

*Experimental.* The Raman spectra were recorded photographically on Ilford Backed Zenith plates with a Model E 612 Raman spectrograph from Hilger & Watts Ltd., London. The exposure times were 30 min.

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Received May 9, 1963.

## NMR-Experiments on Solubilization in Soap Micelles

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To date apparently no investigation has been reported in which the high-resolution NMR technique has been used for studying soap solutions containing micelles. In this communication, however, some findings will be described which indicate that such investigations may give valuable information concerning the nature and structure of micelles.

Fig. 1 displays the relevant parts of the NMR-spectrum of cetyl pyridinium chloride (CPC) when dissolved in water (a) and methanol (b) to equal concentrations

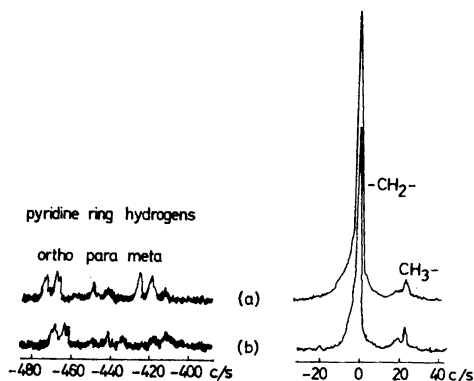


Fig. 1. The spectrum of cetyl pyridinium chloride (except the  $\alpha$ - $\text{CH}_2$ -peak) in water (a) and methanol (b).

(0.1723 M). In these solvents, the triplet of the  $-\text{CH}_2$ -group next to the pyridine ring ( $\alpha$ - $\text{CH}_2$ -) is concealed by the strong water and  $-\text{OH}$  resonance lines. The assignment of the pyridine ring proton peaks was carried out by comparison with the spectrum of methyl pyridinium iodide in water solution and with the thoroughly investigated spectrum of pure pyridine<sup>1</sup>. The critical micelle concentration of CPC in water is, according to the spectrophotometric measurements of Sata and Sasaki<sup>2</sup>,  $0.706 \times 10^{-3}$  M. Because micelles are not formed in methanol, and since a closer examination reveals that the  $-\text{CH}_2$ -peak areas in (a) and (b) are equal to within 2 %, the conclusion must be drawn that it is mainly the hydrogens of the soap molecules in the micelles which contribute to the signal intensity in the case of water solution. The fact that the resonance lines are not much broadened, due to the formation of micelles, may obviously be considered as a consequence of the commonly presumed liquid-like state of micelles in comparatively dilute solutions<sup>3,4</sup>, *i.e.* the interaction between the nuclear magnetic dipoles is effectively averaged as a result of the thermal relative motions of the paraffin chains. However, it may be questioned whether the observed line width could also be accounted for on assuming that the micelle is a microcrystallite, which reorientates under the influence of the thermal fluctuations. Accordingly, from the theory of spin-lattice relaxation given by Bloembergen, Purcell and Pound<sup>5</sup>,

the correlation time  $\tau_c$  for a rigid sphere with the diameter 40 Å turning in water was estimated to be about  $10^{-8}$  sec. Since this correlation time is somewhat larger than  $(2\pi\nu_c)^{-1}$ , we could then expect that the line width would be much broader than is usually found for liquids. The order of magnitude of this line width should be 2000 c/s but actually a line width of about 10 c/s was observed for the  $-\text{CH}_2$ -peak. Thus, since the order of magnitude of the predicted line width is significantly different from the observed, at least a simple micro-crystallite model appears to be inadequate. This conclusion is also confirmed by the fact that the  $-\text{CH}_2$ -line widths for dilute solutions containing micelles of sodium lauryl sulfate and sodium oleate are approximately the same as for the CPC solution, implying that the actual correlation time is almost independent of the hydrocarbon chain length. Moreover, only one resonance line is found for benzene and bromobenzene solubilizates which evidently may be attached to two nonequivalent sites, in the interior and at the surface of the micelles, showing that there is a rapid exchange of solubilizate molecules between these two sites (*cf.* below).

From Fig. 1 it appears that the chemical shift between the  $-\text{CH}_2$ - and pyridine ring hydrogens is larger in case (a) than in case (b). By using an external water standard and correcting for the bulk susceptibility difference, it was found that the ortho, meta and para hydrogens on the pyridine ring in (a) are displaced 2.0, 5.0 and 5.0 c/s, respectively, towards lower field and the  $-\text{CH}_2$ - and  $\text{CH}_3$ -hydrogens 3.4 and 4.4 c/s towards higher field relative to (b). In analogy with the situation usually encountered for liquid solutions, it may be supposed that the magnetic interaction between the aromatic pyridine rings in the micelle-water interface, yields an up-field shift contribution. Due to the presence of counter-ions in the Stern adsorption layer and to the electrostatic repulsion between the charged head-groups, the distance between the pyridine rings is presumably rather large so that the shift in question is likely to be comparatively small. However, it is evident that an additional effect is operative which produces down-field shifts for the hydrogens at the hydrophilic group of the CPC molecule. Although the field intensity in the electric double layer at the micelle-water interface may amount to  $10^6$  V/cm we cannot expect to observe

