AN N.M.R. STUDY IN MOLTEN PYRIDINIUM CHLORIDE SOLUTIONS

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Low-melting organic salts should be especially amenable to proton magnetic resonance studies which have in other solvents proved valuable in elucidating ion–solvent and ion–ion interactions.[1-3] As far as is known, such an investigation has never been conducted in a molten organic salt system *in situ*. This note reports on an n.m.r. spectral analysis of molten pyridinium chloride solutions at 155° with various solutes. Cetyldimethylbenzylammonium chloride (abbreviated CetMe$_2$BzlNCl) was singled out for special attention as a solute because previous studies[4-7] had indicated from several physicochemical techniques that micellization was initiated at $0 \cdot 06$ mol kg^{-1} at 155°.

Experimental

Pyridinium chloride was prepared as described previously.[4] Koch–Light Puriss grade CetMe$_2$BzlNCl was dried intensively before being used. Before the spectral analysis, the mixtures were dried for 24 hr under vacuum. Spectra were obtained with a JEOL JNM-4H-100 n.m.r. spectrometer operating at 100 MHz. Dimethyl sulphoxide was used as an external reference at 155°.

Results

Figure 1 depicts the p.m.r. spectrum for pure molten pyridinium chloride at 155° (m.p. 146°). With dimethyl sulphoxide as reference, the peak assignments in the downfield direction were as follows: β-proton, $5 \cdot 83$ p.p.m. (triplet); γ-proton, $6 \cdot 36$ p.p.m. (triplet); α-proton, $6 \cdot 78$ p.p.m. (doublet); N-proton, $13 \cdot 70$ p.p.m. (singlet).

When CetMe$_2$BzlNCl was added as solute, the pyridine peaks were unaltered in shape and position but the sharp singlet at $13 \cdot 70$ p.p.m. was shifted progressively upfield with increasing solute concentration. An upfield chemical shift of 60 Hz for this peak was registered for a $0 \cdot 168$ mol kg^{-1} solution. The molal chemical shifts

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[1] Craig, R. A., *Rep. Prog. Chem.*, 1962, **59**, 63.

[2] Hinton, J. F., and Amis, E. S., *Chem. Rev.*, 1967, **67**, 367.

[3] Burgess, J., and Symons, M. C. R., *Q. Rev. chem. Soc.*, 1968, **22**, 276.

[4] Bloom, H., and Reinsborough, V. C., *Aust. J. Chem.*, 1967, **20**, 2583.

[5] Bloom, H., and Reinsborough, V. C., *Aust. J. Chem.*, 1968, **21**, 1525.

[6] Reinsborough, V. C., and Valleau, J. P., *Aust. J. Chem.*, 1968, **21**, 2905.

[7] Bloom, H., and Reinsborough, V. C., *Aust. J. Chem.*, 1969, **22**, 519.

are shown in Figure 2. To avoid bulk diamagnetic susceptibility corrections, the most prominent peak of the α-proton spectrum was employed as an internal zero. No peaks peculiar to the solute were observed.
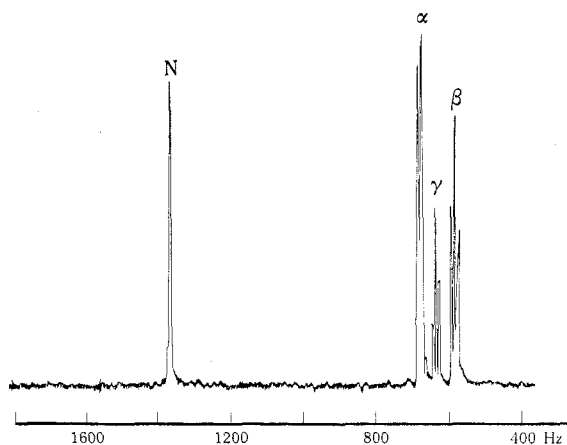

