

Figure 1. Dependence of association constants on dielectric constant in ethanol: curve 1, $(1.0 + \log K_A)$ for $\text{Bu}_4\text{N} \cdot \text{BPh}_4$; curve 2, $(0.5 + \log K_A)$ for Bu_4NBr ; curve 3, $\log K_A$ for Me_4NBr .

that sodium bromide would be much more associated than tetrabutylammonium tetraphenylboride, in a given solvent, while the results of Table III show that precisely the opposite sequence is correct.

The association of the quaternary salts is as expected, as far as the direction and magnitude of the change in association constant with pressure is concerned: association decreases with increasing pressure, corresponding to an increase in dielectric constant. As shown in Figure 1, the logarithm of association constant is linear D^{-1} , as required by the equation¹¹

$$K_A = (4\pi Na^3/3000) \exp(\epsilon^2/aDkT) \quad (3)$$

Also, the slopes (proportional to $1/a$) decrease in the expected sequence $\text{Bu}_4\text{NBPh}_4 < \text{Bu}_4\text{NBr} < \text{Me}_4\text{NBr}$, consistent with \bar{a} values of about 9, 6, and 5 Å. The interesting feature here is the absolute values of the association constants. The values for Me_4NBr and Bu_4NBr are nearly equal, and unmistakably smaller than for the much bulkier $\text{Bu}_4\text{N} \cdot \text{BPh}_4$. The function of eq 3, as a function of a for fixed D , has a minimum at $a_M = \epsilon^2/3DkT$, which in ethanol at 1 atm and 30° is at about 8 Å. The increased association of $\text{Bu}_4\text{N} \cdot \text{BPh}_4$ compared to that of Bu_4NBr is on this basis a consequence of the larger target area offered by the BPh_4^- ion; in other words, here the a^3 in the excluded volume factor has a greater effect than the $1/a$ in the exponential factor.

Finally, we consider the dependence of mobility on

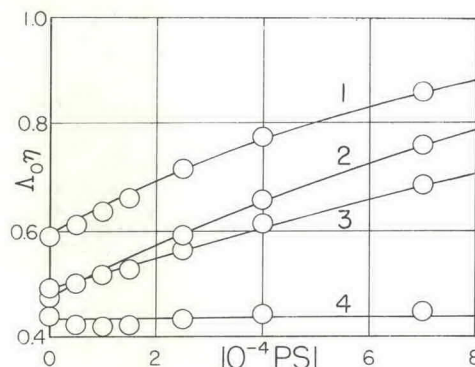


Figure 2. Dependence of Walden products on pressure in ethanol: 1, Me_4NBr ; 2, NaBr ; 3, Bu_4NBr ; 4, Bu_4NBPh_4 .

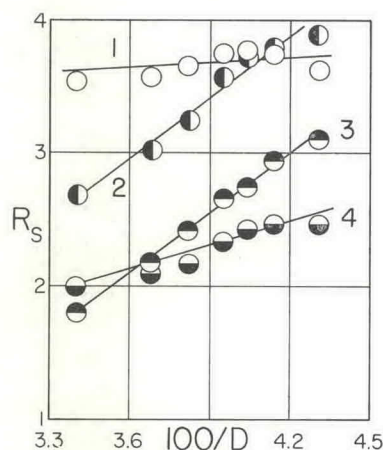


Figure 3. Variation of Stokes radius with dielectric constant in ethanol: 1, Bu_4N^+ ; 2, Na^+ ; 3, Br^- ; 4, Me_4N^+ .

pressure. For $\text{Bu}_4\text{N} \cdot \text{BPh}_4$, the Walden product (Figure 2, curve 4) is substantially independent of pressure, showing that the ions of this salt behave like Stokes spheres in ethanol. For the other three salts, the Walden product increases with increasing pressure. For the two quaternaries, this presumably is due to the bromide ion, since the plot for $\text{Bu}_4\text{N} \cdot \text{BPh}_4$ is flat. Using the value 1.073 for the ratio of the single-ion conductances¹² of Bu_4N^+ and BPh_4^- , the other single-ion conductances can be calculated, and from these, the Stokes radii R_{\pm} are obtained from the equation

$$R_{\pm} = 0.819 \times 10^{-8} / \lambda_{\pm}^0 \eta \quad (4)$$

As shown in Figure 3, these radii decrease with increasing dielectric constant. Part of this change¹³ is

(11) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(12) J. F. Coetzee and G. P. Cunningham, *ibid.*, **87**, 2529 (1965).

(13) R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S. A.*, **45**, 807 (1959); Figure 5B.

caused by a relaxation effect between ions and solvent dipoles; as was observed in methanol and in other

examples, the slope in hydrogen-bonding solvents is considerably larger than in aprotic solvents.