Isopiestic Studies of Non-Aqueous Solutions of Quaternary Ammonium Halides. Comparison of the Degree of Solvations in Methanol and in Acetonitrile

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We wish to report on the result of an application of isopiestic vapor pressure method to estimate the relative stability of halide ions in non-aqueous solvents, methanol and acetonitrile, the former being hydroxylic and the latter a dipolar aprotic solvent. The static data is used to explain the solvent effects on the following equilibrium constant K.

$$CH_3Br + I^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} CH_3I + Br^- \qquad (I)$$

$$K = k_f/k_r$$

Two partially contrary views have been proposed with respect to the effects of solvents on both reactivities and nucleophilic activities for this type of reaction. The views are: (1) anions are "desolvated" in dipolar aportic solvents,[1] (2) small anions are also solvated in these solvents as in protic solvents.[2] A different set of extrathermodynamic assumptions may lead to this contrary conclusion. These assumptions have been used to determine the relative stability of single anions. We wished to provide a conclusion to the subject through an independent method.

For the isopiestic study tetra-n-butylammonium bromide and iodide were taken for their relatively large solubilities in the solvents. We used similar apparatus and procedure to those of Davies and Thomas.[3] The time required for an equilibration process was about ten days. The equilibrium concentrations of these two solutions result in the isopiestic ratio R which is here defined as the ratio of equilibrium molarity of iodide solution to that of bromide solution. Figure 1 shows the plot of R *vs.* equilibrium concentration of bromidesolution.

An attempt to correlate the static data with the rate or eqiulibrium data for reaction (I) is quantitatively made through the activity B coefficient according to the expression of activity coefficient. The difference in B values among two ions I^- and Br^- is obtained by the limiting derivative of R with respect to m, *viz.*,

$$\lim_{m\to 0} \partial R/\partial m = 2.303/2(B_{Br^-} - B_{I^-}) = 2.303/2\Delta B$$

Figure 1 gives the ΔB values of 0.76 and 0.04, in methanol and in acetonitrile, respectively. The rate data for reaction (I) are shown in Table 1 together with the ΔB values.

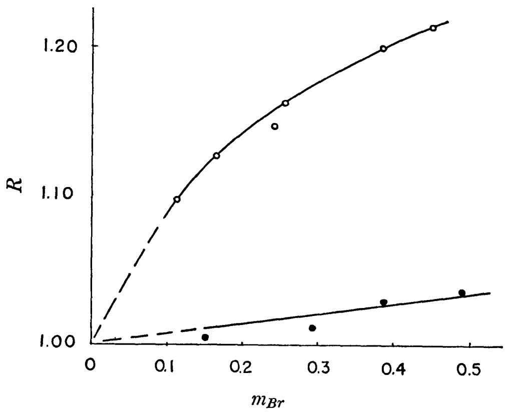

Fig. 1. Relationship between isopiestic ratio, R and molarity of bromide solution. ○, in methanol; ●, in acetonitrile

Table 1. Rate data for reaction (I) and static data in methanol and in acetonitrile at 30°C

	in CH_3OH[a]	in CH_3CN[b]
k_f, $M^{-1}\cdot sec^{-1}$	13.7×10^{-4}	0.091
k_r, $M^{-1}\cdot sec^{-1}$	13.8×10^{-5}	0.292
K	9.9	0.31
ΔB, M^{-1}	0.76	0.04

a) The rate data are taken from E. A. Moelwyn-Hughes. *J. Chem. Soc.*, **1939**, 368.

b) The rate data are taken from K. Uosaki and N. Tokura, unpublished result.

K is split into two terms, *i. e.*, intrinsic (denoted by superscript 0) and solvent-dependent terms, *viz.*,

$$\log K = \log K^0 + \log r_{I^-}/r_{Br^-}$$

where r_i is the solvent activity coefficient of i species. A plot of log K *vs.* ΔB for the changes in solvent results in the intrinsic nucleophilicity K^0. Log K^0 is obtained as the value on the ordinate of this plot at a point where $\Delta B=0$. The result shows that K^0 is smaller than 1.0, which in turn suggests the rate data in acetonitrile may reflect the intrinsic property of the reaction.

From the situations for ΔB and K we conclude as follows. The stability of halide ions is in the order $Br^- > I^-$ in both solvents, but these ions are more stabilized in protic solvents than in dipolar aprotic solvents. The latter explains the solvent effects on k_r or k_f.

1) A. J. Parker, *Quart. Rev.* (London), **16**, 613 (1962).

2) R. F. Rodewald, K. Mahendran, J. L. Beare, and R. Fuchs, *J. Amer. Chem. Soc.*, **90**, 6698 (1968).

3) M. Davies and D. K. Thomas, *J. Phys. Chem.*, **60**, 41 (1956).