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Electrical conductivity of double salts of the silver iodide triethylenediammonium and N,N′-dialkyl triethylenediammonium diiodide types

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The electrical conductivity of the title compounds was studied. Silver iodide-N,N′-dialkyltriethylenediammonium diiodide at 25° C gives a maximum conductivity of 2×10^{-2} (ohm cm)$^{-1}$ with a 92.5 mol % composition of silver iodide. The activation energy is minimum for this composition with a value of 3.4 kcal mol^{-1}. For this type of material the electronic conductivity is very low and can be considered negligible as compared with the ionic conductivity.

1. Introduction

There has been an increasing interest in the study of solid electrolytes in view of their various possible applications. Most of the work to date, pertains to study as cationic conductors which, at moderate to low temperatures, possess interesting conducting properties. A study of such organic/inorganic electrolytes was undertaken in our laboratory. Earlier work with such systems has shown that it was possible to obtain, at ordinary temperatures, high ionic conductivities comparable to those of the best electrolytes in solution. Following the work of Bradley *et al.* [1, 2] and Owens *et al.* [3] on the family MAg_4I_5 (with $M^0 = K^0$, Rb^0, NH_4^0), Owens *et al.* [4, 5] have shown the existence of Ag^+ superionic conductors in silver iodide ammonium iodide complexes. Thackeray *et al.* [6, 7], following the results of de Rossi *et al.* [8] have extended the research in this field. In our earlier study a total electrical conductivity of 0.1 Ω^{-1}cm^{-1} was obtained for the system silver iodide-diiodide of tetramethyl N,N,N′,N′-piperazinium [9]. Takahashi [10] has presented electrical conduction properties of double salts of silver iodide-diiodide of dimethyl N,N′-triethylenediammonium but without giving the experimental curves.

In view of the paucity of available information in the literature we have undertaken a study of the conduction properties, with respect to composition, of the following systems: silver iodide-triethylenediammonium diiodide; silver iodide-diiodide of diethyl N,N′-triethylenediammonium and silver iodide-diiodide of dimethyl N,N′-triethylenediammonium. Studies on samples containing 75–95% of AgI have been carried out since it has been shown that the maximum conductivity is situated in this range.

2. Experimental details

2.1. *Preparation of samples and analysis*

Silver iodide was prepared by pouring a hot solution of silver nitrate, slightly acidified by nitric acid, into a solution of potassium iodide at the same temperature (about 60° C). It was observed that temperature and acidification gave a favourable silver iodide granulometry and permitted better filtration of the product obtained. The precipitate was washed several times with distilled water and then dried at 150° C. X-ray diffraction analysis showed a mixture of beta and gamma phase in the AgI samples.

The diiodides of triethylenediammonium $C_6H_{12}N_2R_2I_2$ with R = H, CH_3, C_2H_5 were obtained by pouring triethylenediamine, preferably diluted in EtOH, in hydroiodic acid or alkyl iodide (methyl or ethyl). The reaction being exothermic, the operation was monitored at temperatures between −10° C and 5° C. The precipitation of organic salts was more or less rapid in accordance with their degree of solubility in ethanol. The solutions, after allowing to stand overnight, were filtered, washed with cold absolute ethanol, recrystallised in a water-ethanol solution, dried at 60° C in a drying-oven and finally under vacuum in the presence of P_2O_5. An NMR analysis of these products and of triethylenediamine was carried out. The 3(trimethylsilyl)-1 propane sulphonic acid

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sodium was used as spectra reference solvent and D_2O as solvent.

The organic salts were mixed with silver iodide in an agate mortar and in preweighed proportions in ethanolic medium. After drying at 80° C, the samples were pressed in the form of cylinder of 10 mm diameter and 7 to 8 mm thickness under $1.2\,T\,cm^{-2}$ pressure in a double effect die. This pressure was selected according to the method of Scrosati [11] who showed that, for a given granulometry (for $RbAg_4I$), the total electrical conductivity was best at the above mentioned pressure.

Silver electrodes were deposited, on each face of the samples so prepared, by evaporation under vacuum with the help of a Trion Alcatel. For the electrical measurements the pellets were placed in a cell in which nitrogen was circulated. The oven used was an Adamel HT 5T.

