PHYSICO-CHEMICAL STUDIES IN ACYL HALIDES
PART-I VISCOSITY OF ELECTROLYTE SOLUTIONS IN ACETYL CHLORIDE

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Relative viscosities of tetraethylammonium chloride, and tetrabutylammonium chloride have been measured in the concentration range 1.756 - 32.16x10^{-3} mole/litre in acetyl chloride at 25°C. A and B parameters of Jones-Dole equation have been estimated and all the salts have been found to act as structure makers and this property increases with the effective increase in the size of the ions.

Physico-chemical studies in solvents[1-4] provide extremely valuable information regarding the behaviour of electrolytes in the solvents, their role in inorganic reactions as well as their use in the industry. Acetyl chloride has been used as solvent[5,6] but all the work has been directed towards elucidation of the mode of ionization, behaviour of Lewis acids and bases and their neturalization reactions, solvolytic reactions and thermochemical studies. No work regarding the fundamental information in the physical properties of electrolytic solutions has so far been carried out inspite of the fact that acetyl chloride has very convenient physical properties m.p.-112.0°C, b.p. 51.8°C d = 1.0983 g/ml at 25°C dielectric constant 15.9 (at 20°C) and conductivity 4.0x10^{-7} ohm^{-1} cm^{-1} . In the present communication,we report the viscosity measurements of some of the electrolytes at 25°C in this solvent.

EXPERIMENTAL

Acetyl chloride (BDH, L.R. Grade) b.p. 50-52°C was distilled over 10% dimethyl aniline and the fraction of b.p. 50.5-51.5°C was refractioned over sodium. Freshly distilled acetyl chloride was used for each run.

Tetraethylammonium chloride, tetrabutylammonium chloride and tetrabutylammoniym perchlorate (Fluka - pure grade) were recrystallized from conductivity water and dried in vaccum at 100°C. Benzyldimethylphenylammonium chloride was prepared from pure dimethyl aniline and benzyl chloride under anhydrous conditions. The product was recrystallised from absolute alcohol and traces of alcohol was removed by heating in vaccum.

The viscosity of the solutions was measured by using modified Ubbelhode capillary type viscometer fitted with silica gel guard tube at 25° ± 0.02°C. Freshly distilled carbon tetrachloride (BDH AnalaR b.p. 78.2°C, η, 9.09x10^{-3} poise; d,1.584 g/ml^{-1}) benzene (BDH AnalaR m.p. 5.51°C ,η = 5.996x10^{-3} poise; d, 0.8737 g/ml) and conductivity water (η=. 8.937x10^{-3} poise, d,= 0.9970 g/ml^{-1}) were used as reference liquids for calibration of the viscometer. The viscosity of the solutions was computed by Poisieuille equation[7] which relates the liquid viscosity to the flow time and dimensions of the viscometer and also include the kinetic energy correction.

Density measurements required for the viscosity calculations were made with the help of bicapillary pycnometer. It was calibrated with fresh distilled mercury.

TABLE 1

VISCOSITY AND RELATIVE VISCOSITY OF ELECTROLYTE SOLUTIONS IN ACETYL CHLORIDE AT 25°C

Electrolyte	Conc.(C) mole/Litre	d (g/ml)	η/η_o
Tetrabutyl-	0.001756	1.09790	1.0040
ammonium	0.006002	1.09799	1.0107
perchlorate	0.011742	1.09806	1.0186
	0.015988	1.09811	1.0244
	0.022313	1.09817	1.0322
Tetrabutyl-	0.005333	1.09765	1.0056
ammonium	0.010954	1.09765	1.0112
chloride	0.014919	1.09746	1.0160
	0.021910	1.09725	1.0227
	0.028468	1.09706	1.0302
Tetraethyl	0.003142	1.09794	1.0029
ammonium	0.005921	1.09798	1.0049
chloride	0.009184	1.09801	1.0069
	0.012205	1.09808	1.0099
	0.015529	1.09813	1.0119
Benzyldimethyl-	0.00226	1.09808	1.0050
phenylammonium	0.00614	1.09819	1.0089
chloride	0.01224	1.09855	1.0152
	0.02024	1.09882	1.0212
	0.03216	1.09927	1.0303

All the solutions were prepared by dissolving the required amount of solute in acetyl chloride in a 100 ml measuring flask. This was kept at 25°C and the solvent at 25°C was added to make the solution to the mark. The transfer of the solution was done in a dry box under an atmosphere of nitrogen.

RESULTS AND DISCUSSION

Viscosity, density and relative viscosity of solutions of tetraethylammonium chloride, tetrabutylammonium perchlorate and benzyldimethylphenyl ammonium chloride have been determined in the concentration range 1.756 - 32.16×10^{-3} mol/litre at 25°C. All the relevant data have been recorded in Table 1.

Plots of viscosity vs concentration for all the electrolytes are linear. A similar behaviour has been observed in other solvents also [7,8].

Semi-empirical Jone-Dole equation[9] has been used to analyse the viscosity data:

$$\eta/\eta_0 = 1 + A\sqrt{c} + B\ c$$

where the symbols have their usual meaning. The values of parameters A and B have been determined from the linear plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ versus $\sqrt{c}$. These values are recorded in Table 2.

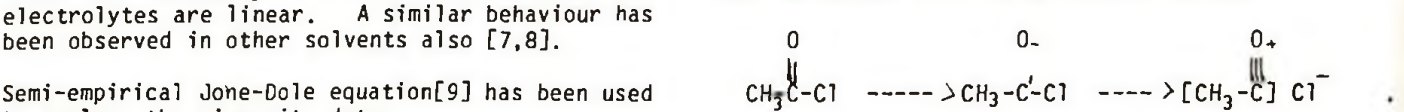
Perusal of Table 2 reveals that the B-values increase with the increase in the size of the ions, showing thereby the increase in the structure making capacity with the increasing size of the ions. . Though tetraalkylammonium salts show a similar behaviour in methanol[10] and acetonitrile[4], the difference in the structure making capacity of these ions in these solvents is much less as compared to that observed in acetyl chloride in the present studies.

TABLE 2

VALUES OF THE PARAMETERS OF JONES-DOLE EQUATION

Electrolyte	$-A$ (moles$^{-1/2}$ litre$^{1/2}$)	B (mole^{-1} litre)
Tetrabutylammonium perchlorate	0.05	1.12
Tetratylammonium chloride	0.002	1.03
Tetraethylammonium chloride	0.018	0.61
Benzyldimethylphenyl ammonium chloride	0.080	0.49

Structure of acetyl chloride can be represented by the following resonating structures[11]



Because of these different resonance structures, the same site of acetyl chloride is capable of interacting with both anions and cations. This large variation in structure making capacity of tetraalkylammonium ions in acetyl chloride may be because of this unique type of solvation of these ions in this solvent. Tetraalkylammonium ions have been found to show anamolous behaviour because of their very large size in the other solvents also [12].

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