Catalysis in Micellar and Liquid-Crystalline Phases. I. The System Water–Hexadecyltrimethylammonium Bromide–Hexanol

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Abstract: The rate of hydrolysis of *p*-nitrophenyl laurate has been determined in liquid and liquid-crystalline phases in the system water–CTAB–hexanol. The reaction rates were of the same magnitude in the various phases. In the lamellar liquid-crystalline phase of the system a pronounced increase in reaction rate occurred within the phase at the same water content where nmr investigations show changes in water mobility and counterion binding.

The catalytic effect of micelles was demonstrated in 1959 by Duynstee and Grunwald[1] and their work has been followed by a steadily increasing number of investigations on the factors which govern the catalytic influence of normal micelles in aqueous solution. Extensive reviews have been published by Cordes and Dunlop,[2] by Morawetz[3] and by Fendler and Fendler.[4] The catalytic action of reversed micelles in a nonaqueous medium was recently displayed by us.[5]

It is well known that systems of surfactants, alcohol, and water contain liquid-crystalline phases in addition to the isotropic solutions.[6] The structure of these phases varies; hexagonal arrays of cylinders, lamellar structures, tetragonal arrays,[7] as well as more complicated associations[8] are known to exist.

Knowledge of these structures enables the influence on the reaction rate of different structural entities to be determined, since the location of reactants within the structure may be determined by means of X-ray diffraction and of molecular spectroscopy techniques. In spite of this fact no kinetic investigations have been performed in lyotropic liquid-crystalline phases. There have been one or two determinations in thermotropic liquid-crystalline phases including a Claisen rearrangement[9] and polymerization reactions.[10]

Under these circumstances it was deemed worth undertaking an exploratory investigation of the reaction rates in the different liquid-crystalline phases of a well-defined system. For this purpose the system water–hexadecyltrimethylammonium bromide–hexanol was chosen because one of the isotropic liquid phases of the system water–hexadecyltrimethylammonium bromide–hexanol was earlier used by us[5] for the demonstration of the catalysis by reversed micelles. Furthermore its phase equilibria and the structure of the different phases have been studied by different methods.[11,12] With regard to the existing knowledge of different factors a continued investigation in the same system was thus considered advantageous. Changes in hydrolysis rate of *p*-nitrophenyl laurate was used as a measure of the catalytic influence in order to facilitate comparison with earlier investigations.[1-3]

Experimental Section

Materials. Analytical reagents *p*-nitrophenyl laurate (Schuchardt, Muchen), 1-hexanol (Fluka, Switzerland), and cetyltrimethylammonium bromide (Merck, Germany) were used. The water was distilled twice and buffered to pH 11.05 with 0.1 *M* sodium phosphate buffer.

Reaction Rates. The reaction rate was followed from the formation of phenolate ion determined by the increase in extinction at 400 mμ by means of a Zeiss PMQII spectrophotometer. The thermostated cells had a distance of 0.2 mm. Initial concentration of *p*-nitrophenyl laurate was 5×10^{-4} *M* in all cases. The solutions were buffered at a pH of 11.05 with phosphate buffer.

The reaction rates were determined in the liquid and liquid-crystalline phases for a number of series with a constant alcohol–CTAB ratio. The phases were highly viscous and a special mixing procedure had to be applied in order to achieve reproducible results. Totally 1 g of the different components according to the actual composition minus equivalent weight of 0.2 ml of hexanol were mixed together and allowed to equilibrate during a 24-hr storage at 25°. Hexanol (0.2 ml) containing the amount of *p*-nitrophenyl laurate to achieve a total concentration of 5×10^{-4} *M* was then added under gentle mixing. The initial turbidity of the mixing disappeared after 2–3 min and the determinations of extinctions commenced.

The pseudo-first-order reaction rate constant was then determined in the usual manner from the slope of extinction *vs.* time. Since the water content varied considerably within each phase, second-order "rate constants" were calculated by division with the molar fraction of water.

Results

Reaction rates were determined in liquid-crystalline phases: the lamellar "neat" phase N, the "middle" phase M, and in the liquid phase L in the system (Figure 1). The hexanol–CTAB ratio was held constant within each series while the water content was varied.

