NMR-measurements on ^{81}Br$^-$-Counterions in Micellar Solutions

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During the last few years several investigations of micellar solutions have been reported which are based upon the application of high resolution NMR-spectroscopy.[1-4] In the present communication we shall briefly discuss some results obtained in a preliminary wide line NMR-study of Br$^-$-counterions in solutions of cationic surfactants. The ion-water interactions are obviously of great importance for the properties of solutions of micelle-forming substances but, unfortunately, the actually available knowledge regarding the details of the interaction between the ionic heads of the micelle-forming molecules, the surrounding water molecules and the counterions at the micelle-water interface is rather restricted. In this context it is of interest to mention that Poland and Sheraga[5] recently presented a theory of micelle formation based on statistical mechanics from which they concluded that the molecular model applied was unsatisfactory, presumably due to the assumption that the ion-water interactions are unaffected when a micelle is formed by the association of the surfactant molecules. Thus, it is evident that additional experimental information about the properties of the counterions in micellar systems, is greatly needed.

For an atomic nucleus of spin quantum number, I, equal to or exceeding unity, the predominant nuclear magnetic relaxation mechanism in the liquid state is often due to the coupling between the nuclear quadrupole moment and fluctuating electric field gradients at the nucleus.[7] When the electronic magnification factor of the atom is large, as is the case for Br, the observed NMR-resonance line is usually quite broad as a result of the rapid quadrupole relaxation. The width of the peak can then be utilized as an experimental parameter characterizing the rate of the relaxation process. Ordinary electrolytic solutions have been investigated in essentially this way by means of, *e.g.*, ^{23}Na, ^{79}Br, ^{81}Br, and ^{127}I resonance.[6-9] It is a general experience that the relaxation rate diminishes with increasing temperature and upon dilution of the ionic solution.

We first made an exploratory study of cetylpyridinium bromide (CPBr) solutions. The critical micelle concentration,[10] CMC, of CPBr is equal to 0.8×10^{-3} M. At a room temperature of ∼30°C the line width of a 0.5 M solution was found to be about 10 gauss, *i.e.* more than two orders of magnitude larger than the line width measured for a 0.5 M NaBr solution. The line width rapidly decreased with increasing temperature, approaching 1 gauss at 80°C. The apparent activation energy of the relaxation process obtained by plotting the logarithm of the inverse line width determined between 40−80°C *versus* $1/T$ was found to be 4.7 kcal/mole. The corresponding figure for the proton magnetic resonance of pure water[11] is 4.5 kcal/mole.

In order to arrive at a better understanding of the above findings we recorded the Br-resonance lines for solutions of octylamine hydrobromide (OAHBr) starting at concentrations slightly below the CMC. The value given in the literature[12] for the CMC of OAHCl is 0.175 M. Since it is well-known that the effect on the CMC of replacing a Cl$^-$ by a Br$^-$-counterion is usually quite small,[13] it is reasonable to assume that the CMC of OAHBr is approximately the same as for OAHCl.
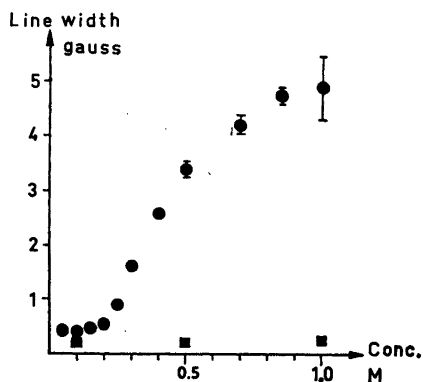

Fig. 1. The dependence of the line width on the concentration, ● = OAHBr, ■ = NaBr.

