

Total electrical conductivity of double salts of the type silver iodide-poly (N-hexylene, N'-alkylene, N,N,N',N'-tetramethyldiammonium diiodide)

J. J. ROSENBERG, A. BENCHETTARA, A. NOUACER

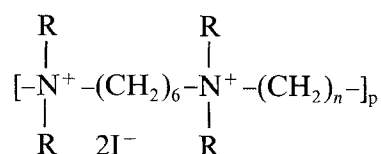
Laboratoire de Chimie des Matériaux Inorganiques, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse-Cedex, France

J. ESTIENNE*

Laboratoire de Chimie Organique Structurale, Université de Provence, Centre Saint-Jérôme - Case 542, Avenue Escadrille Normandie Niemen, 13397 Marseille-Cedex 13, France

Received 10 February 1989; revised 6 October 1989

Some linear ionenes (6-*n*), with the general formula:



(where R = methyl group; *n* = 3, 4, 5, 6; and *p* the degree of polymerization) have been prepared. Their NMR and IR spectra are reported and discussed. These ionic polymers were mixed with silver iodide to investigate their total electrical conductivity. The method of preparation and analysis of these systems is described. Concentrations ranged between 75 and 95 molar % of AgI. The study of the total electrical conductivity with respect to temperature shows that the Arrhenius equation is obeyed. The system silver iodide-polydiiodide of N-hexylene, N'-butylene, N,N,N',N'-tetramethyldiammonium shows a maximum value of $0.05 \Omega^{-1} \text{cm}^{-1}$ at 25°C.

1. Introduction

The interest raised by solid electrolytes lies in their possible applications in many fields such as solid state batteries and sensors. The exceptional conductivity ($1 \Omega^{-1} \text{cm}^{-1}$) [1] of silver iodide in its α phase, above 146°C has led to several studies aimed at maintaining this property at room temperature. Many of the highly conducting solid electrolytes investigated have silver ion migration. These electrolytes have been synthesized through compound formation between AgI and various substituted ammonium monomer iodides [2-10].

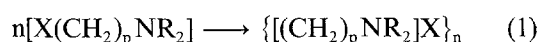
Another interesting series of silver electrolytes are based on polymers particularly the ionenes. The preparation of such polymers was studied intensively by Rembaum *et al.* [11]. These compounds have the following formula:



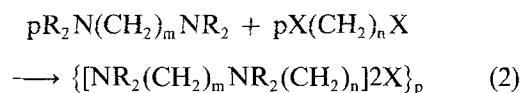
with R generally, a methyl radical and A being a linear chain or a cycle or a combination of both.

Ionenes were first synthesized by Marvel *et al.* [12]

using the reaction:



with *p* varying between 7, 8, 10. For values of *p* strictly less than 7, cyclization occurred [12-16]. This preparation, in which R is an alkyl radical, gives polymers having constant sequences of the methylene group, CH₂, between the quaternary nitrogen atoms. Kern *et al.* [17] have continued this study by preparing the ionenes (*m* - *n*) from the following reaction:



m and *n* are the numbers of (CH₂) in the diamines and the dihalogen. This reaction allows the synthesis of most of the ionenes in which the number of CH₂ groups, between the quaternary nitrogen, is in principle, modifiable. The conditions of reaction in Kern's work, however, appear to be uncertain and the results are less credible. Rembaum and his collaborators have described the parameters which give the expected polymer with certainty [11, 18-32]. The different

*To whom all correspondence should be addressed.

Table 1. Compounds obtained with the reaction between $R_2N(CH_2)_mNR_2$ and $X(CH_2)_nX$ (with $R = CH_3$; $X = Br$ or I ; m and n varying from 1 to 6)

| $(CH_3)_2N(CH_2)_mN(CH_3)_2$ | | | | | | |
|------------------------------|-----------------------------|---|--------|---|----------|-----------------------------|
| m | 1 | 2 | 3 | 4 | 5 | 6 |
| n | | | | | | |
| $X(CH_2)_nX$ | | | | | | |
| 1 | R_2H_2NX | | | | | Linear Diammonium Compounds |
| 2 | Cyclic Diammonium Compounds | | | | | |
| 3 | Cyclic | | | | | |
| 4 | Monoammonium Compounds | | Ionene | | | |
| 5 | | | | | Polymers | |
| 6 | | | | | | |

compounds obtained from the starting reagents of Reaction 2 are depicted in Table 1. For m and n varying from 1 to 6, five types of product were observed:

- the reaction 1-1 which gives bromide or iodide of dimethyl ammonium;
- the diammonium cyclic compounds like imidazolium, piperazinium, diazepinium salts [27];
- the monoammonium cyclic compounds like pyrrolidinium salts, etc. [28];
- the diammonium linear compounds like tetramethylene bis (2-bromoethyl) dimethylammonium salts, etc. [27];
- the ionenes.

The ionic polymers are obtained for m and $n > 3$. These results are confirmed by many authors [18-32]. However, these results are largely confined to the preparation of bromides. In the present study we have prepared iodide polymers (abbreviated as (6- n) with $n = 3, 4, 5, 6$). Organic glasses based on lithium iodide and iodides of ionenes and oxaiionenes, with same ionic conductivity, have been developed [33, 34]. The systems poly (N-hexamethylenetriethylenediammonium dibromide) - CuBr have been studied by Watanabe *et al.* [35]. Further we have reported the electrical conductivity of the systems poly (N-propylene or N-butylene, N,N-dimethylammonium iodide), poly(N-butylene, N'-propylene, N,N,N',N'-tetramethyldiammonium diiodide) [36], poly(N-pentylene, N'-alkylene, N,N,N',N'-tetramethyldiammonium diiodide) [37] and poly(N-alkylene, N, N'-dimethylpiperazinium diiodide) [38]. Dominquez *et al.* [39] have also studied different pristine ionenes as ionic conductors above their T_g .

In view of continued technological interest in these materials, further detailed studies on their preparation and properties are justified. In continuation of our previous studies [36, 38] we report here the methods of preparation and analysis of the precursor compounds and then present results on the total electrical conductivity of the systems iodide-poly(N-hexylene, N-alkylene, N,N,N',N'-tetramethyl diammonium diiodide).

2. Experimental details

2.1. Preparation of ionenes

The ionenes have been synthesized as described earlier [36, 37].

2.2. Analysis of the ionenes

The elementary analysis and potentiometric titration of I^- anions in polymer by $AgNO_3$ confirms the expected sequences. NMR spectra of the samples were recorded with a Perkin-Elmer apparatus equipped with Permalock and working at a frequency of 60 MHz. IR spectra of organic products in the region from 4000 cm^{-1} to 200 cm^{-1} were recorded using the KBr pellet method.