Liquid Isotropic Phase L. The reaction rate constant in the liquid solution is shown as function of the water content in Figure 2. No difference in the rate constant was found when the alcohol–CTAB ratio was varied at water contents in excess of 90 wt %. Compositions containing less water showed a distinct decrease in reaction rate on increasing the relative alcohol content. The "apparent" second-order rate constant is shown in the same figure. The results gave an indication that the rate constant did not change with the water content within certain ranges.

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

(2) E. H. Cordes and R. B. Dunlop, *Accounts Chem. Res.*, **2**, 329 (1969).

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

(4) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).

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(6) A. J. Hyde, D. M. Langebridge, and A. S. Lawrence, *Disc. Faraday Soc.*, **18**, 239 (1954).

(7) L. Mandell, K. Fontell, and P. Ekwall, *Advan. Chem. Ser.*, No. 63, 89 (1967).

(8) P. Ekwall, *Mol. Cryst.*, **8**, 157 (1969).

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(10) A. Douy, R. Mayer, J. Rossi, and B. Gallot, *ibid.*, 7, 103 (1969).

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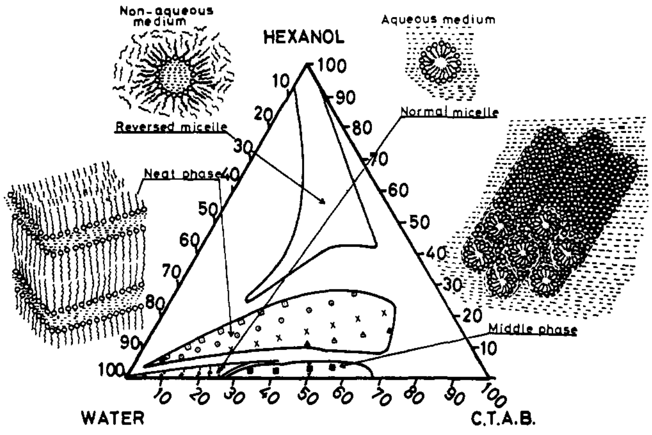

Figure 1. Regions and structure for the phases of the system water–cetyltrimethylammonium bromide–hexanol. The composition of the samples is marked.

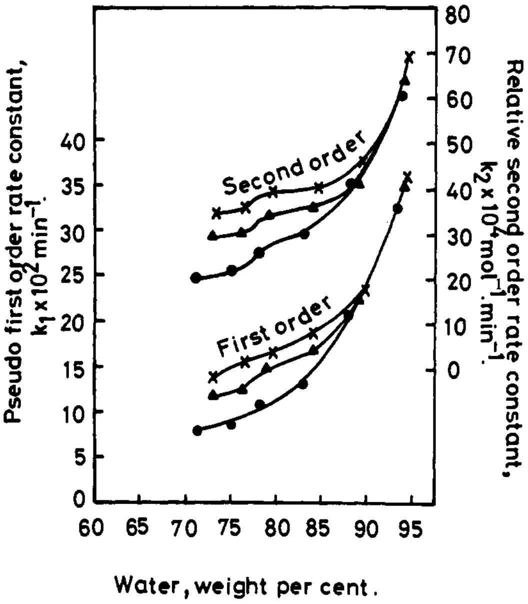

Figure 2. Reaction rates in the aqueous isotropic liquid phase L. The hexanol–CTAB ratios (w/w) were ×0.01 (×), 0.08 ()▲, and 0.13 (●).

Liquid-Crystalline Phase N. Figure 3 displays the variation of the corresponding rate constants for reactions in the liquid-crystalline phase N. All series give the same general pattern; the rate constant undergoes a pronounced increase when the percentage water is increased from 45 to 70 wt %. The second-order rate constant remained approximately unchanged at water contents above or below this range.

The reaction rate increased with the ratio alcohol to CTAB for all compositions. An increase by a factor of 3 may be observed when the ratio hexanol–CTAB was raised from 0.2 to 0.7 (w/w). In general the rates were higher in the liquid-crystalline phase than in the isotropic liquid solution L at the corresponding water content.

Liquid-Crystalline Phase M. This phase is extremely viscous and because of experimental difficulties only a few determinations of the reaction rates were performed. Figure 4 demonstrates an increase of the reaction rate when the water content was raised which is similar to the results obtained for the lamellar phase N. The rates are generally lower than for the liquid-crystalline phase N. On the other hand the second-order rate constant is increased compared to the results obtained in the isotropic liquid region L_1.