2.2. *Total electrical conductivity measurements*

The total electrical conductivity was determined by tracing the impedance diagram by using an impedancemeter ('Radiometer' type GB11). The frequency was varied from 25 Hz to 10^5 kHz. The apparatus used a $32\,\mu A$ alternating current.

The ionic transference number was determined by the Tubandt method [12].

The electronic conductivity was determined by the methods of Hebb [13] and Wagner [14] with cells of type Ag/sample/C in which the carbon electrode was used as the blocking electrode.

3. Results

3.1. *NMR spectra*

NMR spectra of triethylenediamine $C_6H_{12}N_2$, triethylenediammonium diiodide $C_6H_{12}N_2(HI)_2$, diiodide of N,N′-dimethyltriethylenediammonium $C_6H_{12}N_2(CH_3I)_2$ and diiodide of N,N′-diethyltriethylenediammonium $C_6H_{12}N_2(C_2H_5I)_2$ are shown in Figs 1, 2, 3 and 4 respectively.

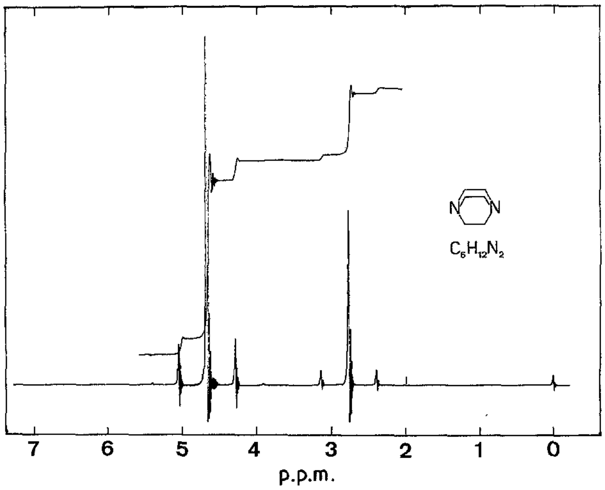

Fig. 1. NMR spectrum of triethylenediamine $C_6H_{12}N_2$.

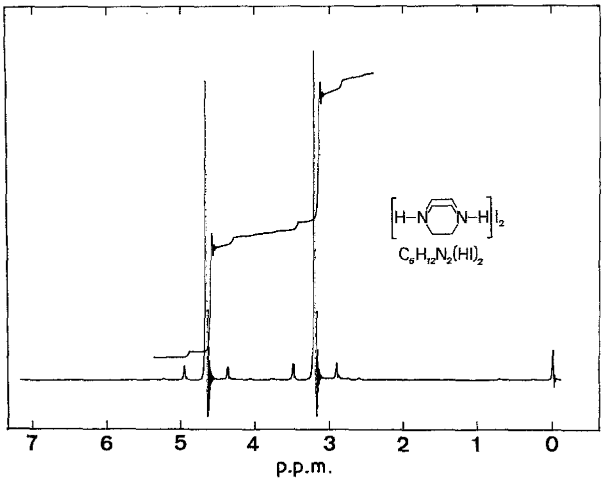

Fig. 2. NMR spectrum of diiodide of triethylenediammonium $[C_6H_{12}N_2(HI)_2]$.

The singlet observed at 2.66 p.p.m. in Fig. 1 can be attributed to the CH_2 groups of the product $C_6H_{12}N_2$. (The peak at 4.66 p.p.m. corresponds to H_2O). In Fig. 2 the protons of the -NH group are rapidly replaced by D (from D_2O). The hydrogen nuclei belonging to methylene groups are less shielded in triethylenediammonium cation (I) than in triethylenediamine: a shift to low fields, from 2.66 to 3.15 p.p.m. is observed.

In N,N′-dimethyltriethylenediammonium cation (II) the CH_3 peak appears at 3.35 p.p.m. and that of the CH_2 bridges at 4 p.p.m. (Fig. 3). By comparison with (I) this shifting to lower fields means less shielded methylene groups in (II).