2.3. Electrical conductivity measurements

The samples were prepared by following the method as described earlier [10]. The total electrical conductivity was determined with the aid of an impedance-meter (Radiometer type GB11).

The ionic transference number was determined by the Tubandt method [40]. The electronic conductivity was studied by the methods of Hebb [41] and Wagner [42, 43] with cells of type Ag/sample/C in which a carbon electrode was used as blocking electrode.

3. Results and discussion

3.1. NMR spectra

The NMR spectra of diiodo alpha omega alkanes show two absorption peaks. The first is due to the methylene protons - CH_2I and the second (generally multiplets) comes from the central chain in $C-(CH_2)_i-C$ (with i varying from 1 to 4). In Table 2, we have reported the NMR peaks obtained for these compounds. The spectrum of TMHDA shows two types of multiplets. The first absorption is composed of a singlet due to methyl protons of $-N(CH_3)_2$ on which

Table 2. Chemical shift (in p.p.m.) of protons in alpha omega alkanes diiodides

| Alpha omega alkanes diiodides | $-\text{CH}_2\text{-I}$ | $\text{C}-(\text{CH}_2)_n-\text{C}$ |
|--|-------------------------|-------------------------------------|
| $\text{I}(\text{CH}_2)_3\text{I}$ (DIP) | 3.3 | 2.3 |
| $\text{I}(\text{CH}_2)_4\text{I}$ (DIB) | 3.2 | 1.9 |
| $\text{I}(\text{CH}_2)_5\text{I}$ (DIPr) | 3.2 | 1.8 |
| $\text{I}(\text{CH}_2)_6\text{I}$ (DIH) | 3.2 | 1.63 |

is superimposed the triplet due to the protons of $>\text{N-CH}_2-$ ($\delta = 2.2$ p.p.m.). The second absorption is that of the methylene in the $>\text{N-C}-(\text{CH}_2)_i-\text{C-N}<$ chain (with i varying from 1 to 4 ($\delta = 1.33$ p.p.m.)).

The existence of polymers (6-n) is attested by the presence of characteristic peaks and multiplets (Figs 1-4). Then,

- the broad band between 1.50 to 1.86 p.p.m. is due to the mutual interaction of methylenes' protons in $\text{C}-(\text{CH}_2)_{m-2}-\text{C}$ (with $m = 4$) and $\text{C}-(\text{CH}_2)_{n-2}-\text{C}$ (with $n = 3, 4, 5, 6$),

- the peak between 2.0 and 2.41 p.p.m. suggest the presence of the $-\text{N}(\text{CH}_3)_2$ radical,

- the peak between 3.00 and 3.20 p.p.m. is attributed to the protons of $-\text{N}^+(\text{CH}_3)_2-$,

- the peak between 3.20 and 3.36 p.p.m. is from the protons of $-\text{CH}_2-$ in $-\text{CH}_2-\text{N}^{\oplus}<$,

- the proton of heavy water gives a peak at 4.5 p.p.m.

The spectra of ionenes and starting products may be compared as follows:

(i) the decrease in the intensity of the peak at 2.41 p.p.m., due to $-\text{N}(\text{CH}_3)_2$, corresponds to completion of the polymerization reaction.

(ii) the disappearance of the peak at 3.3 p.p.m.

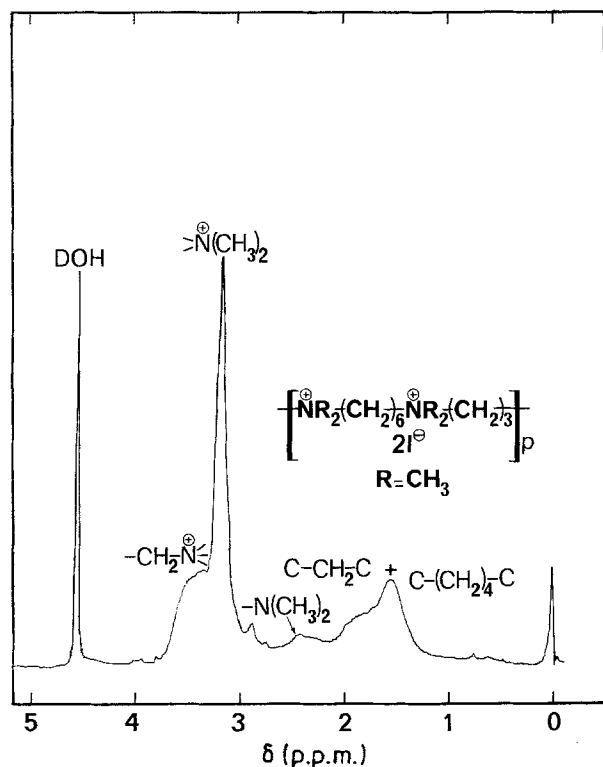


Fig. 1. NMR spectrum of ionene (6-3).

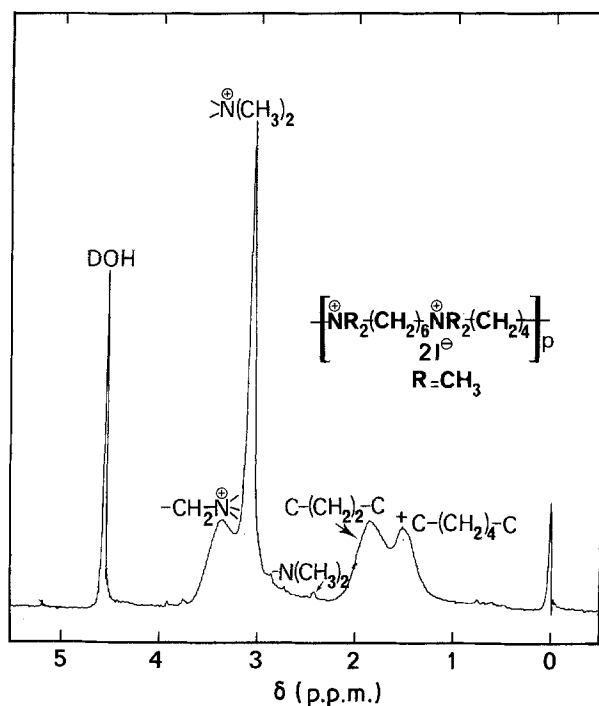


Fig. 2. NMR spectrum of ionene (6-4).

($-\text{CH}_2\text{I}$) shows that the diiodo alpha omega alkane has reacted in totality with the diamine.