In Fig. 1 we have plotted the widths of the resonance lines recorded for several OAHBr solutions. Below the CMC, the line width is approximately constant though somewhat larger than the line width observed for a dilute NaBr-solution. At the CMC the line width starts to increase rapidly and at higher concentrations the resonance line gets very much broader than below the CMC. The dependence of the signal intensity on the concentration is shown in Fig. 2. At concentrations below 0.5 M the intensities of the OAHBr- and NaBr-resonance peaks are equal implying that practically all the Br-nuclei in the OAHBr-solution contribute to the measured intensity of the resonance signal. At higher concentrations the observed OAHBr resonance line intensities appear to be somewhat less than the corresponding NaBr intensities. However, this result is not completely certain as is evident from the indicated magnitude of the experimental errors.

According to the commonly accepted physical picture, some counterions are adsorbed in a Stern layer next to the ionic groups of the surfactant molecules whereas the remaining fraction of the counterions is to be found in the diffuse part of the electric double layer surrounding the micelles.[14] It can be assumed that the electric field gradients operative on the specifically adsorbed ions are comparatively large since these ions are attached to an environment characterized by a distinctly non-spherical distribution of charge. If the average life time at the adsorbed sites were considerably longer than the period of nuclear

Intensity

Fig. 2. The intensity of the resonance line as a function of the concentration, ● = OAHBr, ■ = NaBr.

precession, i.e. much longer than about 10^{-7} seconds, we would expect to observe two superimposed resonance lines, one broad line due to the adsorbed ions in the Stern layer and one narrow line due to the free ions in the diffuse part of the double layer. No detailed study of the signal band shape has been carried out at the present stage of the investigation. However, the behaviour of the observed intensities may indicate the appearance of a broader component that removes intensity from the dominant peak when the concentration increases (Fig. 2). In the case of cetyltrimethylammonium bromide (CTAB) solutions at 75°C a much more pronounced intensity difference was found. We intend to make a complete band shape analysis of each recorded resonance curve using a recent version of a computer program due to Svanson and Forslind[15] in order to scrutinize the deviations from a simple Gauss-shaped resonance absorption curve.

A theory of quadrupole relaxation in liquids has been formulated by Abragam and Pound.[16] The following expression emerges for the inverse relaxation time, which is proportional to the resonance line width

$$T_1^{-1} = \frac{3}{40} \frac{4I(I+1)-3}{I^2(2I-1)^2} \left(\frac{eQ}{\hbar}\right)^2 \langle q^2 \rangle \tau_c$$

eQ is the quadrupole moment of the nucleus and $\langle q^2 \rangle$ is the mean square electric field gradient at the nucleus. τ_c is the correlation time characterizing the random molecular motions that produce fluctuating field gradients. The spinlattice relaxation time T_1 is assumed to be equal to the coherence time T_2, an assumption that has been verified to hold for a few electrolytic solutions.[9] According to the above expression the variable factors that affect the width of the resonance line of a given nucleus are $\langle q^2 \rangle$ and τ_c. It has been shown that both factors play significant roles in the case of ordinary electrolytic solutions.[8] When considering the state of the ions in the double layer we shall have to take into account that τ_c as well as $\langle q^2 \rangle$ are altered in comparison with their values in a homogeneous electrolytic solution. The value of τ_c may well be larger due to attenuation of the thermal movements around the strongly water-coupled and heavy micellar complex. Moreover $\langle q^2 \rangle$ is certainly larger because of the strongly polar endgroups of the surfactant molecules. Since
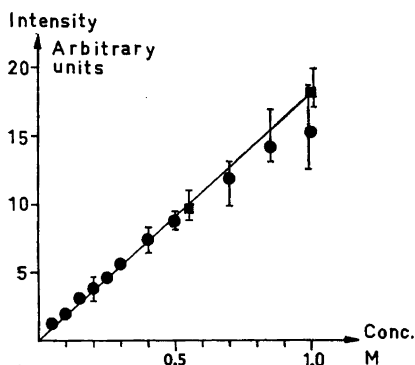
the temperature dependence of the inverse Br line-width of a CPBr-solution resonance is not much different from the temperature dependence of the proton resonance relaxation time in pure water it seems to be plausible that a longer correlation time of the molecular motions is an important cause of the marked increase in the line width around the CMC. This conclusion is supported by the results obtained by Clifford and Pethica [11] showing that micelle formation leads to comparatively shorter relaxation times of the water protons in solutions of sodium alkyl sulphates.

