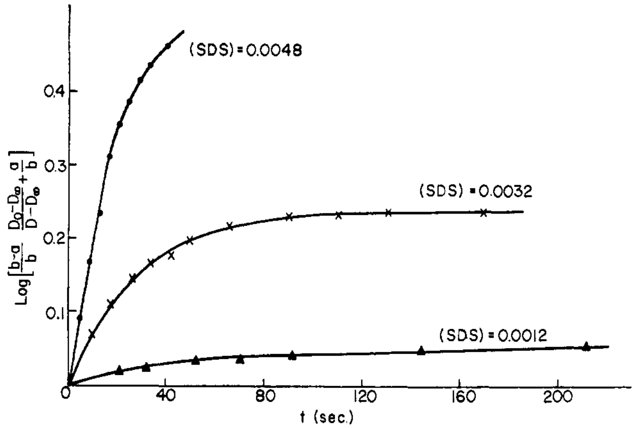

Figure 3. Deviation from second-order kinetics at low SDS concentrations.

The decrease in the catalytic effect at high SDS concentrations is reminiscent of a similar behavior when the reaction of Hg^{2+} with $Co(NH_3)_5Cl^{2+}$ is catalyzed by polyanions.[5] If this catalytic effect is a consequence of a concentration of the reagent ions in the vicinity of the micelles then, at micelle concentrations at which the counterion binding sites are in large excess over the concentration of the reagent ions, the local concentrations of these ions should be inversely proportional to the number of micelles among which the reagents have to be shared. This model would then predict a reaction rate inversely proportional to the micelle concentration under conditions where most of the reagent ions may be considered to have been captured by the micellar domains. The data plotted in Figure 1 show, however, that when the SDS concentration is increased beyond 4.8 × 10^{-3} *M* the reaction rate decreases much more rapidly than in proportion to 1/(SDS). For instance, with (Hg^{2+}) = 2 × 10^{-5} M^{-1}, an increase in the SDS concentration from 6.4 × 10^{-3} to 16 × 10^{-3} *M* leads to a reduction of the reaction rate by a factor of almost 40. We may note that here we are passing into the concentration range in which SDS will form micelles even in the absence of multivalent counterions and the rapid decay of the catalytic effect may, therefore, reflect a rapid increase in the concentration of micelles over which the reagent ions may be distributed.

This interpretation is also consistent with other features of the results. The maximum of the catalytic effect produced by polyions occurs when the binding sites in the polymer domain are approximately equivalent to the reagent ions.[5] The displacement in the maxima of the plots shown in Figure 1 is understandable in terms of the dependence of the concentration of Hg^{2+}-stabilized micelles on the stoichiometric Hg^{2+} concentration. Added electrolytes will provide shielding of the micellar charge and reduce the affinity of the reagent ions for the micelles. This will decrease the catalytic effect at low SDS concentrations but will not affect it when this concentration is sufficiently high to lead to the capture of virtually all divalent counterions by the micelles even in the presence of relatively high concentrations of univalent counterions.

Figure 4 compares results obtained with SDS, sodium tetradecyl sulfate (STS), and sodium hexadecyl sulfate (SHS). The STS data are similar to those obtained with SDS, but the maximum catalytic efficiency is somewhat

(8) H. C. Evans, *J. Chem. Soc.*, 579 (1956).

higher and occurs at a five-times lower detergent concentration. In the concentration range between the normal cmc values of STS and SDS, the former is the less efficient catalyst, presumably because of the higher micelle concentration. At very high concentrations the catalytic efficiency of the two detergents becomes very similar. Data obtained with SHS are much more limited because of precipitation at low detergent concentrations. However, the behavior of this detergent is quite consistent with that of the other two members of the homologous series.