(iii) the presence of the peak at 2.41 p.p.m. indicates that the terminal groups, in the polymer under study, are essentially $-\text{N}(\text{CH}_3)_2$. Similar results have been observed by Yen [44] and Hiraoka [45] in their studies on homopolymerisation of 3-dimethylamino n-propyl chloride $\text{Cl}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$ and the reaction between 4,4' methylene bis (N,N dimethylbenzamine) $\{\text{CH}_2[\text{PhN}(\text{CH}_3)_2]_2\}$ with dibromo alpha omega alkanes.

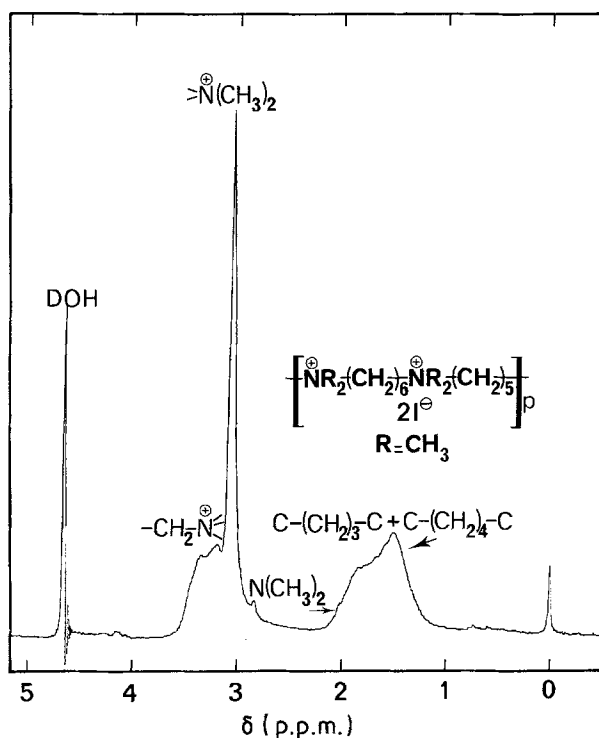


Fig. 3. NMR spectrum of ionene (6-5).

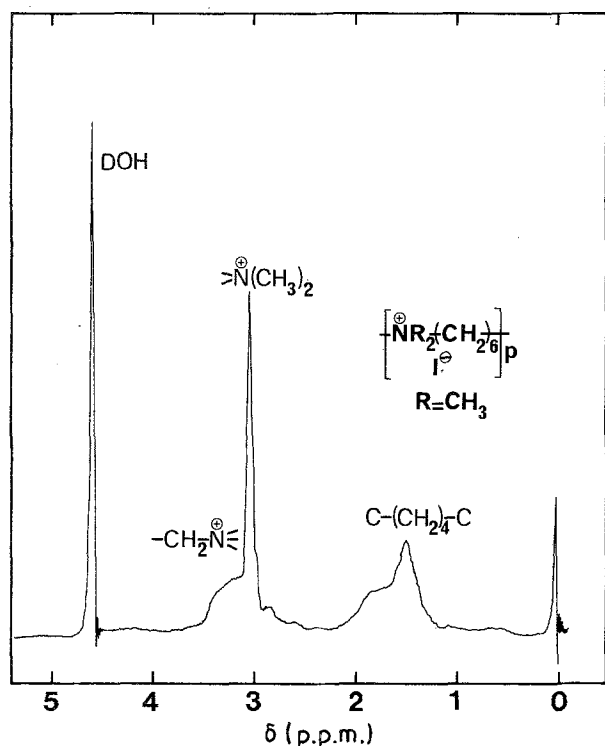


Fig. 4. NMR spectrum of ionene (6-6).

3.2. IR spectra

The diiodo alpha omega alkanes are characterized by the principal absorption bands (Table 3). These are known as:

- stretching band of C-I at 590 cm^{-1} ,
- stretching band of C-C in $(\text{CH}_2)_n$ chain around 720 cm^{-1} (n varying from 3 to 6) [46],
- bending band of CH_2 in $\text{CH}_2\text{-I}$ near 1250 cm^{-1} .

The TMHDA shows:

- a stretching band of CH in $-\text{N}(\text{CH}_3)_2$ at 2760 cm^{-1} ,
- a band of CN in $-\text{CH}_2\text{-N}$ at 1035 cm^{-1} .

The existence of polymers (6- n) is attested by the presence of the following features (Figs 5-8):

- the stretching band of C-I ($500\text{--}600\text{ cm}^{-1}$) and the bending vibration of CH_2 in $-\text{CH}_2\text{I}$ ($\sim 1250\text{ cm}^{-1}$) belonging to the starting reactant (diiodo alpha omega alkane) does not appear further in the ionenes. It can be affirmed that the reaction (ionene formation) attains a high degree of conversion;

- the absorption at $2800\text{--}2950\text{ cm}^{-1}$ attributed to stretching vibration of CH in $-\text{N}(\text{CH}_3)_2$, and present in the TMHDA spectrum, decreases with the appearance of a new band at $1470\text{--}1480\text{ cm}^{-1}$. This latter

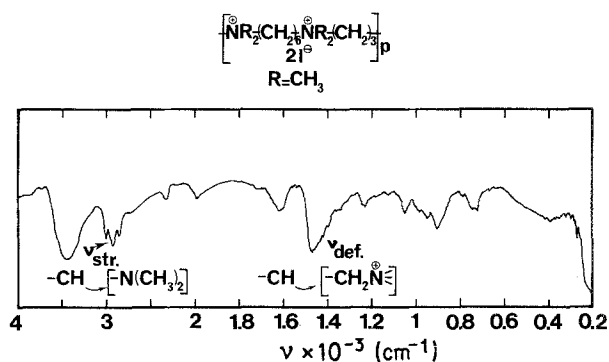


Fig. 5. IR spectrum of ionene (6-3).

absorption is to be linked to the angular deformation (bending) of CH in $\text{CH}_2\text{-N}^{\oplus}$.

- the stretching vibration of C-N in $\text{CH}_2\text{-N}^{\oplus}$ at 1040 cm^{-1} . The presence of these two bands ($2800\text{--}2950\text{ cm}^{-1}$) indicates that the terminal groups are essentially $-\text{N}(\text{CH}_3)_2$.

The results of NMR and IR spectra thus show that Rembaum's method [11, 20-27] permits us to obtain the iodized ionenes (6- n) with $n = 3, 4, 5, 6$.