A few additional observations should be mentioned. In the proton magnetic resonance spectrum of a 0.5 M CPBr solution, the H_2O-line has almost the same width as for pure H_2O independently of the temperature. However, the width of the peak ascribed to the CH_2-groups on the hydrocarbon chains of CPBr diminishes with increasing temperature as does the Br resonance line width. The changes observed in the CH_2-resonance line width are directly related to an increase of the correlation time for the relative thermal motions of the hydrocarbon chains. It is thus reasonable to assume that a continuous transition takes place from a solid-like to a more liquid-like state of the whole micelle, including the double layer, when the temperature is raised. This transition may well be accompanied by changes in the geometrical shape of the micelles and their coupling to the surrounding water due to which the viscosity of the solution rapidly decreases.[2,17]

Experimental. A Varian V-4200 B NMR spectrometer equipped with a 12 inch V-4012 A magnet was used for the measurements. The magnetic field was controlled by a Varian Fieldial. The line width was evaluated directly from the recorded curve. The field modulation amplitude was kept small relative to the line width and the r.f. field was chosen so as to avoid saturation.

The relative signal intensity was calculated by multiplying the peak to peak height with the square of the peak separation of the absorption band derivative. This procedure is exact in the case of Gauss-shaped absorption curves and it constitutes in general a good approximation also for other bell-shaped curves.

For the intensity measurements we used NaBr-solutions as reference solutions. However, due to the circumstance that several instrumental scale factors have to be in-troduced when comparing the intensities of resonance lines of much different width, we found it expedient to broaden the comparatively narrow NaBr resonance line by adding a small amount of the paramagnetic salt $MnSO_4$. The resonance lines of the NaBr-solutions could thus be run at the same spectrometer settings as those used for the surfactant solutions. The experimental points in Figs. 1 and 2 represent average values of 2−5 measurements. The experimental dispersion range is indicated by the bars through the marked points.

The CPBr and CTAB reagents used were of purum grade, containing max. 2 % impurities. The OAHBr solution was prepared through mixing equivalent amounts of octylamine, containing max. 1% of impurities, and a 48 % HBr solution of reagent grade.

1. Mcdonald, J. *Arch. Sci. Genève* **12** (1959) 141.
2. Eriksson, J. C. *Acta Chem. Scand.* **17** (1963) 1478; Eriksson, J. C. and Gillberg, G. *Surface Chemistry*, Proc. of the Second Scandinavian Symposium on Surface Activity in Stockholm, Munksgaard, Copenhagen 1965, p. 148; Eriksson, J. C. and Gillberg, G. *Acta Chem. Scand.* **20** (1966) 2019.
3. Nakagawa, T. and Tori, K. *Kolloid-Z.* **194** (1964) 143; Nakagawa, T. and Inoue, H. *Proc. 4th Intern. Congr. Surface Active Substances. In press.* Inoue, H. and Nakagawa, T. *J. Phys. Chem.* **70** (1966) 1108.
4. Clifford, J. and Pethica, B. A. *Trans. Faraday Soc.* **60** (1964) 1483.
5. Poland, D. C. and Sheraga, H. A. *J. Colloid Sci.* **21** (1966) 273.
6. Itoh, J. and Yamagata, Y. *J. Phys. Soc. Japan* **13** (1958) 1182.
7. Hertz, H. G. *Ber. Bunsen Ges. Physik Chem.* **67** (1963) 311.
8. Deverell, C., Frost, D. J. and Richards, R. E. *J. Mol. Phys.* **9** (1965) 565.
9. Eisenstadt, M. and Friedman, H. L. *J. Chem. Phys.* **44** (1966) 1407.
10. Hartley, G. S., Collie, B. and Sanies, C. G. *Trans. Faraday Soc.* **32** (1936) 795.
11. Clifford, J. and Pethica, B. A. *Trans. Faraday Soc.* **61** (1965) 11.