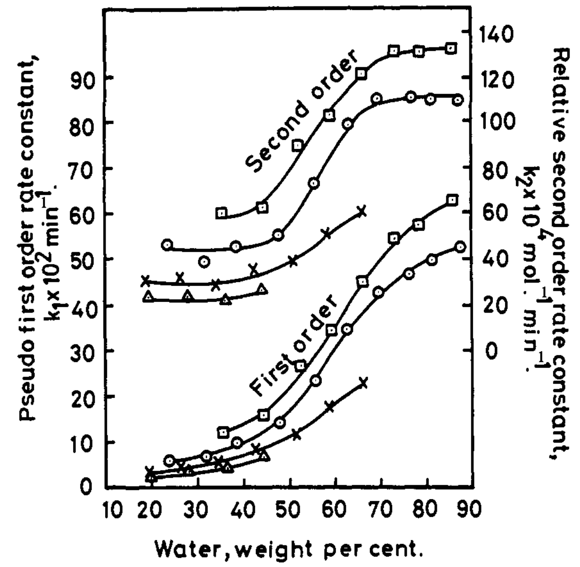

Figure 3. Reaction rates in the liquid-crystalline neat phase N. The hexanol–CTAB ratios (w/w) were 0.77 (□), 0.55 (○), 0.34 (×), and 0.23 (△).

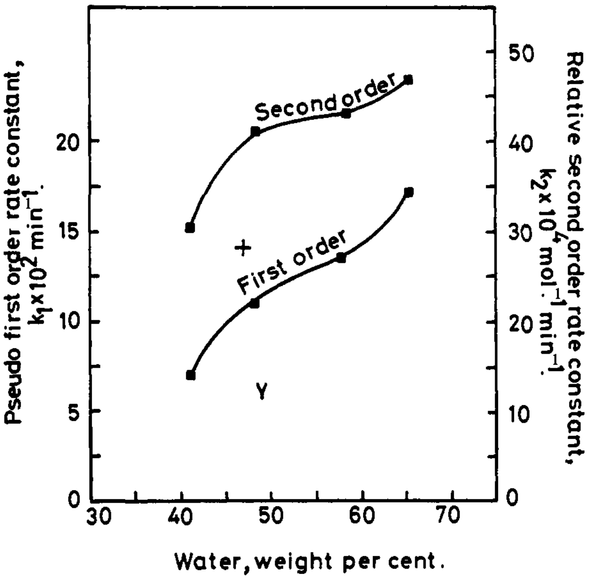

Figure 4. Reaction rates in the liquid-crystalline middle phase M. The hexanol–CTAB ratios (w/w) were 0.02 (Y), 0.06 (■), and 0.10 (+).

Nuclear Magnetic Resonance. The spin–lattice relaxation time T_1 was directly obtained with an accuracy better than 5%. The relaxation time increases smoothly from a value of about 100 msec at the lowest water content to ∼350 msec at the highest water content in the series (Figure 5). This behavior is expected since the relaxation generating mechanism is fast compared to the frequency 13.86 MHz.

The relaxation time T_2 could not be accomplished with corresponding directness or accuracy. In order to measure T_2 it is necessary to use a Carr–Purcell sequence[13]

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(13) S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **29**, 688 (1958).

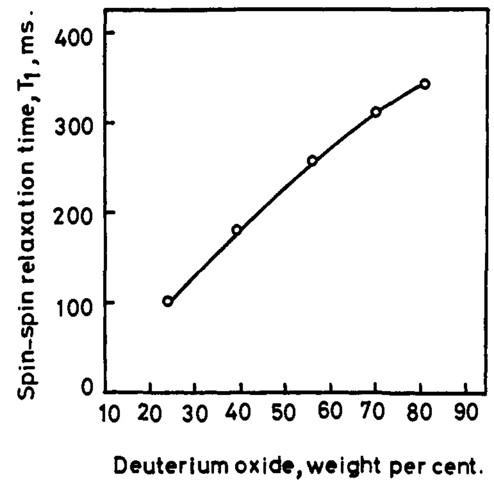

Figure 5. Deuterium spin–spin relaxation times in the liquid-crystalline neat phase. The hexanol–CTAB ratio was 0.55 (w/w).