3.3. Total electric conductivity of AgI-polydiiodides of N-hexylene, N'-alkylene-N,N,N',N'-tetramethyl diammonium systems

3.3.1. Total electric conductivity of the system AgI-(6-3). Our results show that the conductivity of the sample varies with temperature according to an Arrhenius-type law. The conductivity plot as $\log \sigma = f(1/T)$, shows a break in the straight line, for the compositions varying between 75-90 mole % AgI (Fig. 9). This transition is situated around 30°C and this type of phenomenon has already been observed by several authors for systems based on AgI. For example, above 50°C , Ag_2HgI_4 has an alpha phase having electrical conductivity of $0.01\ \Omega^{-1}\text{ cm}^{-1}$ [47-49]. Below this transition point [50-52] a new phase appears which is a very poor conductor. The mercury ions carry 6% of the total charge, the rest being carried by the silver ions. Also, $(\text{C}_5\text{H}_5\text{NH})\text{AgI}_5\text{I}_6$ shows the same property at 52°C . For Geller *et al.* [53, 54] this phenomenon is of a disorder-disorder transition type, that is, from lower to higher disorder. In the lower temperature phase, not all the Ag^+ ions are completely mobile (low disorder), while in the high temperature phases (high disorder), all are mobile. Further the diiodide of N,N,N',N',N',N'-hexamethyl 1,4 butylenediamine linked to 91.5 mole % of AgI

Table 3. Infra-red absorption frequencies (in cm^{-1}) of alpha omega alkanes diiodides

| Alpha-omega alkanes diiodides | Bending of CH_2 in $\text{CH}_2\text{-I}$ | Stretching of C-I | Stretching of C-C in $-(\text{CH}_2)_n-$ |
|--|--|-------------------|--|
| $\text{I}(\text{CH}_2)_3\text{I}$ (DIP) | 1270 | 590 | 730 |
| $\text{I}(\text{CH}_2)_4\text{I}$ (DIB) | 1230 | 580 | 720 |
| $\text{I}(\text{CH}_2)_5\text{I}$ (DIPr) | 1230 | 585 | 720 |
| $\text{I}(\text{CH}_2)_6\text{I}$ (DIH) | 1210 | 590 | 720 |

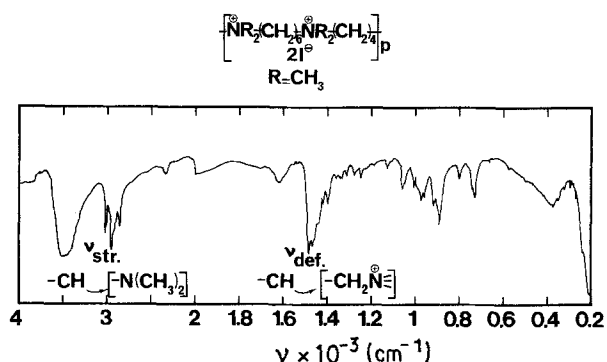


Fig. 6. IR spectrum of ionene (6-4).

shows a break at 58°C, in the graph of $\log(\sigma T)$ with respect to $1/T$. Thackeray gives no information about the exact nature of this transition [55].

In the light of this evidence, and on the basis of the graph of $\log \sigma$ against $1/T$ it appears reasonable that these transitions around 30°C are somewhat related to the passage from high disorder (above 30°C) to a low disorder. For a more conducting composition, containing 87.5 mole % of AgI, a conductivity of $3.8 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ is obtained at 30°C (Fig. 9). When isotherms at temperatures 25, 50 and 100°C with respect to composition equivalent to AgI are drawn, it was observed that the conductivity remains maximum at the composition of 87.5 mole % AgI (Fig. 10). The activation energies of conduction between 100°C and 30°C are shown on the same graph. The minimum value ($4.7 \text{ kcal mol}^{-1}$) corresponds to the maximum conductivity.

3.3.2. Total electric conductivity of the system AgI-(6-4). The curves $\log \sigma = f(1/T)$ shown in Fig. 11 are based on the study of AgI-(6-4) systems. In the studied temperature range, straight lines are obtained. The maximum conductivity is obtained with a system containing 90 mole % of AgI. At 25°C, its value is $5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$. On Fig. 12, we have plotted the electrical conductivity at 25, 50 and 100°C, as a function of the AgI content. At any of these temperatures, the maximum conductivity is observed for the same AgI content. The activation energy of each of the compositions of the system is shown on the same figure. Its value is obtained from the curve $\log \sigma = f(1/T)$. We note that the activation energy is a

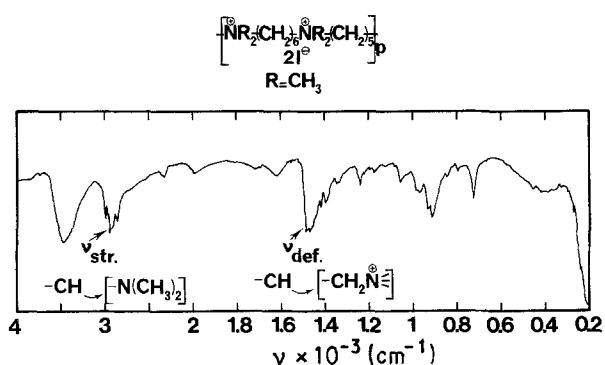


Fig. 7. IR spectrum of ionene (6-5).

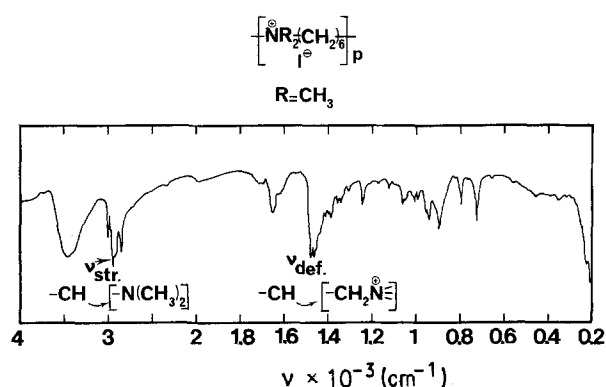


Fig. 8. IR spectrum of ionene (6-6).

minimum ($1.8 \text{ kcal mol}^{-1}$) when the conductivity of the system is maximal (90 mole % of AgI).

