Ultrasonic Absortion Properties of Aqueous Solutions Containing Alkylammonium Salts

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WITHIN the range 1·5—300 Mc./sec., the ultrasonic absorption of aqueous solutions containing 1 : 1 electrolytes such as sodium chloride shows, it is claimed,[1] no evidence for a relaxation process. We have confirmed this observation for aqueous solutions containing either sodium chloride or sodium bromide. Indeed addition of either salt to water at 25° c depresses α/f^2, (α being the sound attenuation coefficient and f the frequency) to values below that for water at the same temperature. However, marked relaxation occurs in this region when tetra-n-alkylammonium (R_4N^+) halides are added (Figures 1 and 2). The results for tetra-n-butylammonium bromide have been analysed by means of a computer and show at least two relaxation processes with relaxation frequencies of approximately 7·5 and 200 Mc./sec. at 25° c. The high-frequency relaxation process increases in magnitude both with decrease in temperatures and with increase in concentration.

A variety of other properties of these two types of solution show similar trends.[2,3] For example,

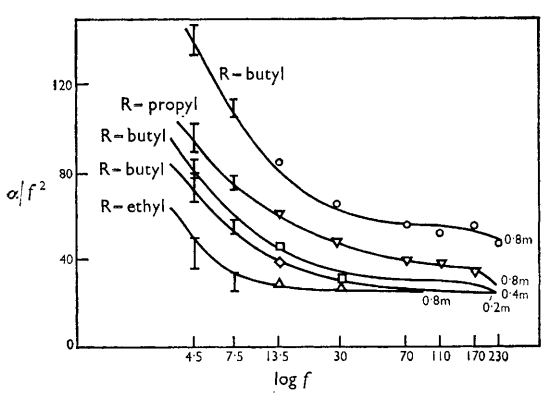

FIGURE 1. *Ultrasonic absorption in aqueous solutions of various tetra-n-alkylammonium (to aid clarity some of the data points at high frequencies have been ommitted).*

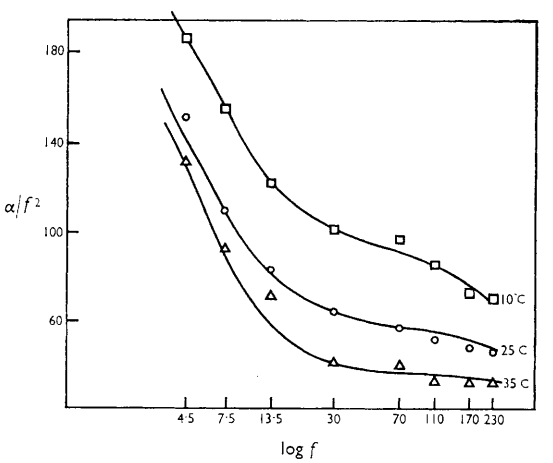

FIGURE 2. *Effect of varying the temperature on the ultrasonic absorption in aqueous solutions of tetra-n-butylammonium bromide.*

the apparent partial molal heat capacities of tetra-alkylammonium halides in dilute aqueous solution are more characteristic of nonpolar than of ionic solutes.[4]

The origin of these relaxations is not clear. At least one might be associated with some conformational changes involving the tetra-alkylammonium ion. Although this cannot be eliminated it seems unlikely in view of the high symmetry of the cations used. We consider that the relaxations are most probably associated with the special hydration properties,[2,3] of the alkylammonium cations. If this is correct then the ultrasonic properties provide a new method of probing the "hydrophobic hydration" of these ions in solution. It is possible that one of the relaxation processes may be associated with an equilibrium between free ions and "structure enforced ion-pairs".[5,6] It is also noteworthy that 2 : 2 electrolytes in water have a characteristic relaxation in the 200 Mc./sec. region and some also show a relaxation at about 10 Mc./sec. This has been discussed[7] in terms of a detailed picture of the association process.

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[2] For key references see: J. L. Kavanau, "Structure of Ice and Liquid Water," Holden-Day, San Francisco, 1964.
[3] W. Y. Wen and G. Saito, *J. Phys. Chem.*, 1964, **68**, 2639.
[4] H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.
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[6] M. J. Blandamer, M. C. R. Symons, and G. S. P. Verma, *Chem. Comm*, 1965, 629.
[7] M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. 8, part 2 (Ed., S. L. Freiss, E. S. Lewis, and A. Weissberger) Interscience, New York, 1963, Ch. 18.