shifts caused by the direct action on the hydrogens of this electric field. Because, from the treatment given by Marshall and Pople<sup>6</sup>, the following formula results for the shift of a free hydrogen atom due to a homogeneous electric field  $E$

$$\delta = -\frac{881 a^3 E^2}{216 m_e c^2}$$

where  $a$  denotes the Bohr radius and  $m_e$  the electron mass. According to this equation the shift,  $\delta$ , would be about  $-10^{-5}$  ppm ( $= -0.6 \times 10^{-3}$  c/s) for  $E = 10^6$  V/cm. The conclusion that the electric field in question (which may be altered significantly by varying the ion strength in the soap solution<sup>7</sup>) has a negligible influence on the relative peak positions was confirmed by measurements on CPC dissolved in NaCl solutions of different salt concentrations. Consequently, an indirect action of the double layer field, *e.g.* through polarization of the  $\pi$ -electrons in the pyridine rings also appears to be of minor importance. It is therefore reasonable to postulate that the relative down-field shifts in (a) are mainly caused by the polarization due to the water molecules and the hydrated counter-ions which surround the ionic soap molecule head-groups in the micelle-water interface. The shifts towards higher field for the  $-\text{CH}_2$ - and  $\text{CH}_3$ -groups obtained as a result of micelle formation should probably be attributed to a change in intermolecular interaction.

When benzene or bromobenzene is solubilized in CPC solution characteristic resonance line shifts occur which have been plotted in Fig. 2 as functions of the solubilizate/soap molar ratio. All peaks are displaced towards higher field, as might be expected, because of the large diamagnetic contribution to the local magnetic field of the anisotropic benzene rings. However, the rates of displacement are of notably different magnitudes so that the shifts of the CPC hydrogens in the micelle surfaces are much larger than the shifts of the CPC hydrogens in the interior of the micelles. (The total dilution shifts for the meta and para hydrogens on the pyridine ring when solubilizing benzene are approximately the half of the corresponding shift for the ortho-hydrogens). The simultaneous water peak shifts, measured against an external chloroform standard, are small, amounting to 0.4 and  $-0.2$  c/s for the highest benzene and bromobenzene concentrations relative to

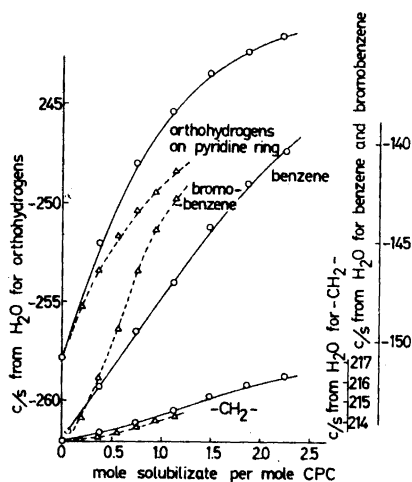


Fig. 2. Resonance line shifts due to solubilization of benzene (o) and bromobenzene ( $\Delta$ ) in 0.1723 M CPC solution relative to water as internal standard.

the pure CPC solution. These shifts can be ascribed mainly to the small changes in magnetic susceptibility obtained on adding the solubilizates. When methyl iodide or cyclohexane is solubilized in CPC solution, much smaller dilution shifts of the CPC hydrogens are generally produced, the order of magnitude being  $-1$  c/s for the saturated solutions relative to the pure soap solution. Moreover, the observed dilution shifts are then not much dissimilar for hydrogens in different positions. An interesting feature which appears from Fig. 2 is that the extrapolated benzene and bromobenzene line positions at zero concentration are  $-155.0$  and  $-156.0$  c/s, whereas for benzene and bromobenzene in cyclohexane the corresponding values, corrected for the bulk susceptibility difference, are  $-147.5$  and  $-144.0$  c/s. For solubilized cyclohexane the extrapolated resonance line is at  $205.3$  c/s and for pure cyclohexane the corrected line position is  $199.2$  c/s, relative to the internal water standard, *i.e.* in this case we have a shift in the opposite direction, towards higher field, for the solubilizate.