We observe for N,N′-diethyltriethylenediammonium cation (III) a quadruplet at 3.6 p.p.m. from the CH_2 groups of the ethyl radical and a triplet at 1.39 p.p.m. from the CH_3 groups (Fig. 4). The CH_2 groups, localized between the N atoms are characterized by a singlet at 3.92 p.p.m.

3.2. *Impedance diagram*

We report in Figs 5a, 5b and 5c the development of

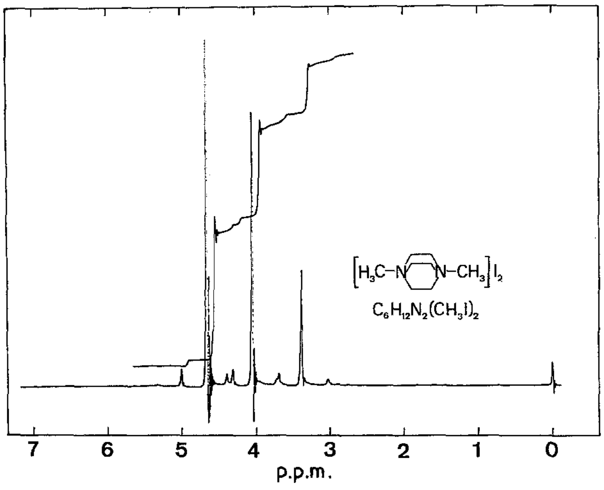

Fig. 3. NMR spectrum of diiodide of N,N′ dimethyltriethylenediammonium.

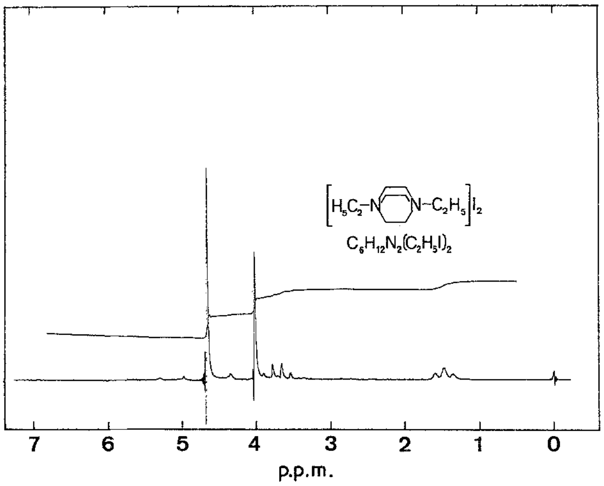

Fig. 4. NMR spectrum of diiodide of N,N′ dimethyltriethylenediammonium.

the impedance diagram obtained at 25° C with cells of the type Ag/electrolyte/Ag for respectively 75, 80 and 92.5% mole compositions of AgI in the silver iodide-N,N′-dimethyltriethylenediammonium diiodide electrolyte. Ravaine *et al.* [15] have shown that the complex impedance can be represented by the analytical expression:

$$Z = \frac{Z_0}{(1 + j\omega\tau_0)^{1-\alpha}} \qquad (1)$$

in which Z_0 is the abscissa of the intersection of the arc of the circle with the real axis, τ_0 is defined as the relaxation times so that $\omega\tau_0 = 1$ at the zenith of the arc and α defines the angle between the real axis and the radius passing through the origin.