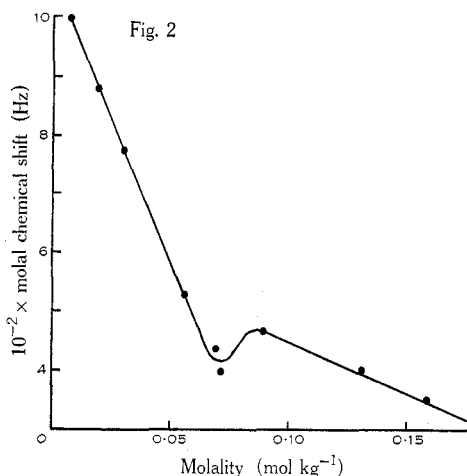Fig. 1.—N.m.r. spectrum for molten pyridinium chloride at 155°.
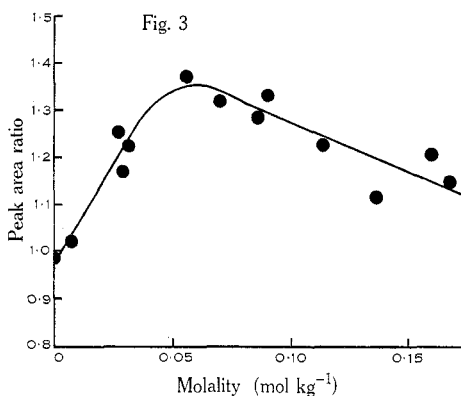

Fig. 2.—Molal chemical shifts in CetMe₂BzlNCl solutions in molten pyridinium chloride at 155°.
Fig. 3.—Changes in peak area ratio, i.e. $4A_N/(A_\alpha+A_\beta)$, with CetMe₂BzlNCl concentration in molten pyridinium chloride.

The instrumentally integrated areas under the N-proton peak and the pyridine proton peaks are compared in Figure 3 by the ratio $4A_N/(A_\alpha+A_\beta)$ where the sub-scripts denote the peaks involved. In pure pyridinium chloride at 155°, this ratio was found to be $1\cdot00\pm0\cdot01$ as would be expected ideally. With increasing solution addition, this ratio increases until at $0\cdot06$ mol kg^{-1} in the neighbourhood of the critical micelle concentration (CMC) it reaches a maximum value of $1\cdot38$ before decreasing once again to almost the pure solvent value at $0\cdot17$ mol kg^{-1}.

Anilinium chloride had been employed as an "ideal" solute in molten pyridinium chloride in previous studies[5-7] to serve as a criterion for the anomalous behaviour of

CetMe₂BzlNCl as a solute in this solvent. It could not be used in this capacity here as the N-protons of both solute and solvent underwent rapid exchange. Instead, tetramethylammonium and tetraethylammonium chloride solutions were examined as comparison systems. With solutions as concentrated as $0 \cdot 25$ mol kg⁻¹ in Me₄NCl, no chemical shift could be detected within experimental error (± 3 Hz) and the area ratio was unchanged from the pure solvent ratio of unity.

Discussion

Physicochemical properties of miscellar solutions generally undergo discontinuities at the onset of micellization, i.e. at the CMC. Both the molal chemical shift and the ratio of the peak area fit this pattern with breaks occurring at $0 \cdot 06$ mol kg⁻¹ which at 155° is the CMC for this system.

The interpretation of the form of the curves is not clear. The upfield shift and the large increase of the peak area of the N-proton spectral line are probably interdependent since micellization causes changes in both properties. Solvent structuring, which has been argued to occur in this system in dilute solution,[5] should lead to a downfield rather than an upfield shift if hydrogen bonding is being enhanced. Solvent structuring could also be responsible for increased ring anisotropy or cation–cation interactions and these could account for an upfield shift. Yet, it is difficult to reconcile these explanations with the increase in the peak area ratio.

Another possibility, suggested by the n.m.r. study of Hofmeister and Van Wazer in molten ammonium chloride and methylammonium chloride mixtures,[8] is that the N-protons of the pyridinium ion and the methyl groups of the CetMe₂BzlN⁺ ion may be undergoing exchange. However, this also should occur when tetramethyl and tetraethylammonium chloride are employed as solutes. This was not found to be the case.

Further investigation in allied systems is being planned. At this stage, some observations can still be made. The CMC is clearly indicated by the chemical shift and the change in the peak area ratio of the N-proton spectral line of the pyridinium ion of the solvent. Of all the protons of the solvent cation, solvation as well as micellization appear to affect the electronic environment of only the N-proton.

Acknowledgments

[8] Hofmeister, H. K., and Van Wazer, J. R., *J. phys. Chem.*, 1965, **69**, 791.