3.3.3. Total electric conductivity of the system AgI-(6-5). The curves $\log \sigma = f(1/T)$ of the system AgI-(6-5) are shown on Fig. 13. The slopes of these straight lines give the activation energy for each composition of the system. A plot of $\log \sigma$ as a function of equivalent AgI content, at 25, 50 and 100°C, (Fig. 14) shows that the maximum conductivity is reached for an equivalent AgI content of 90%; these values are 0.03; 0.042; and $0.072 \Omega^{-1} \text{cm}^{-1}$ respectively. As in the

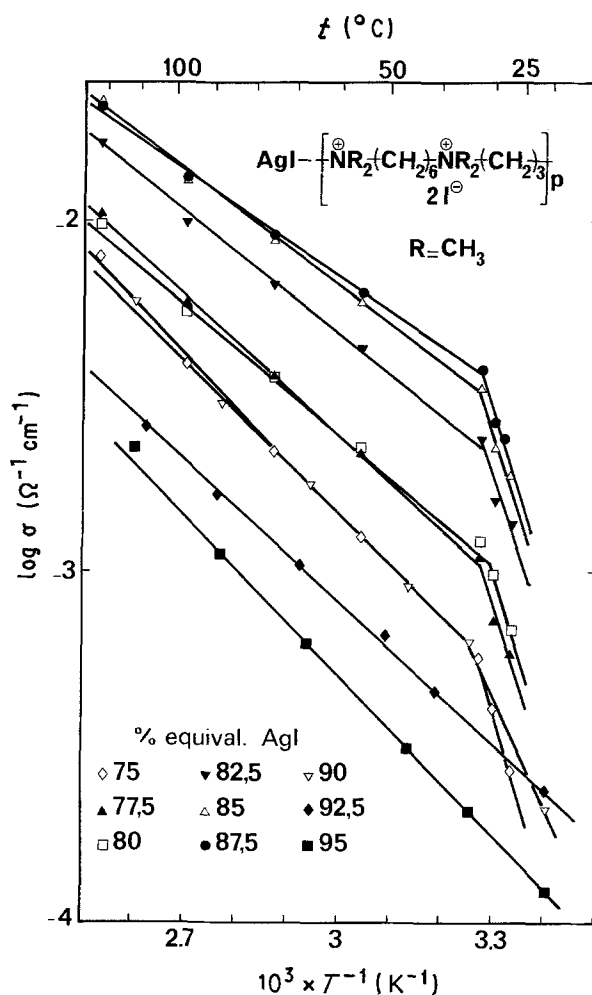


Fig. 9. Total electric conductivity of the AgI-(6-3) system as a function of reciprocal absolute temperature.

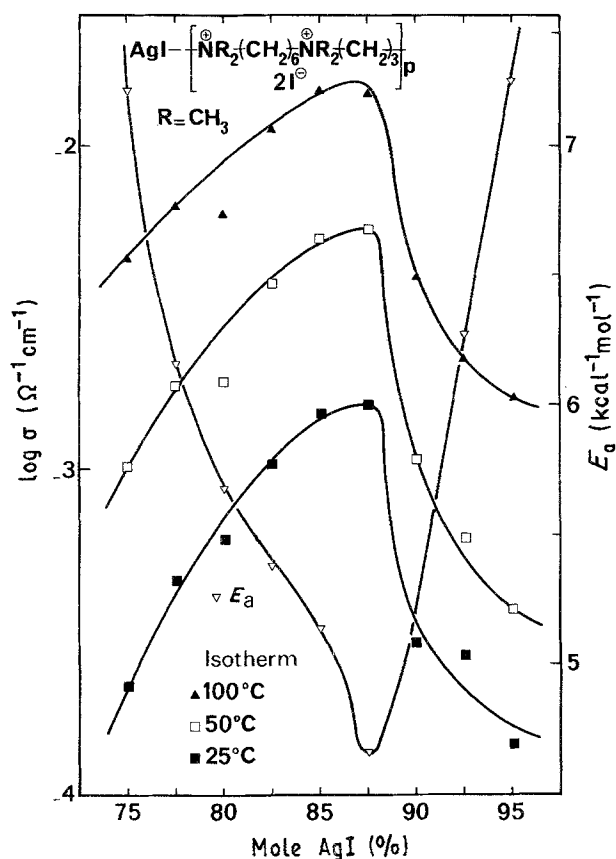


Fig. 10. Isothermal conductivities and activation energy of the AgI-(6-3) system as a function of the equivalent AgI content.

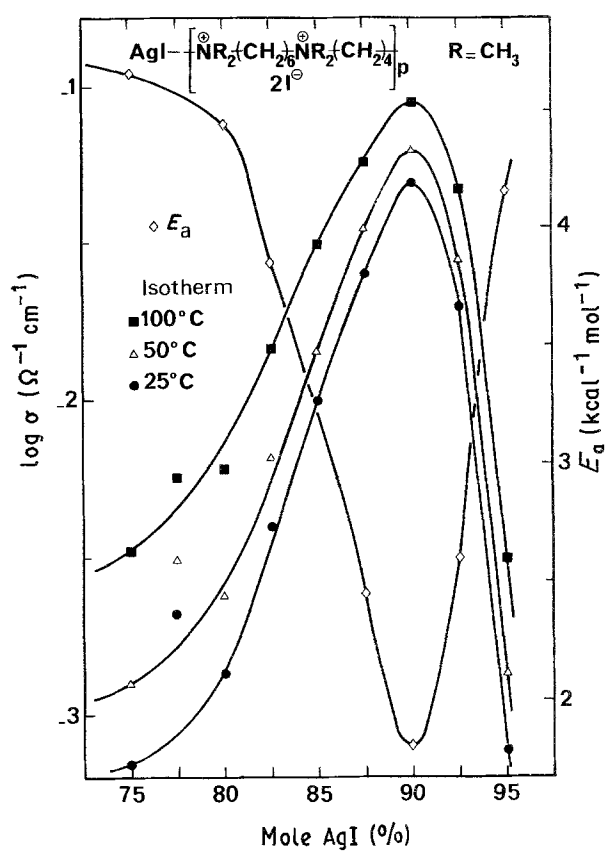


Fig. 12. Isothermal conductivities and activation energy of the AgI-(6-4) system as a function of the equivalent AgI content.

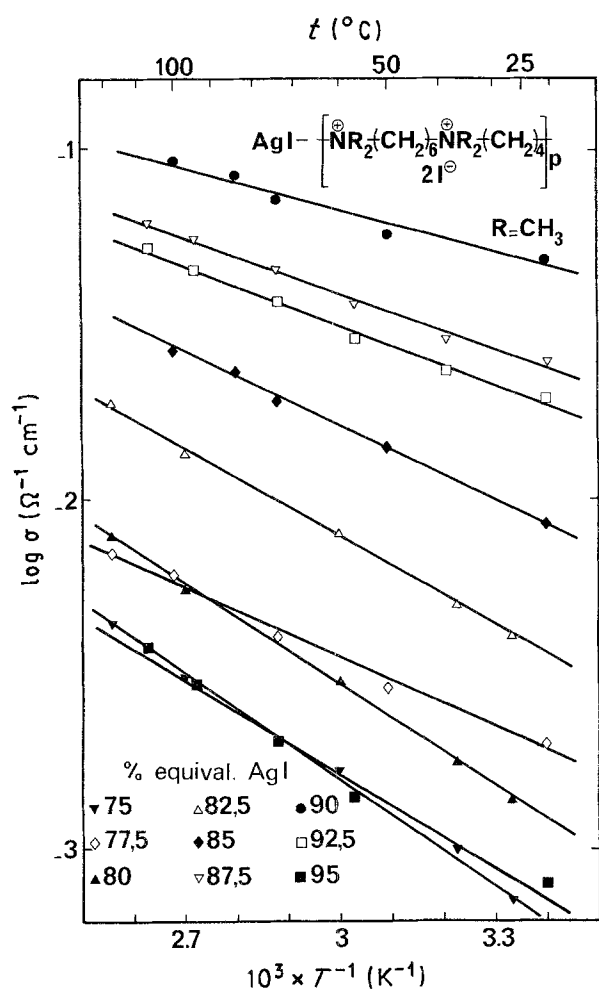


Fig. 11. Total electric conductivity of the AgI-(6-4) system as a function of reciprocal absolute temperature.

