MOLAR VOLUMES OF TETRAALKYLAMMONIUM SALTS IN BENZOYL CHLORIDE

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The determination of thermodynamic property such as partial molar volume of an electrolyte in solution has been of considerable value in understanding the various interactions taking place in the solution.

Survey of literature reveals that a large number of partial molar volume studies have been carried out in aqueous media [1] and to lesser extent in non-aqueous solvents. Such studies have not been attempted in benzoyl chloride. Partially, it is due to a large number of difficulties encountered in handling of this solvent as it is hygroscopic and fumes in moist air. Poor solubility of salt is another problem in this solvent.

Benzoyl chloride has been used as a non-aqueous solvent by Paul and co-workers [8-10] for carrying out solvolylic, metathetical, thermochemical and acid base reactions. Pahil and co-workers have also used this solvent [11].

Molar volume of tetrabutylammonium perchlorate, tetrabutylammonium chloride, tetraethylammonium chloride and benzyldimethylphenylammonium chloride have been determined at various concentrations in benzoyl chloride at 298.15°K and 303.15°K and the results are discussed in this article.

EXPERIMENTAL

Pure samples of tetrabutylammonium perchlorate, tetrabutylammonium chloride, tetraethylammonium chloride were recrystallized from conductivity water and dried in vacuum. Benzyldimethylphenylammonium chloride was prepared in the laboratory and recrystallized twice from alcohol before use. Benzoyl chloride of L.R. grade was purified by distilling over magnesium oxide as described by Paul and co-workers [8-10].

Density was measured in a bicapillary pyknometer. The ends of both capillaries had standard joints. The solutions in the pyknometer was protected from atmospheric moisture by the use of standard joint stoppers during the weighing and by guard tube during the rest of manuplations. The pyknometer was standardized at 298.15°K and 303.15°K with freshly distilled mercury.

RESULTS

The apparent molar volume ϕ_v was calculated from the density data using the following equation

$$\phi_v = \frac{M}{d_o} - \frac{1000}{c}\,\frac{d - d_o}{d}$$

where c is the molar concentration of electrolyte, d is the density of solution and d_o is the density of pure benzoyl chloride and M is the molecular weight of the electrolyte used. The results at 298.15°K and 303.15°K are given in Fig. 1

A plot of apparent molar volume vs square root of molar concentration of electrolyte gave straight line with all electrolytes studied (Fig. 1) suggesting that the data fit into the emperical equation given by Masson [12].

$$\phi_v = \phi_v^\circ + S_v \sqrt{c}$$

where ϕ_v° is apparent molar volume at infinte dilution and is equal to the partial molar volume. S_v is the experimental slope of the plot. The values of partial molar volume and the slope for different electrolytes studied are given in Table 1. A perusal of Table 1 shows that the values of slope are all negative at both the temperatures. Since the

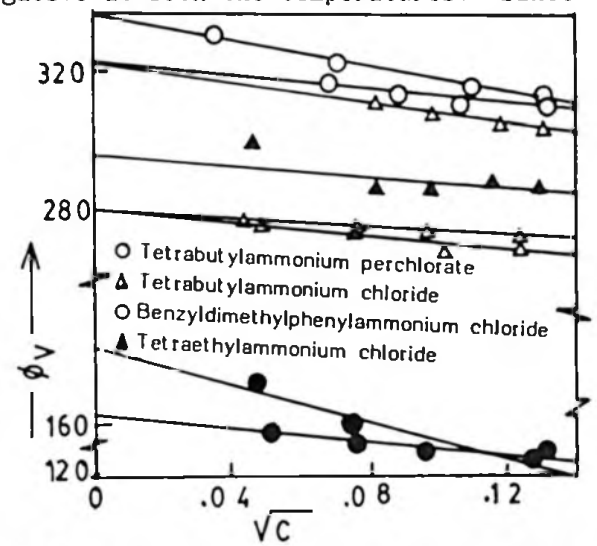


Fig. 1 Plots of apparent molar volume vs $\sqrt{c}$ of tetraalkylammonium salts in benzoyl chloride
(a) at = 298.15°K (b) at = 303.15° K

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TABLE 1

VALUES OF ϕ_v AND SLOPES (Sv) OF ELECTROLYTES AT 298.15°K AND 303.15°K IN BENZOYL CHLORIDE d_o OF SOLVENT 1.2076 g/ml at 298. 15°K, 1.2024 g/ml at 303.15°K

Electrolyte	Molecular weight	At 298.15 K		At 303.15 K	
		ϕ_v° cm^3/mole	Sv (cc/mole)$^{3/2}$	ϕ_v° cm^3/mole	Sv (cc/mole)$^{3/2}$
Tetrabutylammonium perchlorate	341.5	322	-83.33	336	-166.66
Tetrabutylammonium chloride	277.92	296	-66.66	322	-133.33
Benzyldimethyphenyl-ammonium chloride	247.5	220	-90.90	220	-117.64
Tetraethylammonium chloride	165.5	162	-83.33	182	-272.72

slope S_v is a measure of ion-ion interactions, these results point out that such interactions are quite weak and these are further weakened with increase in the temperature. The values of partial molar volumes of all the electrolytes studied are positive and large suggesting large solvent solute interactions.

The partial molar expansibility [$\phi_E^\circ = \Delta\phi^\circ/\Delta T$] is positive indicating that the behaviour of all the electrolytes in benzoyl chloride is like those of symmetrical salts and not like common electrolytes [13]. So it can be concluded that solvent-solute interactions predominate in tetraalkylammonium salts in benzoyl choloride solvent and it confirms our earlier observation that these electrolytes act as structure makers.

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