12. Klevens, H. B. *J. Am. Oil Chemists' Soc.* **30** (1953) 79.
13. Shinoda, K., Nakagawa, T., Tamamushi, B.-I. and Isemura, T. *Colloid Surfactants*, Academic, New York and London 1963, p. 54.
14. Stigter, D. *J. Phys. Chem.* **68** (1964) 3603.
15. Svanson, S. E. and Forslind, E. *Acta Chem. Scand.* **16** (1962) 2149.
16. Abragam, A. and Pound, R. V. *Phys. Rev.* **92** (1953) 943.
17. Götz, K. G. and Heckman, K. *Z. physik. Chem. (Frankfurt)* **20** (1959) 42.

Sur la Structure d'un Dérivé Acétylé de la Phlébiarubrone

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Il y a quelques années McMorris et Anchel [1] ont isolé d'une culture du champignon *Phlébia strigosozonata* un pigment rouge, nommé phlébiarubrone, pour lequel ils ont proposé la structure (*1*) d'une 3,6-diphényl-4,5-méthylènedioxy-1,2-benzoquinone.

Un peu plus tard, la structure proposée fut confirmée par Gripenberg [2] par synthèse à partir de l'acide polyporique (*2*).


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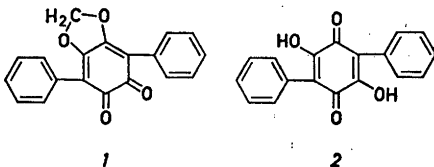
McMorris et Anchel [1] ont constaté qu'avec l'acétate de sodium et l'anhydride acétique la phlébiarubrone donne un

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diacétate incolore (p.f. 115—117°C) non identique au leucoacétate normal (*3*) obtenu avec l'anhydride acétique et la poudre de zinc en présence de pyridine.

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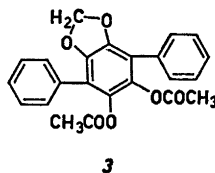
Il y a peu de temps, Gripenberg et Lounasmaa [3] ont montré que l'acide théléphorique (*4*) dans l'anhydride acétique en présence d'acétate de sodium et à reflux donne le 2,3,6,8,9-penta-acétoxy-12-(acétoxyméthyl)-benzo-[1,2-b;4,5-b']-bisbenzofurane (*5*). Cette réaction anormale a été expliquée comme le résultat d'une condensation selon Perkin suivie de décarboxylation et de l'addition de l'anhydride acétique.[3]

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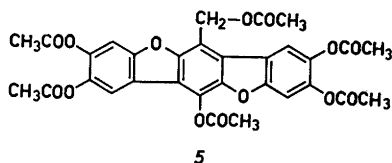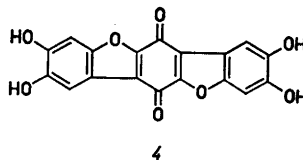
Comme il nous semblait possible que dans le cas de la phlébiarubrone il pouvait s'agir d'une réaction analogue, nous avons répété son acétylation en présence d'anhydride acétique et d'acétate de sodium.

Nous avons obtenu, avec un rendement de 80 %, un produit incolore qui, après une purification chromatographique sur colonne (gel de silice G/benzène) et après une recristallisation dans l'éthanol absolu, fond à 116—117°C. Il s'agit d'un diacétate pour lequel nous proposons la structure (*6*) du 1-acétoxy-2-(acétoxyméthyl)-3,6-diphényl-4,5-méthylènedioxy-benzène ($C_{24}H_{20}O_6$).