II. Ionic Association and Mobility in Propylene Carbonate

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Conductance data are reported for \(\text{Ph}_4\text{AsPic}, \text{Ph}_4\text{PPic}, \text{Ph}_4\text{SbPic}, \text{Hex}_4\text{NPic}, \text{Bu}_4\text{PPic}, \text{Et}_4\text{NSbCl}_6\) in propylene carbonate at 25°C in the concentration range \(1 \times 10^{-4}\) to \(15 \times 10^{-4}\) M. The data were analyzed by the Justice modification of the Fuoss-Hsia equation and all salts studied were found to be associated and to form solvent separated ion pairs. Application of the Barthel-Bjerrum model of ion association permitted calculation of the non coulombic portion of the potentials of mean force, \(W_+\). Ionic limiting equivalent conductances of six ions were calculated using known values of \(R^+_\text{As}\), and \(\text{Pic}^+\) ions. Walden products of ions in propylene carbonate were examined in the light of modern ion mobility theories, including Boyd-Zwanzig, Hubbard-Onsager, and Hubbard-Kayser models of ion solvent interactions.

KEY WORDS: Ionic conductivity; propylene carbonate; ion pairs; nonaqueous solvents.

1. Introduction

Propylene carbonate (PC), \(\text{C}_4\text{H}_6\text{O}_3\), is an aprotic,\(^{(1)}\) dipolar solvent of high dielectric constant (64.92), and a very large dipole moment (4.98D). It is relatively easy to purify, nonhygroscopic, and non toxic. PC is regarded as a moderate Lewis base and a weak Lewis acid, solvating cations and anions slightly. It dissolves a range of inorganic and organic substances and is one of a series of liquids which have been utilized in lithium batteries\(^{(2)}\) as solvents and cosolvents. The mass transport properties of electrolyte solutions of these nonaqueous solvents and electrolyte solution-electrode interactions can limit the efficiency and performance of these batteries. Reviews\(^{(3,4)}\) of the solvent properties of propylene carbonate are available.

As part of a series investigating the influence of the chemical nature and structure of ions on their mutual interactions and their inter-
actions with solvent, we have measured the conductance of a series of quaternary salts of picrate and hexachlorantimonate ions. The results have been interpreted in terms of the specific constitutional and structural factors of the solvent and of the solutes.

2. Experimental

2.1. Solutes

Both tetraphenylarsonium picrate (Ph$_4$AsPic) and tetraphenylphosphonium picrate (Ph$_4$PPic) were prepared as we reported previously. Tetraethylammonium hexachloroantimonate (Et$_4$NSbCl$_6$) was prepared by the method of Ledwith et al. Tetraphenylantimony picrate (Ph$_4$SbPic) was prepared by metathesis from tetraphenylantimony bromide (Alfa) and sodium picrate. A 0.08M solution of the bromide in 70% aqueous acetone was mixed with an equivalent amount of a 0.50M sodium picrate solution in 70% aqueous acetone and cooled to -10°C. After filtration and washing with water the yellow solid was thrice recrystallized from acetone by addition of one half volume of water. The final product was dried in vacuo at room temperature for two days (M.P. 195-197°C).

Tetrabutylphosphonium picrate (Bu$_4$PPic) was prepared from tetrabutylphosphonium bromide (Alfa) and sodium picrate. A 1.33M solution of the bromide in 70% aqueous acetone was mixed with a 0.57M solution of sodium picrate in the same solvent and cooled to -10°C for one hour and a yellow oil separated. The yellow oil was dissolved in acetone and an equal volume of water added and cooled to -10°C for two days. The picrate salt crystallized and was recrystallized from acetone twice in the same manner. The final picrate salt was vacuum dried at room temperature for two days (M.P. 57-58°C).

Tetrahexylammonium picrate (Hex$_4$NPic) was prepared from tetrahexylammonium iodide (Eastman Kodak) and sodium picrate. A 0.035M solution of the iodide in 70% aqueous acetone was added to a 0.035M solution of sodium picrate in the same solvent at room temperature. A yellow oily layer formed. The oil was dissolved in acetone, cooled to -20°C, an equal volume of water added and the salt crystallized. The salt was recrystallized twice from acetone in the same manner as the oil. The crystals were dried in vacuo at room temperature for three days (M.P. 36-37.5°C).

All the salts were analyzed for C, H, N, and P, where possible and agreement between predicted and found values were well within commonly accepted limits. All salts were vacuum dried before use.