

for Pr_4NI at $\epsilon \approx 68$ and for Bu_4NI at about $\epsilon = 57$ (extrapolated value). It, therefore, appears that S_v may change from negative to a positive value provided the dielectric constant of the medium is appropriately reduced. It may be mentioned here that these conclusions are based on density data for higher concentrations and may not be applicable in very dilute solutions in which the limiting slope has been reported to be positive in some R_4NX salts even though the S_v is negative at higher concentrations^{12,13}.

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Apparent Molal Volume of Tetraalkylammonium Iodides in Water-Methanol Mixtures of Varying Dielectric Constants

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Dependence of the slope S_v of the empirical Mason's equation, $\phi_v = \phi_o + S_v\sqrt{C}$, on the dielectric constant of the medium has been examined in methanol-water mixtures. The data obtained suggest a dependence of S_v on dielectric constant of medium.

STUDIES¹ on the variation of apparent molal volume (ϕ_v) on dielectric constant in water-dioxane mixtures¹ indicate a dominant role of the dielectric constant of the medium on the nature (positive or negative) of the limiting slope (S_v) of the ϕ_v versus \sqrt{C} plots. According to Debye-Hückel theory², the slope (S_v) is expected to be positive and this is supported by the experimental data in water^{3,4} and formamide^{5,6} for common electrolytes. However, difficulties arise, at least at the higher concentrations, in the case of tetra-

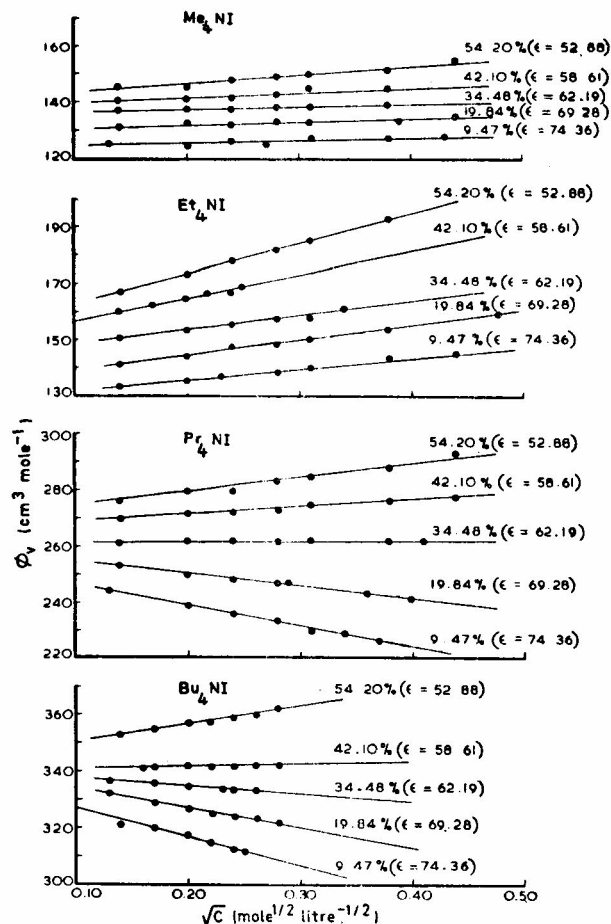


Fig. 1—Variation of apparent molal volume with concentration of some R_4NI salts in methanol-water mixtures at 40°

alkylammonium ions* for which the slope has been found to be negative not only in water but in several other solvents of high dielectric constant investigated so far. Similar studies in solvents of lower dielectric constant like methanol⁷, dimethylsulphoxide⁸, dimethylformamide⁸ and propylene carbonate⁹, indicate that even these salts give a positive slope in these solvents. It may be noted with interest that studies in dioxane-water mixtures¹ indicate that the negative slope in pure water becomes positive as the dielectric constant of the mixture is reduced. In order to ascertain if the electrolytes behave similarly in some other solvent systems, the slope (S_v) of ϕ_v versus \sqrt{C} curves of tetraalkylammonium iodides in methanol-water mixtures of varying dielectric constants have now been obtained. The dielectric constants of water-methanol mixtures have been reported recently¹⁰ and used in this study.

Methanol (AR, BDH) was distilled twice, the middle fraction being retained each time. Conductivity water was used for preparing methanol-water mixtures containing 9.47 ($\epsilon_{25^\circ} = 74.36$), 19.84 ($\epsilon_{25^\circ} = 69.28$), 34.48 ($\epsilon_{25^\circ} = 62.19$), 42.10 ($\epsilon_{25^\circ} = 58.61$) and 54.20% ($\epsilon_{25^\circ} = 52.88$) methanol by weight.

