

of sodium chloroacetate⁸ and sodium α -chloropropionate⁸ in water at 25°.

All solutions were prepared on molar basis in doubly distilled water and were deaerated. The time of flow measurements on solutions were made using Tuan and Fuoss⁹ type viscometer having a flow time of 717.6 sec for water at 25° in a thermostat with temperature fluctuations less than $\pm 0.005^\circ$. Prior to the measurements, the viscometer was calibrated using 20% sucrose solution at 25°. The density measurements were carried out using 25 ml calibrated pycnometer. The accuracy in density measurement was of the order of 5×10^{-5} g/cc.

The data were analysed in terms of Jones-Dole equation⁷. The values of A and B coefficients were 0.004 and 0.208 dm³ mol⁻¹ for sodium chloroacetate and 0.004 and 0.508 dm³ mol⁻¹ for sodium α -chloroacetate respectively at 25°. It is observed that values of A -coefficient in the present case are positive and equal which is in accordance with the behaviour of 1:1 electrolytes and in confirmation with the Debye-Hückel theory. The B -coefficients are found to be positive for both the salts and it is larger for sodium α -chloropropionate as compared to sodium chloroacetate. Since B -coefficient is an additive property, one can calculate the ionic B -coefficient. Subtracting the value for sodium ion as (0.086 dm³ mol⁻¹)¹⁰, the individual ionic B -coefficient for chloroacetate (CH₂ClCOO⁻) and the α -chloropropionate (CH₃CHClCOO⁻) obtained are 0.1220 and 0.4220 dm³ mol⁻¹ respectively.

The value of B -coefficient for acetate ion (0.25) reported by Laurence and Wolfenden¹¹ has been interpreted by Gurney⁵ as not due to partial localization of negative charge over the entire acetate ion, thereby rendering it a structure-forming ion. In the presently studied chloroacetate ion, the heavy and large size of chlorine atom makes the ion more polarizable as also the negative charge may spread all over the ion. Hence one expects a smaller B -coefficient value for the chloroacetate ion and it is indeed the case. Further, it has been established that introduction of an hydrophobic group (-CH₂-) in an ion¹² or in a molecule¹³ results in a more positive B -coefficient. This fact corroborates with the large B -coefficient (0.42) obtained for α -chloropropionate ion. It appears that a large increase in hydrophobic surface of the ion results in a feeble ionic charge and enforcement of water structure around the large size anions.

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Viscosity of Ternary Electrolytes in Dioxane-Water Mixtures

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The viscosity and density data of seventeen electrolytes in 10, 20 and 30% (by wt) in dioxane-water mixtures have been analysed. The values of the B coefficient and V_e , the effective rigid molar volume have been found to increase with the increase in dioxane content in the medium. This increase occurs due to the formation of more and more hydrogen bonded dioxane-water molecules, with the increase in dioxane content.

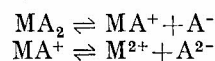
THE viscosity data of electrolyte solution in aqueous and non-aqueous media can be analysed in terms of modified Jones-Dole equation¹,

$$\eta_r = 1 + AC^{1/2} + BC^x \quad \dots(1)$$

where x is an empirical constant and is near about unity, and by Eq. (2) proposed by Das².

$$\eta_r = 1 + A(\alpha C)^{1/2} + B_i \alpha C + B_{ip}(1 - \alpha C) \quad \dots(2)$$

For an electrolyte,



If α is the degree of dissociation of MA^+ , then, Eq. (2) can be written as

$$\eta_r = 1 + A(\alpha C)^{1/2} + B_{A^-}(1 + \alpha C) + B_{M^{2+}}\alpha C + B_{MA^+}(1 - \alpha C) \quad \dots(3)$$

$$\text{or } \eta_r - 1 - A(\alpha C)^{1/2}/C = (B_{MA^+} + B_{A^-}) + \alpha(B_{M^{2+}} + B_{A^-} - B_{MA^+}) \quad \dots(4)$$

The plot of LHS vs α should have a slope of $(B_{M^{2+}} + B_{A^-} - B_{MA^+})$ and an intercept at $\alpha = 0$, of $(B_{MA^+} + B_{A^-})$ and at $\alpha = 1$, the intercept is $(B_{M^{2+}} + 2B_{A^-})$, since there is no ion pair formation. Hence B could be computed at $\alpha = 1$.

Fuoss and coworkers^{3,4} have confirmed Einstein's equation⁵:

$$B = 2.5V \quad \dots(5)$$

where V is the molal volume of the solute particles. Kuruscev *et al.*⁶ reported that Eq. (5) is valid for ions of radii $> 5 \text{ \AA}$. Breslau and Miller⁷ designate V as the effective rigid molar volume, V_e and

calculated it with the help of Eq. (6).

$$V_e = \frac{-2.5C + [(2.5C)^2 - 4(10.05C^2)(1-\eta)]^{1/2}}{2(10.05)C^2} \quad \dots(6)$$

V_e has been strictly defined as the volume which a mole of solute particles occupies when considered, from purely hydrodynamic reasons, as rigid microscopic spheres. Since B coefficient is a measure of ion-solvent interaction, Breslau and Miller⁷ have obtained the relationships (7) and (8) for monovalent and bivalent ions:

$$B = 2.90V_e - 0.018 \quad \dots(7)$$

$$B = 6.06V_e - 0.041 \quad \dots(8)$$

In this note an attempt has been made to find a correlation of the B coefficient obtained from our data⁸ by utilizing the Eq. (2) at $\alpha = 1$ with V_e for seventeen electrolytes at 10, 20 and 30% (by wt) in dioxane-water mixtures at $35^\circ \pm 0.005^\circ$. The values of B and V_e thus obtained are recorded in Table 1.

