Dielectric Relaxation Studies of Tin(IV) Chloride in some Non-polar Solvents

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TIN(IV) chloride possesses a symmetrical tetrahedral structure in the gas phase.[1] A zero dipole moment is observed for the molecule in the gas phase,[2] and in carbon tetrachloride,[3,4] and hexane solutions.[4] This confirms the essential symmetry of the molecule in these media. Solutions of tin(IV) chloride in solvents capable of acting as donor molecules in charge-transfer interactions (*e.g.* benzene, dioxan) show a non-zero orientation polarization. Dipole moments of 0·8 D,[3] 0·87 D,[5] and 0·96 D [6] have been reported for benzene solutions and 3·84 D [7] and 5·1 D [8] for dioxan solutions. Dielectric relaxation measurements provide a means of investigating the stability of charge-transfer complexes.[9,10] Stable complexes behave in the same way as do rigid molecules and relax by molecular reorientation. The decomposition of a polar complex into its nonpolar constituents provides another relaxation mechanism. This mechanism predominates over the molecular reorientation if the life-time of the complex is sufficiently short. The observed relaxation time will then be shorter than that expected from a rigid entity of similar dimensions to that of the complex.

The dielectric properties (permittivity and dielectric loss factor) were measured at 1, 3, 8·5, and 35 GHz by using techniques described previously.[10] The variation of the dielectric loss factor (ϵ'') with frequency (f) is given by the Debye equation

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\frac{\omega\tau}{1 + \omega^2\tau^2}$$

where ϵ_0 is the permittivity at low (or static) frequencies, ϵ_∞ is the permittivity at high frequencies where the orientation polarization has ceased to contribute, τ is the relaxation time, and $\omega = 2\pi f$. Values of $(\epsilon_0 - \epsilon_\infty)$ and τ are chosen to give the best fit between the experimental results and the Debye equation. Dipole moments (μ) were calculated with the equation,

$$\mu^2 = \frac{(\epsilon_0 - \epsilon_\infty)\, 6750\, \boldsymbol{k}T}{(\epsilon_0 + 2)^2\pi \boldsymbol{N}c}$$

where c is the solute concentration in mole l.$^{-1}$. All materials were dried and purified before use, and an excess of donor solvent (benzene or dioxan) was used to ensure maximum complex formation. A solution of tin(IV) chloride in carbon tetrachloride gave no significant loss ($\epsilon'' \leqslant 0{\cdot}5 \times 10^{-3}$) over the frequency range studied. This confirms the zero dipole moment observed earlier[3,4] for tin(IV) chloride in carbon tetrachloride.

The observed dipole moment in benzene solution (Table) is slightly higher than the values previously reported in the literature. These literature values made some allowance for atomic polarization contributions to the total polarization. This correction is unnecessary here as the dipole moments are calculated from the maximum loss factor which is a direct measure of the orientation polarization. The dipole moment of the dioxan complex agrees better with the value of 5·1D obtained by Osipov *et al.*[8] than it does with the 3·4D obtained by Lane *et al.*[7] However, this dipole moment is concentration dependent. The presence of both 1 : 1 and 1 : 2 complexes between tin(IV) chloride and dioxan has been reported,[11] and the 1 : 1 complex isolated as a solid.[12] The structure of the 1 : 1 complexes is undecided. One theory[11] suggests a dioxan molecule in the boat configuration forms a bidentate linkage with the tin atom, another theory[12] suggests a polymeric form with each dioxan molecule forming a connecting link between two tin(IV) chloride molecules. By using the relation $\tau = 3V\eta/\boldsymbol{k}T$ (where V is the molecular volume, and η the solution macroscopic viscosity) and by assuming a spherical shape (radius 3·4 Å) for the bidentate model a relaxation time of 156×10^{-12} sec. is calculated for the complex in dioxan solution. It is well established[13] that the use of the macroscopic viscosity instead of the microscopic (or internal) viscosity in the above equation produces calculated relaxation times which are often greater than the experimentally observed times by a factor of three or four. The observed relaxation time of 190×10^{-12} sec. for the dioxan complex is thus associated with the relaxation of a stable (probably polymeric) complex.

Relaxation parameters for tin(IV) *chloride in donor solvents at* 293°K

Donor	Concentration $SnCl_4$ (mole l.$^{-1}$)	$(\epsilon_0 - \epsilon_\infty)$	$10^{12}\,\tau$ sec.	μ (D)
Benzene ..	0·26	0·038	15·5	0·99
Dioxan ..	0·034	0·156	195	5·9
	0·046	0·152	191	5·2
	0·053	0·192	193	5·3
	0·074	0·216	185	4·9

The relaxation time for the benzene complex is much shorter than expected for a rigid 1 : 1 complex. This suggests the presence of a short-lived entity whose life-time is of the order of pico-seconds. Charge-transfer interactions in this system are of the contact charge-transfer type[14] and no stable complex is formed. The charge-transfer band observed between 320—360 nm.[15] does not distinguish between the formation of stable and contact charge-transfer interaction.

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