All these findings indicate that the aromatic solubilizates, benzene and bromobenzene, are solubilized to a large extent

in the micelle-water interface. This conclusion gives experimental support for the corresponding assumption stated by other investigators, in order to account for the anomalous viscosity maximum<sup>8</sup> and the ultracentrifugal pattern<sup>9</sup>, observed for polysoap and CPC solutions on solubilizing benzene, toluene, chlorobenzene and trichlorobenzene. The downfield shifts for benzene and bromobenzene at zero concentration in CPC solution, relative to cyclohexane solution, may thus be accounted for by considering that the major portion of these solubilizates is attached to the micelle surface, where the benzene rings are electrically polarized by the ionic groups and the water molecules\*. It would then also be required that this effect is more important than the magnetic interaction with the aromatic pyridine rings which probably produces an up-field shift. For cyclohexane the corresponding shift is towards higher field, *i.e.* in the same direction as for the paraffin chains due to micelle formation, showing that the state of solution in a CPC micelle is different from that in cyclohexane.

Although the experimental material presented here is incomplete, it is tempting to speculate on the mechanism responsible for the preferential attachment of the aromatic solubilizates to the micelle surface. This behaviour is presumably connected with the aromatic property, *i.e.* the easily polarized  $\pi$ -electrons of the benzene rings. It is possible that a specific interaction can be established through formation of a charge transfer complex with the aromatic solubilizate and the ionic pyridine group. However, Snyder<sup>10</sup> has recently shown that in most cases the mechanism of adsorption of unsubstituted aromatic hydrocarbons on alumina does not involve the formation of charge transfer complexes. Instead, this adsorption is ascribed to the polarization caused by the adsorbant surface. In order to gain a better insight into these and related questions, further studies are required where different aromatic solubilizates, hydrophilic soap

\* The solubility of benzene in pure water at  $25^\circ\text{C}$  is  $1.79$  g/l<sup>11</sup>, implying that about 94 % of the total amount of dissolved benzene is solubilized by the CPC micelles. The corrected peak position for benzene in water is  $-163.0$  c/s. Thus, the water-dissolved benzene presumably gives a minor contribution to the observed mean resonance frequency for benzene.

molecule head-groups and counter-ions are employed.

*Experimental.* The measurements were made at 31°C on a Varian A-60 spectrometer, equipped with a Hewlett Packard 202A audio oscillator and a Hewlett Packard 5512A electronic counter. The chemicals used in the reported measurements were of reagent grade except for cetyl pyridinium chloride which was of *purum* grade (m.p. 79–81°C) obtained from Kebo AB, Stockholm. The required magnetic volume susceptibility values were calculated from the data compiled by Foëx<sup>12</sup>.

*Acknowledgements.* Drs Erik Forslind and Gunnar Aniansson are thanked for their kind interest in this investigation and for helpful discussions. The cost of the NMR-apparatus has been defrayed by a generous grant from the *Knut and Alice Wallenberg foundation*.

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Received May 16, 1963.

## Kinetics of the Alkaline Hydrolysis of 3-Acetoxy-quinuclidine Hydrochloride and Methiodide

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It has been observed that esters of the structure dialkyl-NR(CH<sub>2</sub>)<sub>n</sub>OCOCH<sub>3</sub>, V,  $n = 2$  or  $3$ , are 20–30 and 10 times, respectively, more rapidly hydrolyzed in alkaline solution when R=H than when R = alkyl<sup>1</sup>. The pH-dependence of the reaction rate can be explained either as a first order reaction of the amine form of the ester where the rate determining step should be the formation of a cyclic intermediate, I, or a reaction with hydroxyl ions under catalysis by an intramolecular hydrogen bond, II. By varying the alkyl groups it was possible to show that the latter mechanism is the most likely one<sup>1</sup>. In the present communication the rates of the alkaline hydrolysis of the hydrochloride, III H, and the methiodide, III Me, of 3-acetoxy-quinuclidine, are reported. In III H both intramolecular hydrogen bonding and the formation of an intermediate resembling I are impossible for steric reasons.

3-Quinuclidinol, prepared according to Sternbach's and Kaiser's method<sup>2</sup>, was dissolved in ethanol and neutralized with HCl. The solvent was evaporated under vacuum at room temperature. The solid residue dissolved when refluxed for 1 h in acetyl chloride. After a further half hour the excess of acetyl chloride was evaporated. The residue, recrystallized from anhydrous ethanol/ligroin 3:7, was III H. (Found: C 52.4; H 7.70. Calc. for C<sub>9</sub>H<sub>16</sub>ClNO<sub>2</sub> (205.7): C 52.6; H 7.84).

3-Acetoxy-quinuclidine, prepared according to the method reported by Grob *et al.*<sup>3</sup>, was dissolved in acetone and excess methyl iodide was added. The crystals of III Me formed in 24 h were recrystallized from anhydrous ethanol/acetone 1:1. M.p. 165°. Grob *et al.*<sup>3</sup> found m.p. 165–166°.

The kinetic experiments were carried out using a pH-stat and were run in 0.07 M

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