Counter-ion Nuclear Magnetic Resonance Chemical Shifts in Micellar Solutions

BY HANS GUSTAVSSON and BJÖRN LINDMAN*

(*Division of Physical Chemistry* 2, *The Lund Institute of Technology, Chemical Center, P.O.B.* 740, *S*-22007 *Lund* 7, *Sweden*)

Summary It is demonstrated that the binding of alkali and halide ions to micellar aggregates may be followed by studying n.m.r. chemical shifts of alkali and halide nuclei.

THE attachment of alkali or halide ions to macromolecules or molecular aggregates of colloidal dimensions results in considerable changes in the nuclear magnetic resonance parameters of the ions. Extensive use has been made of the quadrupole relaxation method to study ion binding in protein,[1] polyanion,[2] and association colloid solutions.[3a,b] Recently, it was shown that for anisotropic systems the quadrupole splitting method is a promising possibility for studying the interaction between small ions and association colloids.[4] The interaction between counter-ions and ionic amphiphiles is also expected to affect the electronic shielding of the counter-ion nuclei. We demonstrate here the feasibility of this method for studying ion binding in micellar solutions.

We have examined the $^{23}Na^+$, $^{35}Cl^-$, and $^{133}Cs^+$ resonance signals in aqueous solutions of short-chain soaps with a Varian V-4200 wide-line spectrometer. In order to improve homogeneity and stability we used shim coils, a flux stabilizer, and a frequency stabilizer. External reference solutions were inserted coaxially in the sample tubes. Each sample was swept at least five times in both increasing and decreasing field directions to negate field drift. The estimated accuracy of the shift measurements is better than $\pm$ 0·15 p.p.m. Spectrum calibration was achieved with the conventional side-band technique. Corrections due to differences in bulk susceptibilities between sample and reference are assumed to be negligible.[5] From ref. 6 it appears that the appropriate correction is only a small fraction of our experimental error. A positive chemical shift, δ, corresponds to a shift to higher field. The sample temperature was 27 $\pm$ 2 °C.

We may safely assume (*cf.* refs. 3a and b) that the lifetime of the counter-ion in a particular binding site is small compared to the inverse difference in resonance frequencies characterizing different binding sites. If we assume that there are two binding conditions for the counter-ions, one corresponding to a free ion (subscript f) and one corresponding to a counter-ion attached to a micellar aggregate (subscript m), the observed chemical shift is $\delta = \rho_f\delta_f + \rho_m\delta_m$, where the time-fractions ρ_f and ρ_m equal the fractions of counter-ions in the different binding sites and δ_f and δ_m are the intrinsic chemical shifts of the sites.

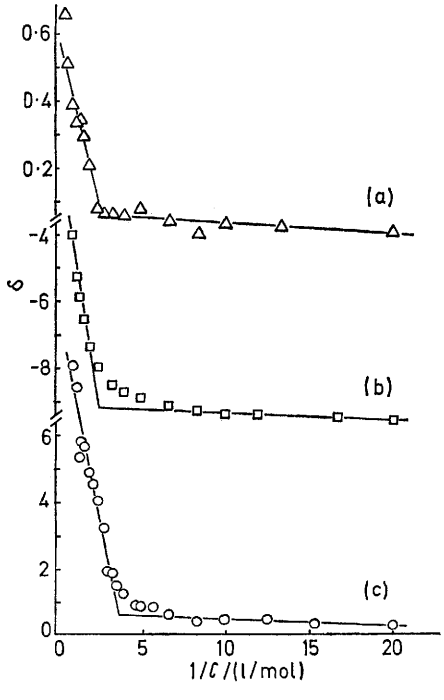

FIGURE. *Counter-ion n.m.r. chemical shifts,* δ, *in soap solutions plotted against the inverse soap concentration.* (a) ^{23}Na *n.m.r. in sodium n-octanoate solutions;* (b) ^{133}Cs *n.m.r. in caesium n-octanoate solutions;* (c) ^{35}Cl *n.m.r. in n-octylamine hydrochloride solutions. Reference solutions were* 0·5M-NaCl(a,c) *or* 0·5M-CsCl (b).