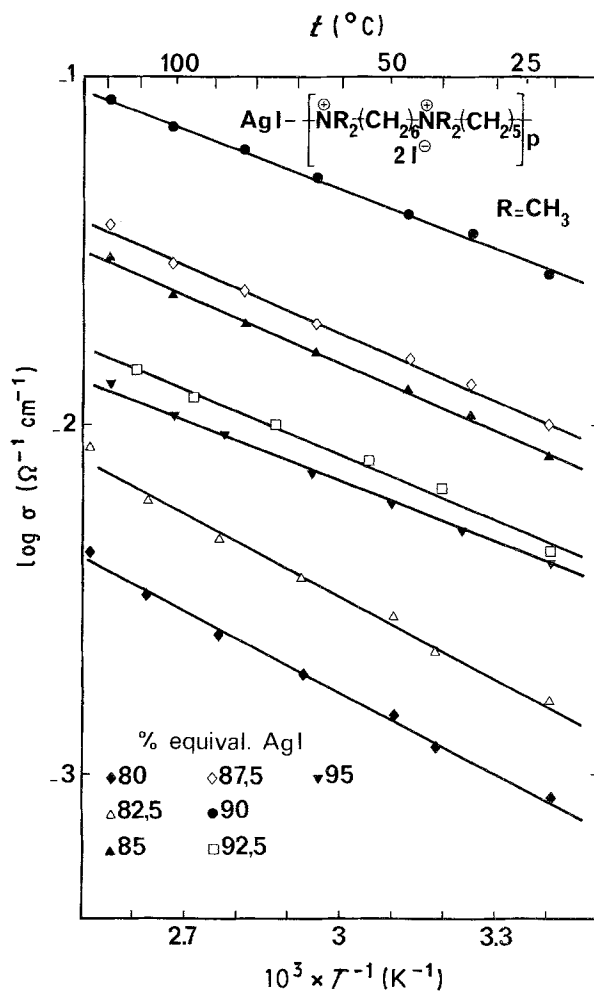


Fig. 13. Total electric conductivity of the AgI-(6-5) system as a function of reciprocal absolute temperature.

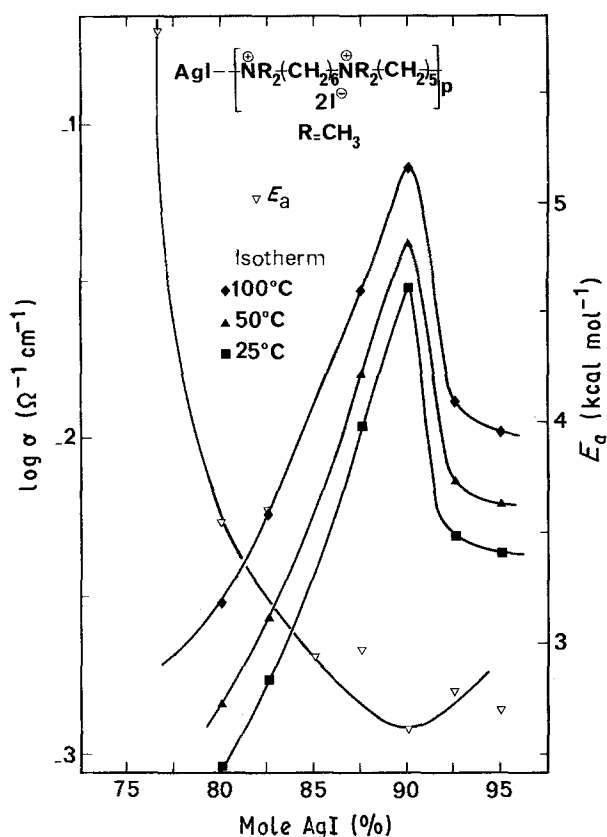


Fig. 14. Isothermal conductivities and activation energy of the AgI-(6-5) system as a function of the equivalent AgI content.

case of the preceding systems, the activation energy is minimum ($2.6 \text{ kcal mol}^{-1}$) for the composition having the maximum conductivity.

3.4. Total electric conductivity of the system AgI-(6-6)

The results for the total electrical conductivity and the activation energy are shown on Figs 15 and 16. On the former are plotted the curves $\log \sigma = f(1/T)$. The study of the variation of the total electrical conductivity with respect to the concentration allowed us to plot the isothermal conductivity curves at 25, 50, 100°C (Fig. 16). We note that, in all the studied temperature range, the maximum conductivity is reached for the composition containing 82.5% of equivalent AgI. For this composition, the minimum value of the activation energy is reached. The maximum conductivity is $0.0133 \Omega^{-1} \text{ cm}^{-1}$ at 25°C, and the corresponding activation energy is $2.6 \text{ kcal mol}^{-1}$.

4. Nature of conduction

We have studied the nature of the conduction at 25°C of the system AgI-(6-4) containing 90% of equivalent AgI.

4.1. Ionic conduction

The Ag^+ transport number in AgI-(6-4) (90%) was determined by passing a current density of 0.25 mA