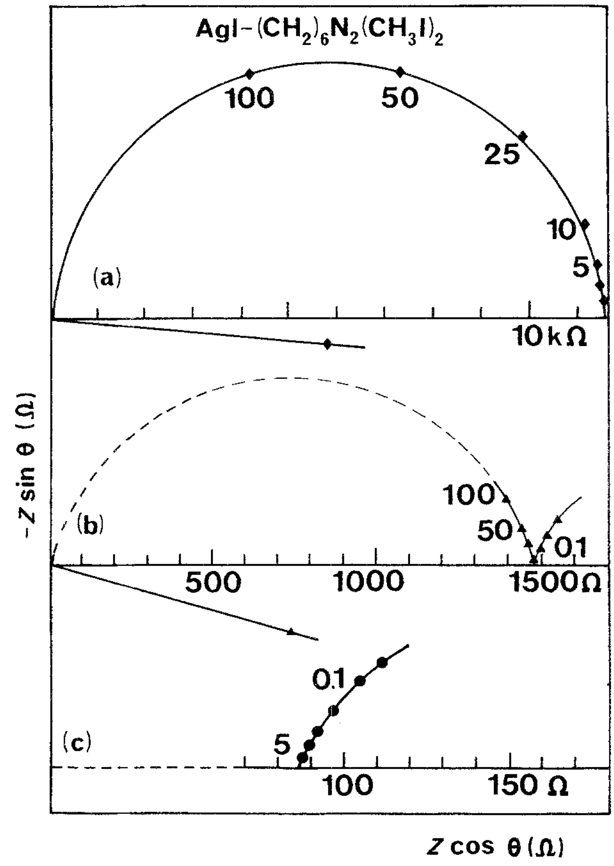

Fig. 5. Complex impedance plots at 25°C for AgI-$[(CH_2)_6N_2(CH_3I)_2]$ electrolyte with 75, 80 and 92.5 composition in mol % AgI respectively in (a), (b) and (c). Frequencies are in kHz.

For 75 mole % AgI (Fig. 5a) the general trend of the experimental data of complex conductance is represented by one semicircle having its centre somewhat under the real axis of the complex plane which fitted the experimental data in the frequency range 100 kHz – 25 Hz. The straight line connecting the origin of the complex plane to the centre of the semicircle formed an angle of 5° with the real axis: such distortion is probably due to an eventual small asymmetry between the electrodes [16]. We can assume a very simple equivalent circuit: a parallel combination C_1R_1 followed by a resistance R_2, where C_1 and R_1 represent the double layer capacitance and the charge transfer resistance at the electrodes respectively and R_2 represents the overall resistance of the elecrolyte. As the semicircle in the complex plane passes close to the origin we can assume $R_1 \gg R_2$.

For the same frequency range Equation 1 does not hold for materials richer in AgI and having better conductivity. Thus, for the compositions containing 80–92.5% of AgI another curve appears which is attributed to an electrode phenomena (Figs 5b, c).

3.3. *Total electrical conductivity measurements*

3.3.1. System AgI-$C_6H_{12}(HI)_2$. Fig. 6 represents the variation of total electrical conductivity with inverse of absolute temperature for compositions varying from 82.5 to 95 mol % silver iodide. The samples between 75–80% being too resistive, their conductivity was not determined.

Straight line curves are obtained following the Arrhenius law:

$$\sigma = A \exp(-E/RT) \qquad (2)$$

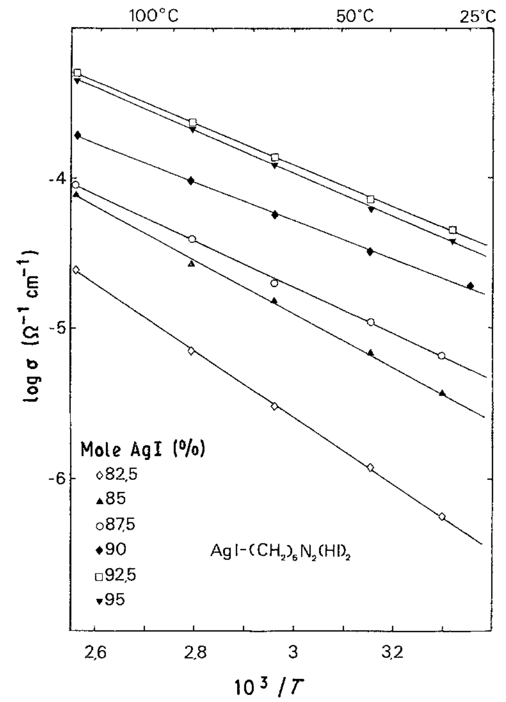

Fig. 6. Conductivity curves for the AgI-$[(CH_2)_6N_2(HI)_2]$ system.