*Some common salts have a negative slope in N-methylacetamide [*Z. phys. Chem.*, **75** (1971), 7] and in N-methylpropionamide [*Z. phys. Chem.*, **91** (1974), 98; *J. phys. Chem.*, **72** (1968), 3209].

The R_4NI salts (M/s Distillation Products Industries, USA) were purified in the usual manner¹¹. Solutions were prepared on molal basis and the density was determined with a dilatometer of about 40 ml capacity, the stem of which was graduated in 0.01 ml so that volume could be read with ease up to 0.003 ml within an error not exceeding 0.002 ml with a magnifying glass. Rest of the experimental procedure was the same as given in earlier communications from this laboratory. From the density data at 40°, apparent molal volume was obtained in the usual manner. Only Me_4NI , Et_4NI , Pr_4NI and Bu_4NI could be studied since the higher homologues have little solubility in this solvent medium.

The linear plots of ϕ_v versus \sqrt{C} (Fig. 1) indicate the applicability of the Mason's equation, $\phi_v = \phi_0 + S_v\sqrt{C}$, to these solutions within the concentration range studied. The slope of the curves for Me_4NI and Et_4NI is positive in all the five mixtures. However, for Pr_4NI , it is negative in mixtures containing 9.47 and 19.84% methanol and becomes positive at higher concentrations of methanol. The slope is negative for Bu_4NI in mixtures containing 9.47, 19.84 and 34.48% methanol and then becomes positive. Comparing the results obtained in the present study with those in water-dioxane mixtures¹, it appears that change over of the negative slope to a positive one, occurs at $\epsilon \simeq 60$ for Bu_4NI in both water-dioxane and water-methanol mixtures and for Pr_4NI , it appears at $\epsilon \simeq 63-64$ in water-methanol and at $\epsilon \simeq 69$ in water-dioxane mixture. In view of the approximate nature of these estimates, it is justified to assume that change over from a negative to a positive slope for a given salt occurs around the same approximate value of the dielectric constant. The change in the nature of the molecular species (dioxane is non-polar and without hydrogen bonding whereas methanol is polar with hydrogen bond interaction) does not seem to have any appreciable effect. It is only the dielectric constant of the medium which matters. With the limited data in a few solvent systems, it is not possible to make any generalization.

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Kinetics of Reaction Between *o*-Substituted Benzoate Ions & Phenacyl Bromide

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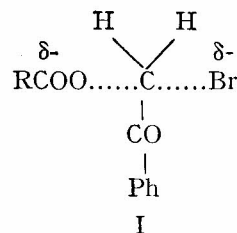
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The rate of reaction of phenacyl bromide with various *o*-substituted benzoate ions has been measured in 90% (v/v) acetone-water mixture at 30°, 35° and 40°. Arrhenius parameters as well as the enthalpies and the entropies of activation have been evaluated. The reaction does not obey the Brønsted relationship. The isokinetic temperature unexpectedly is found to be well below the ambient temperature. Though the behaviour of *o*-substituents is correlated with their polar effects by the Taft equation, it appears that some substituents behave quite unexpectedly. This may be due to the fact that the values of k are all obtained above the isokinetic temperature. The polar substituent constants, σ_p^* , for SCH_3 and SO_2CH_3 groups are evaluated by interpolation in the Taft plot. Variation in ΔS^\ddagger has been explained in terms of the bulk effect of the groups.

KINETICS of reaction of *m*-, *p*- and a few *o*-substituted benzoate ions with phenacyl bromide have been recently reported by Rout and coworkers¹. But a systematic study on the influence of *o*-substituents has not so far been made in this reaction and thus a study to understand the effect of *o*-substituents in this reaction appeared necessary.

The kinetics of the reaction between a number of *o*-substituted benzoate ions and phenacyl bromide are presented in this paper.

The kinetic results are summarized in Table 1. Based on the results obtained by Ananthakrishna Nadar and Gnanasekaran² in the reaction of 6-substituted ω -bromo-2-acetonaphthones with benzoate ion, we have proposed transition state (I) in this reaction.



This shows that the attack is at a point remote from *o*-substituents in the benzene ring. This means that the primary steric effect³ is absent in this reaction and its contribution to the total effect of the substituents is also absent. But the secondary steric effect⁴ of the *o*-substituents may be expected to make contribution. Presumably conjugation between ring and carboxy side-chain will stabilize the ester product and some sign of this might appear in the transition state and be subject to steric inhibition which will lead to retardation. Therefore, the major effects of