Fractionation Factor for L_3O^+ in H_2O–D_2O Mixtures

By A. JERRY KRESGE
(*Illinois Institute of Technology, Chicago, Illinois* 60616)
and W. JOHN ALBERY*
(*Physical Chemistry Laboratory, South Parks Road, Oxford* OX1 3QZ)

Summary A recent approach based on curve-fitting of solvent isotope curves in H_2O and D_2O mixtures by computer analysis, which leads to a revised value for l, the fractionation factor for L_3O^+, is shown to be erroneous.

BATTS and KILFORD have recently suggested[1] that the value of l, the fractionation factor for L_3O^+, in H_2O mixtures should be increased from 0·69 (ref. 2) to 0·72. Their argument is based on curve fitting by computer to the results of six different reactions. We believe that their approach leads to erroneous results.

The variation of a reaction rate or an equilibrium constant with the isotopic composition, x, of H_2O–D_2O mixtures is a smooth curve. Families of such curves for different values of the fractionation factors often lie close together.[3] Any smooth curve passing through the points at $x = 0$, $x = \frac{1}{2}$, and $x = 1$ will fit the data at other values of x within the limits of the experimental precision.[4] Thus even with the most accurate data the curve by itself can at best give information about the values of two fractionation factors. Batts and Kilford have attempted to find values for up to four factors from a single curve. This is equivalent to trying to distinguish between smooth curves that all pass through the points $x=0$, $x=\frac{1}{4}$, $x=\frac{1}{2}$, $x=\frac{3}{4}$, and $x=1$; existing experimental data are not precise enough to make this very fine distinction. For instance, they find that results for the hydrolysis of ethyl diazoacetate[5] do not yield a convergent set of values for four factors; this failure is not surprising and does not throw doubt on the conclusion that the mechanism is A-2, which was reached using independently determined values for three of the four factors. A further problem is that several sets of different possible values for the fractionation factors may exist. For instance even for two factors there will be two different curves that both pass through $x=0$, $x=\frac{1}{2}$, and $x=1$ where the values of the fractionation factors correspond to two completely different roots of a quadratic equation. It is unlikely that the experimental data at other values of x are sufficiently precise to distinguish between the two different roots.[4] This type of problem has arisen in the fractionation

TABLE

Comparison of fractionation factors

Reaction	Factor from ref. 1	Experimental value
Hydrogen exchange in 1,3,5-trimethoxybenzene	0·793	0·12 ± 0·01[a]
Dissociation of acetic acid	1·237	0·96 ± 0·02[b]
Hydration of isobutene	0·205	0·26 ± 0·01[c]

[a] A. J. Kresge and Y. Chiang, *J. Amer Chem. Soc.*, 1967, **89**, 4411. [b] V. Gold and B. M. Lowe, *J. Chem. Soc. (A)*, 1968, 1923. [c] V. Gold and M. A. Kessick, *J. Chem. Soc.*, 1965, 6718.

of the hydroxide ion.[6] The approach used by Batts and Kilford may find a set of possible values, but there is no guarantee that this is the correct set. Indeed, in three out of six of the systems used by Batts and Kilford for their new value of *l* one of the other fractionation factors determined by the computer disagrees with a separate experimental determination as shown in the Table. They analyse the fourth of their six systems, the dissociation of boric acid, using the structure H_2O^+–$B(OH_3)^-$, but recent investigations, summarized by Bell,[7] have shown that this is incorrect. In general the more factors that Batts and Kilford try to determine, the larger is the discrepancy between their value and the experimental value, which suggests that they are indeed trying to extract values for too many factors from a single curve. Unfortunately they have not given any estimates for the precision of their suggested values. However, the results in the Table, particularly for 1,3,5-trimethoxybenzene with a proposed factor of 0·79 for a proton in flight, show that little confidence can be placed in the computer analysis, and therefore we suggest that the experimentally determined value[2] of $l = 0{\cdot}69 \pm 0{\cdot}01$ should continue to be used.

(*Received, 8th March* 1974; *Com.* 273.)

[1] B. D. Batts and J. Kilford, *J.C.S. Faraday I*, 1973, **69**, 1033.
[2] V. Gold, *Adv. Phys. Org. Chem.*, 1969, **7**, 259.
[3] A. J. Kresge, *Pure Appl. Chem.*, 1964, **8**, 243.
[4] W. J. Albery and M. H. Davies, *J.C.S. Faraday I*, 1972, **68**, 167.
[5] W. J. Albery and M. H. Davies, *Trans. Faraday Soc.*, 1969, **65**, 1066.
[6] V. Gold and S. Grist, *J.C.S. Perkin II*, 1972, 89.
[7] R. P. Bell, 'The Proton in Chemistry,' 2nd edn., Cornell University Press, 1973, p. 9.