Dielectric Measurements on Solutions of Electrolytes in 1,2-Dichloroethane

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RECENT interest in the structure of electrolyte solutions in solvents of low permittivity,[1] particularly when these are employed in kinetic studies, *e.g.*, cationic polymerisation,[2] prompts us to report briefly the results of some measurements of the permittivity (ϵ') and loss (ϵ'') of tetra-alkylammonium salts in 1,2-dichloroethane. Measurements were made in the frequency range 1—3000 Mc./sec., and the general features of the dielectric absorption are similar to those reported for tetrabutylammonium bromide in acetone.[3] Longer relaxation times are, however, generally observed and if the data are represented by the usual Cole–Cole relation[4]:—

$$\epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (j\omega\tau_0)^{1-\alpha}}$$

then non-zero values of the distribution parameter, α, are required. The relaxation time, τ_0, is defined as $1/\omega_0$, where ω_0 is the angular frequency ($2\pi f$) at which ϵ'' has its maximum value; ϵ_0 and ϵ_∞ are the low- and high-frequency limiting values of ϵ' and the operator j is $\sqrt{-1}$.

The existence of a distribution parameter is sometimes considered to be the result of non-exponential decay of electric polarisation.[5] In systems where there is a possibility of more than one relaxation process occurring, however, it is reasonable to analyse the data into the sum of two or more dispersion regions,[6] each governed by an exponential law and characterised by a single relaxation time, τ_k, and an amplitude constant, C_k, such that $\sum_k C_k = 1$, *i.e.*,

$$\epsilon' - j\epsilon'' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\sum_k C_k/(1 + j\omega\tau_k).$$

We have accordingly analysed our data by means of an unweighted "least-squares" procedure,[6] employing an I.C.T. 1900 computer for the purpose, and find that they are adequately represented as the sum of two relaxation processes. The sums of the squared deviations between calculated and observed values, *i.e.*, $\sum(\epsilon'_{\text{calc}} - \epsilon'_{\text{obs}})^2 + \sum(\epsilon''_{\text{calc}} - \epsilon''_{\text{obs}})^2$ lie between 0·02 and 0·05.

Some derived parameters for solutions of various concentrations of tetrabutylammonium bromide in 1,2-dichloroethane at 25° are summarised in the Table, although for the two lowest concentrations studied the experimental data are considered to be insufficiently accurate to warrant analysis. The estimated uncertainties in τ_0 are $\pm 5\%$ and in τ_2, and τ_1 $\pm$ 10%.

TABLE

Concn. (M)	$10^{12} \times \tau_0$ (sec.)	α	C_1	$10^{12} \times \tau_1$ (sec.)	$10^{12} \times \tau_2$ (sec.)
0·4	211	0·07	0·30	100	280
0·3	217	0·07	0·24	85	285
0·2	235	0·05	0·20	75	295
0·1	225	(0·06)	—	—	—
0·05	264	(0·06)	—	—	—

Other tetrabutylammonium salts examined *e.g.*, nitrate and perchlorate, have similar values of τ_0 but somewhat larger distribution parameters.

The sets of values of C_1, τ_1, and τ_2 reported here do not in themselves constitute a unique analysis of our experimental data. An alternative resolution into two relaxations is possible with $1 > C_1 > 0{\cdot}5$ and with appropriate modifications to the values of τ_1 and τ_2 ($\tau_1 < \tau_2$). We prefer the values reported here because of their greater consistency with previously published results.[3] In either case, the possible existence of two dispersion regions, each characterised by a single relaxation time, could be interpreted as indicating the presence of two distinguishable types of ion-pair in the electrolyte solution.

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