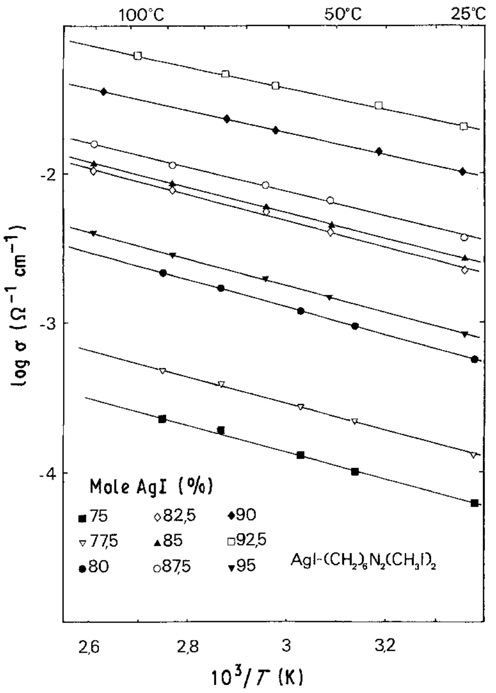

Fig. 7. Conductivity curves for the AgI-$[(CH_2)_6N_2(CH_3I)_2]$ system.

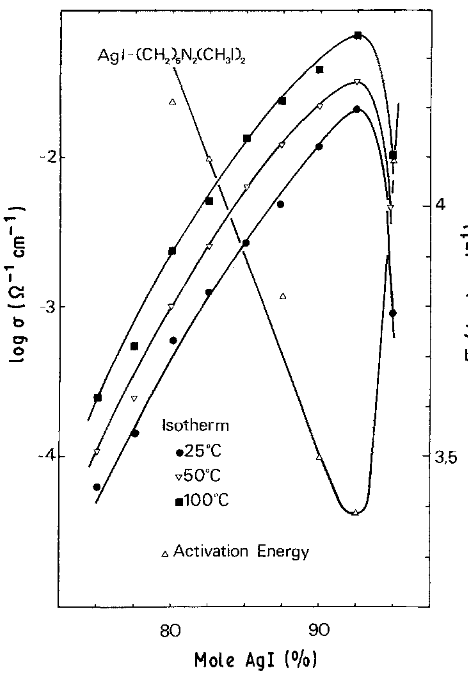

Fig. 8. Composition dependence of electrical conductivity and activation energy of the AgI-$[(CH_2)_6N_2(CH_3I)_2]$.

where A is the pre-exponential term, E is the activation energy of conduction and R is the gas constant.

The maximum conductivity is obtained at all temperatures for a composition of 92.5 mol % of silver iodide. The conductivities at 25°, 50° and 100° C are 3.9×10^{-5}, 9.6×10^{-5} and $3.3 \times 10^{-4} \Omega^{-1} cm^{-1}$ respectively. The activation energy, calculated between 25° C and 100° C for the same composition, has a minimum value of 6.3 kcal mol^{-1}.

3.3.2. System AgI-$C_6H_{12}N_2(CH_3I)_2$. Figure 7 represents the variation of conductivity against $(1/T)$ for compositions between 75 and 95 mol % silver iodide.

As in the previous case the maximum conductivity is obtained for 92.5 mol % of silver iodide at 25°, 50° and 100° C, the respective values being 0.0207, 0.032 and $0.0655 \Omega^{-1} cm^{-1}$. The maximum conductivity is therefore superior to that obtained previously for the system silver iodide-triethylenediammonium diiodide. The activation energy is lower with a value of 3.4 kcal mol^{-1} (Fig. 8).

3.3.3. System AgI-$C_6H_{12}N_2(C_2H_5I)_2$. The variation of total conductivity was studied as a function of temperature for samples containing between 77.5–90 mole % silver iodide. The results are presented in Fig. 9. As previously, straight lines are obtained. Maximum conductivity is noted for the composition 92.5 mole % silver iodide with the values being $0.015 \Omega^{-1} cm^{-1}$ at 25° C; $0.026 \Omega^{-1} cm^{-1}$ at 50° C, $0.063 \Omega^{-1} cm^{-1}$ at 100° C. The activation energy calculated between 25 and 100° C for the same composition has a value of 4.82 kcal mol^{-1}

3.4. *Nature of conduction*

We have studied the nature of the conduction at 25° C, of the system AgI-$C_6H_{12}N_2(CH_3I)_2$ containing 92.5 mol % of AgI.

