MOLAR VOLUMES OF TETRAALKYLAMMONIUM SALTS IN ACETYL CHLORIDE

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Acetyl chloride has been used as non-aqueous solvent by Paul and co-workers [1] for carrying out solvolytio, matathetical, acid-base and thermochemical reactions. This solvent has also been used by the present authors for the study of relative viscosities of various tetraalkyl salts and found that all these salts are structure makers [2].

EXPERIMENTAL

Salt samples are the same as in ref[3]. Acetyl chloride (BDH LR grade) b.p. 50-52°C was distilled over 10% dimethyl aniline and the fraction boiling between 50.5-51.5°C was refluxed over sodium. Freshly distilled acetyl chloride was used for each run.

Details of the density measurements and calculation of apparent molar volumes are as in ref. [3]. The temperatures of study were 293.15°C and 298.15°C.

RESULTS

The plot of apparent molar volume vs square root of molar concentration of electrolyte gives straight lines in all the cases (Fig.1).

The values of partial molar volume and the slope for different electrolytes studied are given in Table 1. The value of S_v is found to be positive in all cases and this indicates that ion-ion interactions exist in the case of solutions of electrolytes in acetylchloride solvent. Further these interactions are weakened with the increase in the temperature.

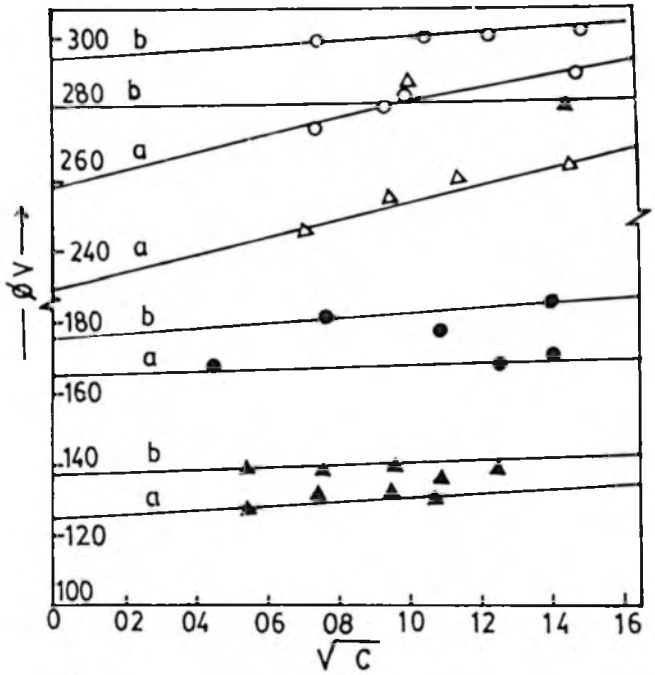


Fig. 1 Plot of apparent molar volume vs square root of concentration of tetraalkylammonium salts at 293.15°K and 298.15°K in acetyl chloride.

- ○ Tetrabutylammonium perchlorate
- △ Tetrabutylammonium chloride
- ● Benzyldimethylphenylammonium chloride
- ▲ Tetraethylammonium chloride

TABLE 1

VALUES OF PARTIAL MOLAR VOLUMES ϕ_v° AND SLOPES (S_v) OF ELECTROLYTES IN ACETYL CHLORIDE

Electrolytes	Molecular weight	At 293.15°K		At 298.15°K	
		ϕ_v° cm³/mole	S_v (cc/mole)$^{3/2}$	ϕ_v° cm³/mole	S_v (cc/mole)$^{3/2}$
Tetrabutylammonium perchlorate	341.5	258	250	293	55.55
Tetrabutylammonium chloride	277.92	230	230	270	27.27
Benzyldimethylphenyl-ammonium chloride	247.5	165	50	175	62.5
Tetraethylammonium chloride	165.5	125	50	137	28.57

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TABLE 2

VALUES OF PARTIAL MOLAR VOLUMES ϕ_v OF ELECTROLYTES IN BENZOYL CHLORIDE AND ACETYL CHLORIDE

Electrolyte	ϕ_v' cm3 /mole		ϕ_v° cm3 /mole	
	Benzoyl chloride		Acetyl chloride	
	At 298.15°K	At 303.15°K	At 293.15°K	At 298.15°K
Tetrabutyl-ammonium perchlorate	322	336	258	293
Tetrabutyl-ammonium chloride	296	322	230	270
Benzyldimethyl-phenylammonium chloride	220	220	165	175
Tetraethyl-ammonium chloride	162	182	125	137

The partial molar volumes are large and positive. They increase with increase in molecular weight and temperature as can be expected. However, the increase with temperature in the case of benzyldimethylphenylammonium chloride is small. The partial molar expansibility has been found to be positive for all the electrolytes in acetyl chloride indicating the behaviour of the electrolytes in acetyl chloride is like those of symmetrical salts and not like common electrolytes [4]. So it can be concluded that in acetyl chloride solvent system, tetraalkylammonium salts, solvent-solute interactions predominate and it confirms our earlier observation that these electrolytes act as structure makers.

It may be interesting to compare the partial molar volumes of various electrolytes in acetyl chloride with benzoyl chloride [3]. It is evident from Table 2 that partial molar volumes of all the electrolytes are larger in benzoyl chloride than those of acetyl chloride. So, it can be concluded that these electrolytes behave as structure maker more in benzoyl chloride than acetyl chloride. This difference in behaviour of electrolytes in these two solvents may be due to the difference in their dielectric constants (Benzoyl chloride = 22.9, Acetyl chloride = 15.8).

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