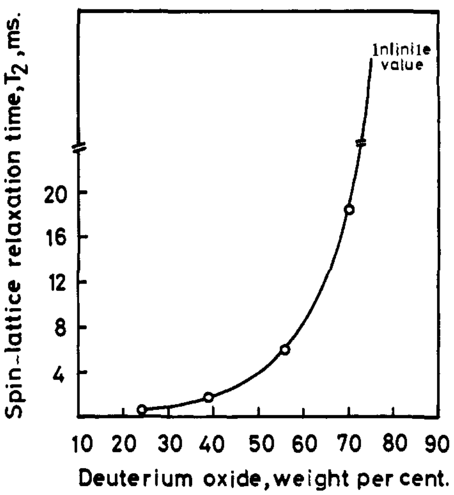

Figure 6. Deuterium spin–lattice relaxation times in the liquid-crystalline neat phase. The hexanol–CTAB ratio was 0.55 (w/w).

with pulse spacings less than T_2. This, however, is also the condition for obtaining dipolar echoes from a dipolar solid.[14] In the present case pronounced dipolar echo trains were obtained from the Waugh sequences with time constants close to those yielded by the Carr–Purcell sequences. Regarding this the only possibility to obtain information on T_2, appeared to be measurements of the decay preceding the dipolar echoes. These T_2 values could be determined for deuterium oxide contents lower than 70 wt %. Contents of deuterium oxide in excess of this value resulted in T_2 values so high that all feasible pulse spacings were much lower than T_2 and only the dipolar echoes could be observed. Figure 6 demonstrates the pronounced decrease of the T_2 values at water percentages of about 70 wt %.

Discussion

The results gave evidence of a catalytic effect of cationic substances associated into liquid-crystalline phases. The effect is comparable to the effect in micelles. They also gave evidence of the changes of the catalytic effect with structural changes of the associated substances.

Before discussing the results with relation to the conditions in the different phases the structures of the actual phases will be reviewed. In the system water–CTAB–hexanol[11] two liquid phases L_1 and L_2 and two liquid-crystalline phases M and N have been found. The two liquid phases contain "normal" (L_1) and "reversed" micelles (L_2). Phase M consists of cylinders with a hydrophobic core packed in a hexagonal array. Phase N forms a lamellar structure, where the hydrophobic parts of the surface active substance face each other. Figure 1 demonstrates the regions and the structures of the different phases. The present discussion will be confined to the dependence of reaction rate on the composition within each phase. The variation of reaction rate between different phases is presently studied using compositions in the different phases where equilibria between them is obtained.

Liquid Isotropic Phase L_1. A great deal of work on the enhancement of the reaction rates at the CTAB critical micelle concentration has been demonstrated earlier.[2-4] Recently, also the effect of micellar structural changes on the reaction rate has been mentioned[2] but no relationship with changes in micellar structure has been shown.

The critical micelle concentration of CTAB in aqueous solution is 0.99×10^{-3} M.[15] At concentrations in excess of this value the micellar structure changes with the concentration of surface active agent. The structure conditions in post micellar range in the system water–CTAB–hexanol has been studied by Lindblom[16] and Ekwall.[12] An examination of the reaction rates obtained in the present investigation in the light of the information on structures of micelles[12,16] shows a pronounced dependence of the reaction rate on variations in micellar structure. The pronounced decrease in the rate constant between 6 and 12% of the cationic surfactant was parallel to the increase in binding of counterions[16] in that range. At concentrations above 13%, counterion binding has been shown to be constant[16] and the reaction rate was also approximately constant. At 20% CTAB the reduction of the intensity of perpendicularly scattered light has been found[12] to increase. At that concentration the reaction rate suddenly dropped. These results demonstrated that rather small changes in micellar structure may give rise to a pronounced influence on the reaction rate.

No difference in reaction rate with the alcohol content was found at a water percentage of 94. This fact indicated that the alcohol–CTAB ratio does not influence the catalytic activity in this system prior to mutual micellar interaction which is sufficient to modify the shape of the micelles. When this is the case the alcohol–CTAB ratio has a distinct effect on the reaction rate. The precise mechanism for this influence is obscure but is certainly associated with the inclusion of the alcohol molecules in the micelles with their polar parts located at the micelle surface. This would presumably decrease the surface potential of the micelle.

