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High-Conductivity Solid Electrolytes. Tropyllium Iodide–Silver Iodide System

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Since the discovery[1-3] of the family of high-conductivity solid electrolytes MAg_4I_5 (M = K, Rb, NH_4), we have carried out an extensive search for high ionic conductivity in other AgI double-salt systems. We have previously reported the discovery of many compounds of high ionic conductivity in the systems QI–AgI, where Q^+ is an ammonium ion[4-6] or a sulfonium ion.[7] The high Ag^+ mobility in these compounds has been attributed to the unique crystal structures characterized by face-sharing iodide polyhedra, forming channels of Ag^+ sites through the structure, and by a large excess of vacant Ag^+ sites in the unit cell.[8-11]

In this paper we report our investigation of the tropyllium iodide (C_7H_7I)–silver iodide system, the first examination of a stable carbonium ion system.

Experimental Section

Using the method of Kursanov and Vol'pin[12] for the preparation of tropyllium chloride, a stirred mixture of 41 g of PCl_5 in 500 ml of CCl_4 was treated dropwise with 9 g of cycloheptatriene in 50 ml of CCl_4. The system was protected by a $CaCl_2$ tube. After addition of the triene was complete, the heavy slurry was stirred for 2 hr at room temperature and was then filtered through a coarse frit. The collected filtrate was cooled in Dry Ice and 20 ml of H_2O was added dropwise with stirring. Much heat and HCl were evolved. After warming to 25°, 50 ml of 55% HI was added to the solution of C_7H_7Cl, followed by 200 ml of acetone. Bright red crystals of C_7H_7I separated, were collected, washed with acetone, and stored in vacuo.

Mallinckrodt reagent grade AgI was used without further purification. The AgI–C_7H_7I compositions were prepared by the paste preparation procedure previously described.[4] The measurement of the density of the electrolytes has also been described.[4] The conductivities were measured using the cell Ag, $RbAg_4I_5$–sample–Ag, $RbAg_4I_5$ as previously reported.[4,13] All measurements were made at 22°.

Results

The experimentally determined densities and specific conductivities are shown in Table I. Contact resistances[13] were not determined; the reported values for the specific conductivities therefore represent a lower limit. Our experience[4] indicates that the corrected values would be 5–8% higher.

Discussion

The observed maximum in specific conductivity around 80–85 mol % of AgI, while not as sharp as that observed in other systems,[4,6-8] indicates that at least one compound with specific conductivity greater than that of AgI is formed in this system. More work would be necessary to establish the exact stoichiometry of the conductive compound (or compounds). The fact that the electrochemical cell Ag–$C_7H_7I \cdot 4AgI$–C, $(CH_3)_4NI_9$ has the correct potential of 0.63 V indicates that the conduction is primarily ionic, rather than electronic.[14]

Table I. Density and Specific Conductivity in the Tropyllium Iodide–Silver Iodide System

Mol % of AgI	Density, g/cm^3	Specific conductivity, (ohm cm)$^{-1}$
75	4.16	5.04×10^{-3}
80	4.42	5.84×10^{-3}
85	4.69	5.78×10^{-3}
90	4.97	5.30×10^{-3}
95	5.33	1.94×10^{-3}
100	5.75	4.00×10^{-4}

The highest conductivity we have observed for onium iodide–silver iodide compounds is 0.06 (ohm cm)$^{-1}$ (e.g., for diethyldimethylammonium[4] and quinuclidinium[6]); the maximum conductivity shown in Table I is an order of magnitude less, but still an order of magnitude greater than the conductivity of pure AgI. The inorganic compound $RbAg_4I_5$ has a specific conductivity of 0.26 (ohm cm)$^{-1}$.

The work presented here supports our previous conclusions[4,6,7] that there are a multitude of QI–AgI solid electrolytes exhibiting high ionic conductivity and that the Q^+ ion, whether ammonium, sulfonium, or, as in this case, carbonium, serves merely to stabilize a structure through which the Ag^+ ion can move freely.[15] The most important characteristic of the Q^+ ion seems to be its size, rather than its composition and structure.[4,6]

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Registry No. AgI, 7783-96-2; C_7H_7I, 1316-80-9.

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Interaction of Cobalt(II)–Glycylglycine Chelates with Molecular Oxygen. Species in Solution[1a]

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The nature of the factors governing the properties of cobalt oxygen complexes has recently elicited considerable interest.[2-4]