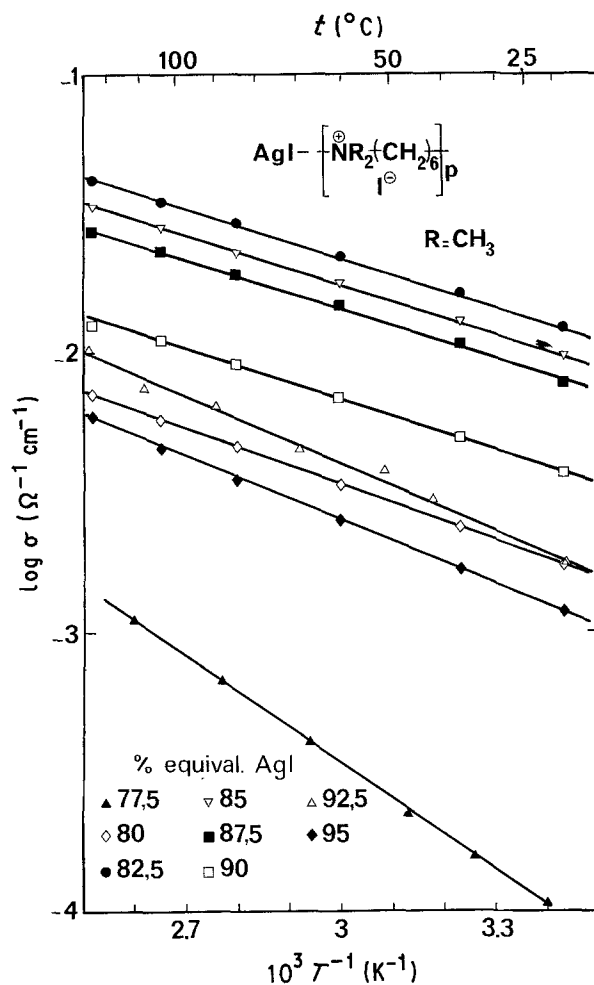


Fig. 15. Total electric conductivity of the AgI-(6-6) system as a function of reciprocal absolute temperature.

cm^{-2} for 14 hours through a cell made of two metal-electrolyte (1-1 in weight) composite electrodes in contact with the solid electrolyte pellet. The transport number was obtained by measuring the weight loss of the anode. This method is similar to that used by Bradley *et al.* for KAg_4I_5 solid electrolyte [2]. The number of faradays passed through the experimental cell was given by an electronic coulometer (Tacussel I.G.6N).

The transport number of the Ag^+ thus determined is 0.99 ± 0.01 . This value shows that the contribution to the passage of current within the electrolyte is essentially due to migration of Ag^+ ions alone.

4.2. Electronic conduction

Wagner [43] has shown the total electronic current, passed through the cell (I), follows the relation

$$\begin{aligned} I &= I_e + I_t \\ &= \frac{RTA}{LF} \left\{ \sigma_e \left[1 - \exp\left(-\frac{EF}{RT}\right) \right] \right. \\ &\quad \left. + \sigma_i \left[\exp\left(\frac{EF}{RT}\right) - 1 \right] \right\} \end{aligned} \quad (3)$$

where I_e and I_t are, respectively, electrons and electron hole currents, A and L are the sectional area and the

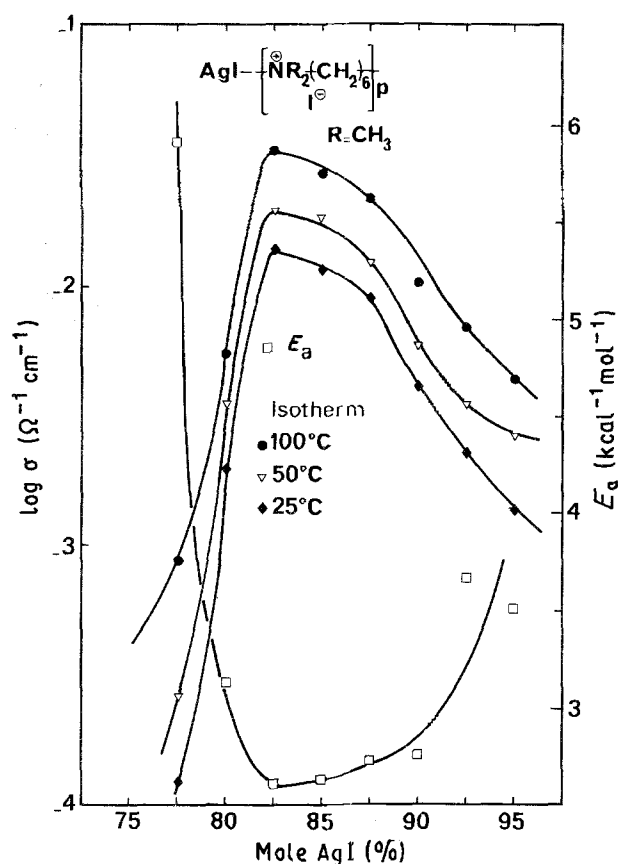


Fig. 16. Isothermal conductivities and activation energy of the AgI-(6-6) system as a function of the equivalent AgI content.

length of the electrolyte respectively; R the ideal gas constant, F the Faraday constant and T the absolute temperature. The specific conductivities of electrons and holes are denoted by σ_e and σ_t . Generally, the conductivity due to the electrons or holes is predominant and we have

$$\begin{aligned}
 I &\approx I_e \\
 &= \frac{RTA}{LF} \sigma_e \left[1 - \exp\left(-\frac{EF}{RT}\right) \right] \\
 &\quad \text{when } \sigma_e \gg \sigma_t
 \end{aligned} \quad (4)$$

or

$$\begin{aligned}
 I &\approx I_t \\
 &= \frac{RTA}{LF} \sigma_t \left[\exp\left(\frac{EF}{RT}\right) - 1 \right] \\
 &\quad \text{when } \sigma_t \gg \sigma_e
 \end{aligned} \quad (5)$$

If the applied potential, E , is high enough we have $EF \gg RT$ and Equations 4 and 5 may be simplified. Then

$$\begin{aligned}
 I &\approx I_e \\
 &= \left(\frac{RTA}{LF}\right) \sigma_e
 \end{aligned} \quad (6)$$

$$\begin{aligned}
 I &\approx I_t \\
 &= \left(\frac{RTA}{LF}\right) \sigma_t \exp\left(\frac{EF}{RT}\right)
 \end{aligned} \quad (7)$$

These results show that the current varies exponentially with the voltage and the electron conduction is negligible. This relation (7) permits us to calculate the total electronic conduction. At 25°C, the electronic conductivity is $10^{-9} \Omega^{-1} \text{cm}^{-1}$. This value is comparable to that of RbAg_4I_5 [56-59], and is negligible when compared with the ionic conduction. In conclusion, the electrical conductivity behaviour of the four AgI based ionenes (6- n) systems studied in the present work shows that in each case the total electrical conductivity goes through a maximum, and the largest value is observed in the case of the AgI-(6-4) system. At 25°C, the maximum value is $0.05 \Omega^{-1} \text{cm}^{-1}$ which is obtained with a composition containing 90 mole % of AgI. This value is quite close to those previously reported for different organic-mineral systems. In particular, the behaviour of the composition with 90 mole % of AgI is shown to be that of a purely ionic conductor. Further studies on related systems are in progress.