Such a decrease of the surface potential would cause a reduction of the concentration of an activated complex ester–cationic surfactant–hydroxide ion. Considering that the formation of this complex has been envisioned

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[14] J. S. Waugh and C. H. Wang, *Phys. Rev.*, 162, 209 (1967).

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[16] G. Lindblom, B. Lindman, and L. Mandell, *J. Colloid Interface Sci.*, 34, 215 (1970).

as the rate-determining step in the catalyzed hydrolysis,[17] a reduction of the surface potential by a reduction of the charge density would certainly be expected to decrease the reaction rate. However, several factors connected with the specific structure at the surface may also have an influence and definite conclusions must await more detailed analysis of the situation.

Liquid-Crystalline Phases. The second-order rate constant, which accounts for the present fraction of water, rose when the liquid isotropic solution was transformed to the middle phase M. This is demonstrated by a comparison of the curve marked by triangles in Figure 2 with the rate constant denoted by squares in Figure 4. The reason for this is obscure; the form factor which is operative has yet to be evaluated.

In the phase N, on the contrary, a pronounced decrease of the rate constants was observed when reducing the water content in the same range. This behavior could be related to the bonding condition of the water molecules. Thus, the enhancement of reaction rate when the water content is increased above 45% was accompanied by a decrease of the ^{81}Br nuclear magnetic resonance line width.[14] The changed line width implies a reinforced hydration of the bromide ions accompanied by a decreased binding to the cationic group of the surfactant. Such a structure change will facilitate the formation of charged activation complexes in the vicinity of the polar layer which should enhance the catalytic effect.

Increased ratios of hexanol–CTAB gave rise to an increased reaction rate at all water concentrations in the lamellar phase. This fact may be connected with the position of the water molecules in the liquid-crystalline structure. The X-ray determinations by Ekwall[12] and Luzzatti[18] demonstrated that the distance change between polar groups *vs.* water content changed markedly with the amount of alcohol present. At low per cent alcohol alteration of water content does not cause much variation of the distance; at high alcohol content the distance varied linearly with the water content. The first result has been interpreted as due to the fact that all water molecules are situated around the polar groups within the amphiphilic layer. The corresponding interpretation of second result has given a localization between the amphiphilic layers.

This implies release of water molecules from the charged layers when alcohol is added to the liquid-crystalline phase. The release of water molecules would then be the basic reason for the reduction of ^{81}Br nuclear magnetic resonance line width when the hexanol–CTAB ratio is varied[16] since the release gives rise to enhanced hydration of the bromide ions and their transfer from the charged surfaces.

Comparing these results it appears highly probable that the alcohol molecules are substituted for water molecules in the charged layer. The excluded water molecules have a higher chemical potential than when in the amphiphilic layer. This is verified by the fact that the tie lines between the lamellar phase N and the phase L_1 are connected with compositions of lower water content in the latter phase,[12] which has a lower alcohol–CTAB ratio. Basically the increased chemical potential of the water molecules can be explained from the *hydrophobic* contributions to the bonds alcohol–CTAB; strong bonds between the polar parts of the two amphiphiles cannot be expected to release water at all.

The released water changes the properties of the system in the same manner as further addition of water (Figure 3). The water which is released from the polar parts of the layers enhanced the activity of the water molecules in the equilibrium $(OH^-)(H^+)/(H_2O) = K$, and since pH and with this (H^+) is kept constant by the buffer an increase of the activity of the water molecules gave rise to increased activity of the hydroxide ions. This mechanism serves as a reasonable explanation of the enhancement of the hydrolysis rate when alcohol is added to the system.

These investigations are continued with comparisons of the rate constants in compositions, where different phases are in equilibrium with each other. The increase of reaction rate when the system changes from liquid isotropic phase to the middle phase indicated the presence of "form factors" and these would be of high interest in connection with studies on the enzymatic mechanism.

Acknowledgment. The authors are grateful to Drs. L. Ödberg and T. E. Bull for their advice and experimental assistance in connection with the nmr determinations. The investigation was supported by Swedish Board for Technical Development.

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