Comparison of Catalysis by Sodium Alkyl Sulfates and by Poly(vinylsulfonate). In comparing the present results with a previous study[5] of the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ in poly(vinylsulfonate) solutions the following points may be made. (a) While polyion catalysis is observed even at extreme dilution of the polyelectrolyte, catalysis by detergent is limited to the concentration range in which stable micelles can be formed. (b) The maximum observed acceleration factors in the presence of the polyion were 1.76×10^5 and 5.8×10^4 if the only added electrolyte was 10^{-3} *M* $HClO_4$ or if 10^{-2} *M* $NaClO_4$ was also present. The corresponding values for catalysis by SDS are 4.2×10^4 and 7.9×10^3. The maximum catalytic efficiency increases with the chain length of the detergent and an acceleration factor as large as 1.4×10^5 was found with STS in 10^{-3} *M* $HClO_4$. When the detergent is present at high concentrations, *i.e.*, under conditions when most of the reagent ions may be considered bound to the micelles, the detergents are distinctly less effective catalysts then the polyion. For instance, in the presence of 0.03 *M* SDS and 0.01 *M* $NaClO_4$, the acceleration factor is 260 while extrapolation of the data of Morawetz and Vogel[5] for poly(vinylsulfonate) catalysis at the same salt concentration leads about to 1000-fold acceleration. This implies that concentration of the reagent ions at the micellar surface provides a less favorable reaction medium than concentration in the polyion domain.

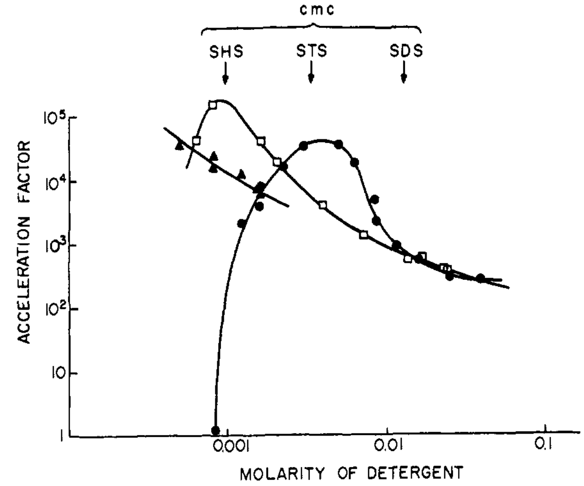

Figure 4. Comparison of catalytic effects of SDS (●), STS (□), and SHS (▲). The critical micelle concentrations are also indicated.

Experimental Section

Materials. Practical grade sodium dodecyl sulfate (Fisher Scientific Co.) was purified by the method of Duynstee and Grunwald.[4] Sodium tetradecyl sulfate and sodium hexadecyl sulfate were recrystallized from hot water. Chloropentaamminecobalt(III) perchlorate was prepared as reported previously[5] and was characterized by ϵ_{max} 1.88×10^4 at 229 nm. Analytical reagent grade mercuric perchlorate (Alfa Inorganic Co.) was used as the source of Hg^{2+}.

Rate Measurement. The reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} was determined at 35° by following the absorption at 230 mμ in a Cary-14 spectrophotometer. For slow reactions a 10-cm water-jacketed cell was used. Faster reactions were followed in a 1-cm cell in a water-jacketed holder, using a small magnetic stirrer for mixing the solution. All solutions contained 10^{-3} *M* $HClO_4$ and 5×10^{-6} *M* $Co(NH_3)_5Cl^{2+}$; the Hg^{2+} concentration was 2×10^{-5} *M* unless stated otherwise. The data were used to plot $[1/(b - a)] \ln [(b - a)(D_0 - D_\infty)/b(D - D_\infty) + a/b]$ as a function of time, where a and b are the initial concentrations of the reagents and D_0, D, and D_∞ are the optical densities at the outset of the reaction, at time t, and at the completion of the reaction. As specified in the text, many of the runs followed second-order kinetics to high conversion. Wherever the plots were curved, the initial apparent second-order rate constant was reported.