"PRESSURE AND TEMPERATURE EFFECTS ON THE WALDEN PRODUCT OF TWO TETRA-ALKYL AMMONIUM SALTS IN DIFFERENT SOLVENTS"

by

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Most of electrolytes in non-aqueous solvents have much lower electrical conductivity than in pure water and so measurements can be made at lower concentrations without serious loss of accuracy. On the other hand, these solvents have to be very purified and they require careful protection from atmospheric moisture. This last requirement is very important specially for alcoholic solution considering that very small amounts of dissolved water can minimize the values of experimental conductances (1).

Investigations on transport properties in alcoholic solutions are less frequent than in other non-aqueous systems perhaps on account of the hydrogen bonding which can favour certain types of structural effects which can difficult data interpretation. The majority of these studies have been made at room temperature and atmospheric pressure.

In this work pressure and temperature effects on the Walden product of tetra-ethyil and tetra-n-butyl ammonium salts in six different protic solvents are studied.

The data of limiting molar conductivities were treated by both the appropriated Fuoss-Onsager equation (2)

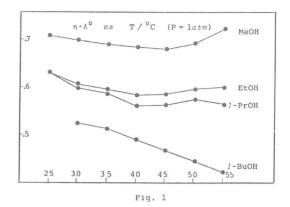
and a quadratic (3) where $c^{1/2}$ was taken as the independent variable. Both methods have given similar results and they are comparable to those few cases (4) where such comparison was possible.

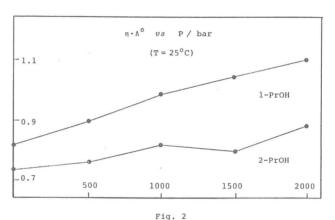
The Walden product in general has several types of behaviours according this is plotted <u>versus</u> temperature, <u>versus</u> pressure or as function of carbonic length of the solvent (Fig. 1 , 2 and 3), and the interpretations for it can be found in the effects of pressure and temperature on the ion mobility and on the electroforetic and relaxation effects.

Association constants were also determined as a function of temperature and pressure.

References

- (1) Murray-Rust, T. M. and Hartley, H., Proc. Roy. Soc., 1930, A-126, 84
- (2) Fuoss, R. M. and Onsager, L., J. Phys. Chem., 1957, 61, 668
- (3) Calado, A. R. T., "Reacções de Menschutkin em Alcoóis: Termodinâmica e Cinética", Tese de doutoramento, Lisboa, 1986
- (4) Evans, D. F. and Gardam, P., J. Phys. Chem., 1968, 72, 3281





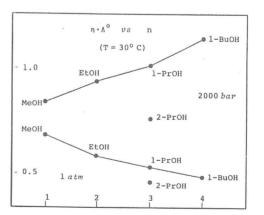


Fig. 3