References

- [1] C. Tubandt and E. Lorenz, *Z. Physik Chem.* **87** (1914) 513.
- [2] J. Bradley and P. Greene, *Trans. Faraday Soc.* **62** (1966) 2069.
- [3] J. Bradley and P. Greene, *Trans. Faraday Soc.* **63** (1967) 424.
- [4] B. Owens and G. Argue, *Science* **157** (1967) 308.
- [5] B. Owens, *J. Electrochem. Soc.* **117** (1970) 1536.
- [6] B. Owens, *J. Electrochem. Soc.* **118** (1971) 1144.
- [7] M. De Rossi and M. Berardelli, *J. Electrochem. Soc.* **119** (1972) 114.
- [8] M. Thackeray and J. Coetzer, *Electrochim. Acta* **21** (1976) 37.
- [9] T. Takahashi, *Japan Kokai* 74-61 697 (June 1974), *C.A.* **81** 180 369 f.
- [10] G. Robert, J. Faucheu and J. J. Rosenberg, *J. Power Sources* **1** (1976-77) 359.
- [11] A. Rembaum, W. Baumgartner and H. Eisenberg, *J. Polym. Sci.* **B6** (1968) 159.
- [12] C. Marvel, M. Lehman and C. Thompson, *J. Am. Chem. Soc.* **55** (1933) 1977.
- [13] C. Marvel and E. Littmann, *J. Am. Chem. Soc.* **52** (1930) 287.
- [14] C. Marvel and C. Gibbs, *J. Am. Chem. Soc.* **57** (1935) 1137.
- [15] C. Marvel and C. Gibbs, *J. Am. Chem. Soc.* **56** (1934) 725.
- [16] L. Knorr, *Ber.* **37** (1904) 3507.
- [17] W. Kern and E. Brenneisen, *J. Prakt. Chem.* **159** (1941) 193.
- [18] U. Horn, H. Berendt, P. Liechti and H. Wegmuller, Swiss Pat. no. 606 191 (1975).
- [19] J. Haase, U. Horn and H. Berendt, Brazilian Pat. no. P.I. 7 803 709 (1979).
- [20] A. Rembaum, *J. Macromol. Sci.* **A3** (1969) 87.
- [21] H. Noguchi and A. Rembaum, 158th National Meeting, American Chemical Society (NY) (Sept. 1986) Polym. Preprints. **10** (no. 2), (1969) 718.
- [22] H. Noguchi and A. Rembaum, *J. Polym. Sci.* **B7** (1969) 383.
- [23] A. Rembaum, H. Rile and R. Somoano, *J. Polym. Sci.* **B8** (1970) 457.
- [24] V. Hadek, H. Noguchi and A. Rembaum, *Macromolecules* **4** (1971) 494.
- [25] D. Casson and A. Rembaum, *Macromolecules* **5** (1972) 75.
- [26] A. Rembaum and H. Noguchi, *Macromolecules* **5** (1972) 253.
- [27] A. Rembaum and H. Noguchi, *Macromolecules* **5** (1972) 261.
- [28] T. Tsutsui, T. Sato and T. Tanaka, *Polym. J.* **5**, **3** (1973) 332.
- [29] K. Mizoguchi, T. Suzuki, E. Tsuchida and I. Shinohara, *Nippon Kagaku Kaishi* **9** (1973) 1756.
- [30] K. Sanada, N. Eda, E. Tsuchida and I. Shinohara, *Nippon Kagaku Kaishi* **3** (1974) 584.

- [31] T. Tsutsui, R. Tanaka and T. Tanaka, *Polym. J.* **8**, **6** (1976) 487.
- [32] H. Noguchi and Y. Uchida, *J. Polym. Sci.* **B15** (1977) 31.
- [33] E. Cooper and C. A. Angell, '4th International Conference on Solid State Ionics', Grenoble, (July 1983).
- [34] E. Cooper, Personal Communication -- 4th International Conference on Solid State Ionics, Grenoble, (July 1983).
- [35] M. Watanabe, M. Kanba, J. Ikeda, E. Tsuchida and I. Shinohara, *Electrochim. Acta* **27**, **8** (1982) 1153.
- [36] A. Benchettara, A. Nouacer and J. J. Rosenberg, *Electrochim. Acta* **31**, **2** (1986) 155.
- [37] G. Schmitt and J. J. Rosenberg, *J. Applied Electrochem.* **16** (1986) 505.
- [38] J. J. Rosenberg, A. Benchettara, A. Nouacer and J. Estienne, *Electrochim. Acta* (in press).
- [39] L. Dominquez and W. H. Meyer, *Solid State Ionics* **28-30** (1988) 941.
- [40] C. Tubandt and E. Lorenz, 'Nernst's Festschrift', W. Knapp, Halle (1912) p. 446.
- [41] M. Hebb, *J. Chem. Phys.* **20** (1952) 185.
- [42] C. Wagner, *J. Chem. Phys.* **21** (1953) 1819.
- [43] C. Wagner, 7th C.I.T.C.E., Lindau, (1955), Butterworths, London (1957) p. 361.
- [44] S. Yen, D. Casson and A. Rembaum, *Polym. Sci. Technol.* **2** (1973) 291.
- [45] K. Hiraoka and T. Yoroyama, *J. Polym. Sci.* **B16** (1978) 401.
- [46] C. Pouchert, The Aldrich Library of Infrared Spectra, Vol. 2, 2nd ed, Aldrich Chem. Co., Milwaukee (1975).
- [47] J. Ketelaar, *Z. Physik. Chem.* **B26** (1934) 327.
- [48] J. Ketelaar, *Trans. Faraday Soc.* **34** (1938) 874.
- [49] R. Weil and A. Lawson, *J. Chem. Phys.* **41** (1964) 832.
- [50] L. Suchow and G. Pond, *J. Amer. Chem. Soc.* **75** (1953) 5242.
- [51] J. Jaffray and R. Jouanisson, *C.R. Acad. Sci.* **245** (1957) 40.
- [52] J. Jaffray, *J. Rech. CNRS (Lab. Bellevue, Paris)* **39** (1957) 125.
- [53] S. Geller and B. B. Owens, *J. Phys. Chem. Solids* **33** (1972) 1241.
- [54] S. Geller, 'Topics in Applied Physics 10' **3** (1977) 40-66.
- [55] M. Thackeray and J. Coetzer, *Electrochim. Acta* **24** (1979) 495.
- [56] J. Oxley and J. Humphrey, 'Atomics Int. Final Rep'. 22 July, 22 October 1968.
- [57] G. Argue, I. Groce and B. B. Owens, Proc. 22nd Ann. Power Sources Conference, New Jersey (1968) p. 103.
- [58] G. Argue, I. Groce and B. B. Owens, in 'Power Sources 2', 1968, (edited by D. H. Collins), Pergamon Press, Oxford, (1970) p. 389.
- [59] M. De Rossi and B. Scrosati, *Electrotechnica* **52** (1970) 1.