

Proton Nuclear Magnetic Resonance Shifts for Water containing Alkylammonium Ions

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Summary In contrast with previous results, proton chemical shifts for water are found to move to lower applied fields as the size of the alkyl group in symmetrical

tetra-alkylammonium ions is increased for temperatures below 300 K, although the trend is reversed at higher temperatures.

MUCH controversy has centred around the paradox presented by the ^1H n m r shifts for water protons on the addition of tetra-alkylammonium salts^{1,2}. Thus although there is considerable evidence that these ions ($R > \text{Me}$) are 'structure making'³ the ^1H n m r results seem to show the opposite since relative upfield shifts were obtained on increasing the bulk of the cations¹. Attempts have been made to rationalise these results in terms of different types of hydrogen bond, some of which can cause upfield ^1H n m r shifts whilst others cause downfield shifts⁴. If this is correct then all deductions about hydrogen bonding based upon ^1H n m r shifts must be treated with considerable reserve.

We have repeated this work over a wide temperature range and the results are in the Table. These show that

TABLE

Molal salt shifts determined by extrapolation to infinite dilution for alkylammonium bromides at various temperatures (Signals from protons nearest to nitrogen were used as an internal reference)

T/K	Molal salt shifts (p p m)					
Salt	273	285.5	298	313	333	353
Me_4NBr	0.091	0.083	0.080	0.073	0.061	0.050
Et_4NBr	0.075	0.077	0.071	0.078	0.073	0.067
Pr^n_4NBr	0.057	0.064	0.072	0.077	0.085	0.097
Bu^n_4NBr	0.042	0.060	0.073	0.103	0.115	0.121
$\text{C}_8\text{H}_{17}\text{NMe}_3\text{Br}$	0.108	0.125	0.137	0.133	0.130	0.123

at low temperatures, at which water structural effects are always most marked, the trends are, after all, to low field with increasing size of the alkyl group, and by use of what we consider to be values close to absolute ion shifts for Br^- ,⁵ these alkylammonium ion shifts are in fact downfield. As the temperature is increased, however, the shifts for the more bulky ions pass through zero and become positive (see Figure 1). This behaviour is comparable

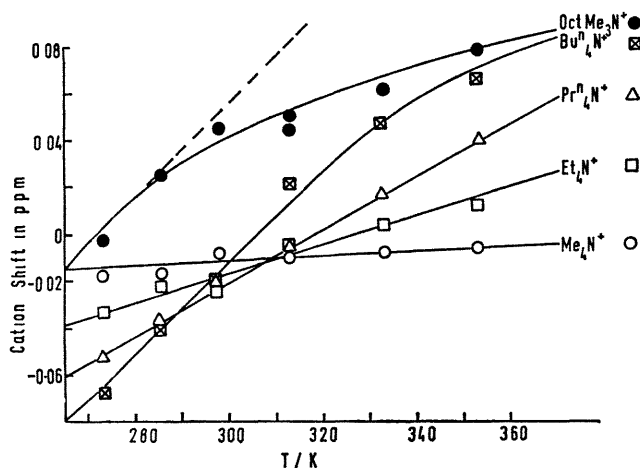


FIGURE 1 Molal ion shifts (p p m) vs temperature

¹ H G Hertz and W Spalthoff *Z Elektrochem Ber Bungsengesellschaft Phys Chem*, 1959, **63**, 1096

² E Wicke, *Angew Chem Internat Edn*, 1966, **5**, 106

³ M J Blandamer and M C R Symons, 'Hydrogen Bonded Solvent Systems', eds A K Covington and P Jones, Taylor and Francis, London, 1968, p 211

⁴ J Clifford and B A Pethica, *Trans Faraday Soc*, 1964, **60**, 1483

⁵ J Davies, S Ormondroyd, and M C R Symons, *Trans Faraday Soc*, in the press, *Chem Comm*, 1970, 1426

⁶ R G Anderson and M C R Symons, *Trans Faraday Soc*, 1969, **65**, 2550

⁷ F Franks and D J G Ives, *Quart Rev*, 1966, **20**, 1

⁸ M J Blandamer, D E Clark, N J Hidden, and M C R Symons *Chem Comm*, 1966, 342.

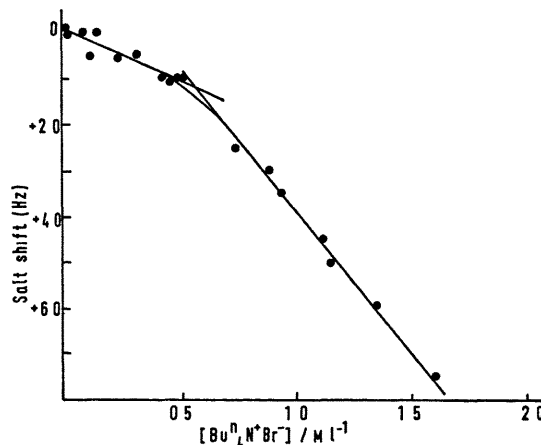
⁹ R N Butler and M C R Symons, *Trans Faraday Soc*, 1969, **65**, 945, 2559

with that for neutral molecules such as t-butyl alcohol⁶. It is also found to a more marked extent for asymmetric alkylammonium ions containing one long chain alkyl group. Such behaviour is understandable in terms of the 'clathrate' structural theory that we have used to explain other spectroscopic and ultrasonic relaxation data⁶⁻⁸. Enclathration of alkylammonium ions requires considerable organisation by neighbouring water molecules, and even the transient structural effects envisaged for aqueous solutions will be strongly opposed by increased thermal motion and loss of bulk water structure. At elevated temperatures it seems that disorganisation is somewhat enhanced, especially by long chain alkyl groups, and this overshadows any residual structuring effects. We suggest that these very marked temperature effects are strongly diagnostic of water-structure phenomena.

One reason why our results differ from those previously reported¹ is that, for the higher homologues, plots of shift against concentration are non-linear (Figure 2) the slopes changing from those used in this work to those quoted previously as the concentration increases¹.

Another reason is that in the former work¹ low temperatures were not investigated and the methyl protons of t-butyl alcohol were used as reference despite the fact that the addition of this alcohol causes the water proton resonance to shift⁶. Use of the methyl protons of the alkylammonium ions avoids this difficulty.

The non-linearity noted in Figure 2 is of interest also in

FIGURE 2 Salt shift vs molality for Bu^n_4NBr at 273 K

that the slopes observed for the concentrated solutions are close to those previously calculated for the bromide ion alone⁵. In other words, the specific shifts for the higher symmetric of alkylammonium ions appear to have become zero.

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