3.4.1. Ionic conduction. The transport number of the Ag^+ was determinated by passing a current density of 0.25 mA cm^{-2} for 14 hours through a cell made of two silver-electrolyte (1-1 in weight) electrodes in contact with the solid electrolyte pellet. The Ag^+ transport number was 1 ± 0.01. This value shows that the current within the electrolyte is essentially due to migration of Ag^+ ions alone.

3.4.2. Electronic conduction. The results show that the electronic conductivity is $10^{-9} \Omega^{-1} cm^{-1}$ at 25° C. this value is comparable to that of $RbAg_4I_5$ [17–20] and is negligible when compared with ionic conduction.

4. Discussion

As regards the maximum conductivity of the silver iodide-diiodide of N, N′-dimethyltriethylenediammonium system values identical to those of Takahashi [10] are obtained, with a slight difference in mole percentage of AgI (namely 92.5%, as compared to 95%, reported by Takahashi).

Cations (I), (II) and (III) have a quasi-D_{3h} symmetry. Owing to methyl and ethyl groups on the onium nitrogen atoms, (II) and (III) deviate more from this ideal symmetry. Yet rotational disorder along the three-fold symmetry axis induces, for these two last cations in the solid state, the same high degree of symmetry as observed in (I). In spite of this same type of symmetry we note that (I) does not have good conductivity. A similar result is observed for the quinolinium cation (IV) which exhibits a specific conductivity of $4 \times 10^{-3} \Omega^{-1} cm^{-1}$ [5]. With Geller [21] and Owens [4, 22] we estimate that the presence of the NH bond in the organic cation induces asymmetric polarization which destabilises the iodide network through which the mobile Ag^+ ions circulate.

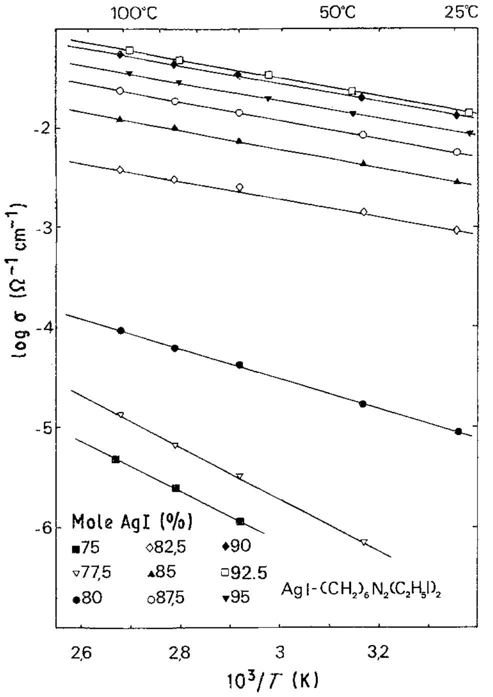

Fig. 9. Conductivity curves for the AgI-$[(CH_2)_6N_2(C_2H_5I)_2]$ system.

With the same reasoning, 1-methylquinolinium (V) has a conductivity with an order of magnitude equal [5] to that observed in (II), but differs in symmetry by the absence of a mirror-plane of symmetry perpendicular to the three-fold axis. Such a lowering of the overall symmetry does not induce a significant lowering of conductivity.

If we compare the conductivity of the cyclic tetramethylpiperazinium cation (VII) ($\sigma: 0.1\,\Omega^{-1}\mathrm{cm}^{-1}$ [9]) with that of (II), we observe the same order of conductivity. One might infer that the removal of the cage structure does not prevent the stabilization of the conductive phases.

The activation energy of (II) is lower than that of (III): this observation suggests that there may be more mobile silver ions in the former material. It seems that high molecular symmetry in the substituted organic ammonium cations appears to give a lower E value for silver ion migration in the solid phase. The introduction of larger groups on the onium nitrogen atom, which induces some lowering of the overall symmetry, leads to larger E values.

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