As a first approximation we assume that the pseudo-phase separation model[7a] is applicable and that β, the molar ratio of counter-ions to surfactant ions in the micellar complexes, is independent of concentration. With these assumptions we have $C_m = \beta(C_t - \text{c.m.c.})$, where C_m is the concentration of micellarly bound counter-ions, C_t the total soap concentration, and c.m.c. the critical micelle concentration. This gives us the following expression (*cf.* ref. 3a) for δ above the critical micelle concentration

$$\delta = \delta_f + \beta(\delta_m - \delta_f) - \beta(\text{c.m.c.})(\delta_m - \delta_f)C_t^{-1}$$

According to the model adopted we expect to obtain two straight lines intersecting at the c.m.c. if the observed chemical shift is plotted against the inverse of the total soap concentration. As can be seen in the Figure our model is in reasonable agreement with the experimental data except in the region of the c.m.c. where deviations are expected to occur due to the oversimplified model used as well as the neglect of pre-micellar association. The c.m.c. values obtained from the intersection points are 0·37M for sodium octanoate, 0·40M for caesium octanoate, and 0·27M for octylammonium chloride. The c.m.c. value obtained for octylammonium chloride is the same as that obtained from the relation given by Shinoda.[7b] For sodium octanoate excellent agreement with previous determinations[8] is found, whereas for caesium octanoate no c.m.c. value has been found in the literature.

It is evident from the Figure that counter-ion chemical shifts may conveniently be used to study counter-ion binding to micelles. However, the method should be equally applicable to investigating the binding of small ions in other colloidal solutions, such as polyanion solutions, lyotropic liquid crystalline solutions, and model membrane systems.

Apart from being used to follow association processes the method can also give information on the mode of interaction between the counter-ions and the micelles. This information is contained in δ_m. Unfortunately, the understanding of n.m.r. chemical shifts for alkali and halide nuclei is far from complete (*cf.* refs. 9a and b) and it is at present impossible unambiguously to interpret the observed upfield chemical shift obtained on micelle formation. It may be noted that on binding to micelles the $^{23}Na^+$ chemical shift changes in the same direction as when the sodium ion is transferred from water to, for example, acetic acid.[9a] By studying how the counter-ion chemical shift depends on soap end-group we hope to clarify the factors determining alkali and halide chemical shifts in solution.

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[1] T. L. James and J. H. Noggle, *Proc. Nat. Acad. Sci. U.S.A.*, 1969, **62**, 644; E. Chiancone, J. E. Norne, S. Forsén, E. Antonini, and J. Wyman, *J. Mol. Biol.*, 1972, **70**, 675.
[2] B. Lindman and I. Lindqvist, *Chemica Scripta*, 1971, **1**, 195.
[3] (a) B. Lindman and I. Danielsson, *J. Colloid Interface Sci.*, 1972, **39**, 349; (b) G. Lindblom, B. Lindman, and L. Mandell, *ibid.*, in the press.
[4] G. Lindblom, H. Wennerström, and B. Lindman, *Chem. Phys. Letters*, 1971, **8**, 489; G. Lindblom, *Acta Chem. Scand.*, 1971, **25**, 2767.
[5] G. J. Templeman and A. L. Van Geet, *J. Amer. Chem. Soc.*, 1972, **94**, 5578.
[6] M. S. Bergqvist and E. Forslind, *Acta Chem. Scand.*, 1962, **16**, 2069; L. Ödberg, B. Svens, and I. Danielsson, *J. Colloid Interface Sci.*, 1972, **41**, 298.
[7] K. Shinoda, T. Nakagawa, B.-I. Tamamushi, and T. Isemura, 'Colloidal Surfactants,' Academic Press, New York, 1963, (a) p. 25; (b) p. 43.
[8] B. Lindman and B. Brun, *J. Colloid Interface Sci.*, in the press, and references therein.
[9] (a) E. G. Bloor and R. G. Kidd, *Canad. J. Chem.*, 1968, **46**, 3425; (b) G. W. Canters, *J. Amer. Chem. Soc.*, 1972, **94**, 5230.