The electrolytes used were of extra pure quality (E. Merck). Experimental technique adopted has been described earlier¹. The time of flow has an accuracy of ± 0.04 to 0.08% and density readings are accurate up to 4 in 10^6 .

The plot of B vs V_e is found to be linear and the following equations fit the data (both graphically and by least square methods):

$$B = 1.33V_e - 0.020 \quad (\text{in } 10\% \text{ dioxane})$$

$$B = 2.19V_e - 0.033 \quad (\text{in } 20\% \text{ dioxane})$$

$$B = 3.25V_e - 0.100 \quad (\text{in } 30\% \text{ dioxane})$$

This indicates that the slope of the plot of B versus V_e changes with the change in the dielectric constant. This can be explained as follows: As a result of solute-solvent interaction small density changes take place at the interface in the solute and the solvent molecules. These density changes lead to changes in the microscopic viscosities of the solvent at the interface. This is reflected either as an increase or decrease in Einstein's slope, depending upon whether the microscopic viscosities are, respectively, higher or lower than the pure

solvent value. As the dielectric constant decreases, the divalent ion as a result of higher charge density, tends to induce much more structuring in the solvent at the interface. This results in an increase in microscopic viscosity of the solvent at the interface.

A gradual increase in viscosity and hence an increase in the B value is observed as the dioxane content of the solvent medium is increased (Table 1). This phenomenon seems obvious in terms of increasing intermolecular association⁹ between water and dioxane with the formation of bigger molecules.

The value of V_e decreases with the decrease in dioxane content of the solvent, in agreement with the theoretical expectation. This may be interpreted in terms of the bond formation between water and dioxane molecules. As dioxane content is increased more and more hydrogen bonded dioxane-water molecules are formed resulting in an increase in V_e (Table 1).

The values of B and V_e for the same solvent composition and for the same anion are not the same for different cations. The magnitude of B and V_e is higher for cations carrying greater charge and hence these are more structure-forming than the ions carrying lower charge which give higher value of V_e . The order is: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$; $Zn^{2+} > Ni^{2+} > Mg^{2+}$; and $Na^+ > K^+$.

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Reactions of Organotin Isopropoxides with Acetyl Pseudohalides

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Reactions of trialkyltin isopropoxides, R_3SnOPr^i (where $R = Et, Pr^n$ or Bu^n) and dialkyltin diisopropoxides, $R_2Sn(OPr^i)_2$ (where $R = Me, Et$ or Bu^n) with acetyl pseudohalides, CH_3COX (where $X = CN$ or NCS) give compounds of the types R_3SnX , $R_2Sn(OPr^i)(X)$ and $R_2Sn(X)_2$. The compounds have been characterized on the basis of molecular weight, infrared spectral and volatility data.

TRIETHYLTIN cyanide is one of the earliest known organometallic pseudohalides¹. Later on, many more organotin pseudohalides have been

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TABLE 1 — VALUES OF B AND V_e IN DIFFERENT DIOXANE-WATER MIXTURES (WT %)

Electrolyte	B			V_e		
	10%	20%	30%	10%	20%	30%
BaCl ₂	0.211	0.364	0.514	0.112	0.152	0.186
SrCl ₂	0.308	0.412	0.512	0.118	0.154	0.199
CaCl ₂	0.276	0.368	0.518	0.128	0.164	0.201
MgCl ₂	0.430	0.458	0.742	0.190	0.244	0.292
BaBr ₂	0.202	0.393	0.534	0.130	0.197	0.286
MgBr ₂	0.356	0.542	0.779	0.191	0.247	0.358
Ba(ClO ₄) ₂	0.218	0.318	0.495	0.123	0.154	0.226
Mg(ClO ₄) ₂	0.271	0.412	0.684	0.122	0.210	0.270
Ba(NO ₃) ₂	0.110	0.280	0.330	0.064	0.122	0.153
Sr(NO ₃) ₂	0.200	0.270	0.400	0.107	0.128	0.157
Ca(NO ₃) ₂	0.340	0.390	0.433	0.130	0.156	0.194
Mg(NO ₃) ₂	0.380	0.420	0.500	0.161	0.195	0.216
Na ₂ SO ₄	0.255	0.264	0.313	0.130	0.148	0.156
K ₂ SO ₄	0.228	0.238	0.288	0.122	0.138	0.141
MgSO ₄	0.610	0.660	—	0.258	0.269	—
NiSO ₄	0.690	0.710	—	0.292	0.297	—
ZnSO ₄	0.670	0.680	—	0.269	0.287	—