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High-conductivity solid copper ion conductors: the sulphonium halide-copper(I) halide systems

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The electrical conductivities of the copper (I) halide-sulphonium halide systems were measured and high conductivity copper ion conductors were found in the copper (I) iodide-1-methyl-1-thioniacyclohexane iodide ($C_5H_{10}SCH_3I$) and copper (I) iodide-4-methyl-1, 4-oxathianium iodide ($C_4H_8OSCH_3I$) systems. The dependence of electrical conductivity on the composition showed that the maximum conductivity appeared at 83·4 mol% CuI for these two systems. The highest conductivities of the systems, CuI-$C_5H_{10}SCH_3I$ and CuI-$C_4H_8OSCH_3I$, were $1{\cdot}4 \times 10^{-3}$ and $7{\cdot}2 \times 10^{-4}$ $(\Omega\,\mathrm{cm})^{-1}$ at 25° C, respectively. The conduction in these systems was essentially ionic.

1. Introduction

During the past decade, a search for high conductivity solid ion conductors has been carried out and high copper ion conductivity compounds have been found in the CuX-substituted ammonium halide systems at room temperature [1–4]. In this paper, the copper ion conductivities of the CuX-sulphonium halide systems are described.

2. Experimental

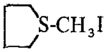
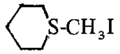
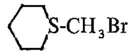
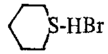
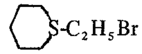
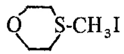
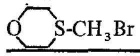
Copper (I) halides were purified by recrystallizing in the corresponding hydrohalogenic acid. After drying under vacuum, the copper (I) halide was annealed under oxygen-free nitrogen to remove the excess halogen.

Sulphonium halides were prepared by the method described in the literature [5]. A typical example of synthesis is as follows:

To a solution containing 7·1 g (0·12 mol) of dimethylsulphide in 50 ml of ethyl alcohol was slowly added 17·9 g (0·13 mol) of methyl iodide and the mixture was refluxed for 90 min. After being filtered and dried, the precipitate was purified by recrystallizing three times in ethyl alcohol. A yield of 7·3 g of trimethylsulphonium iodide (about 30% yield) was obtained.

The decomposition temperatures of each sulphonium halide are shown in Table 1.

Table 1. The decomposition temperatures of sulphonium halides

Sulphonium compounds	*Decomposition temperature* (° C)
$(CH_3)_3SI$	146
$(CH_3)_2C_2H_5SI$	89
	133
	156
	147
	115
	114
	147
	150

The CuX-sulphonium halide double salts were synthesized by combining two corresponding halides. The appropriate quantities of sulphonium halide and CuX were thoroughly ground together in an agate mortar with a small amount of ethyl alcohol and dried completely under vacuum before being pressed to form a pellet under a pressure of 3000 kg cm^{-2}, and then heated in a sealed evacuated Pyrex vessel. The reactions were carried out for 20 h below the decomposition temperatures of the corresponding sulphonium iodide shown in Table 1, which were determined by thermogravimetric analysis.

The reaction product was ground and pressed under a pressure of 4000 kg cm^{-2} to form a conductivity cell of the configuration of

Cu, electrolyte (2 : 1 weight ratio)/electrolyte/Cu,

electrolyte (2 : 1 weight ratio).

The conductivity was measured under a nitrogen gas flow with a 1000 Hz conductance bridge. The resistance was not frequency-dependent in the 1000–10 000 Hz range.

The electronic conductivities of some of the samples were measured by the Wagner polarization method [6]. The sample was formed in the shape of pellet, about 3 mm thick and 13 mm in diameter, by pressing at a pressure of 4000 kg cm^{-2}. A constant current supplier was used and the resulting voltage was measured with a high impedance digital voltmeter. The X-ray diffraction patterns of the powdered samples were obtained using CuKα radiation.

Differential thermal analysis (DTA) was carried out for the sample which was sealed in a Vycor tube under vacuum. The heating rate was 3·5° C min^{-1}. The decomposition temperature of the samples was measured by thermogravimetric analysis (TGA) in air, the heating rate being 7·5° C min^{-1}.

3. Results and discussion

The electrical conductivity values obtained for the various systems are shown in Table 2. Of these systems, the CuI-$C_5H_{10}SCH_3I$ and CuI-$C_4H_8OSCH_3I$ systems give relatively high conductivities of 1·4 x 10^{-3} (Ω cm)$^{-1}$ and 7·2 x 10^{-4} (Ω cm)$^{-1}$ at room temperature, respectively. The specific conductivities for two systems, namely the CuI-$C_5H_{10}SCH_3I$ and CuI-$C_4H_8OSCH_3I$ systems, are plotted as a function of the composition of CuI in Fig. 1. The maximum conductivity values are found at the composition of about 83·4 mol% CuI, in agreement with the CuI contents in the corresponding ammonium iodide-CuI systems, that is, the $C_5H_{11}NCH_3I$-CuI and $C_4H_9ONCH_3I$-CuI systems, reported previously [4]. The temperature dependence of the conductivities of CuI 83·4 mol%-$C_5H_{10}SCH_3I$ 16·6 mol% and CuI 83·4 mol%-$C_4H_8OSCH_3I$ 16·6 mol% were measured under a nitrogen atmosphere. The logarithmic conductivity versus the reciprocal of the absolute temperature curves for these samples give straight lines over the temperature range 20–130° C. The values for the Arrhenius activation energy were calculated from the expression

$$\sigma = \sigma_0 \exp(-E/RT)$$

where R is the gas constant, σ_0 the pre-exponential term and E the activation energy. A value of 22 kJ mol^{-1} was obtained consequently for these compounds. The maximum conductivities and the activation energies for these compounds were comparable to those of the corresponding compounds reported previously [4]. The electronic conductivities of the CuI-$C_5H_{10}SCH_3I$ and CuI-$C_4H_8OSCH_3I$ systems were measured by Wagner's polarization method. The logarithmic current versus cell voltage curves for the cell, Cu/sample/graphite, give straight lines in the temperature range of 90–130° C. Therefore, the electronic conductivities were calculated with the help of the Wagner theory [6]. The value of the electronic conductivity obtained for CuI 83·4 mol%-$C_4H_8OSCH_3I$ 16·6 mol% at 110° C is about 10^{-7} (Ω cm)$^{-1}$ and that of CuI 83·4 mol%-$C_5H_{10}SCH_3I$ 16·6 mol% is too small to measure with this method, so that the conduction in these new compounds is essentially ionic.

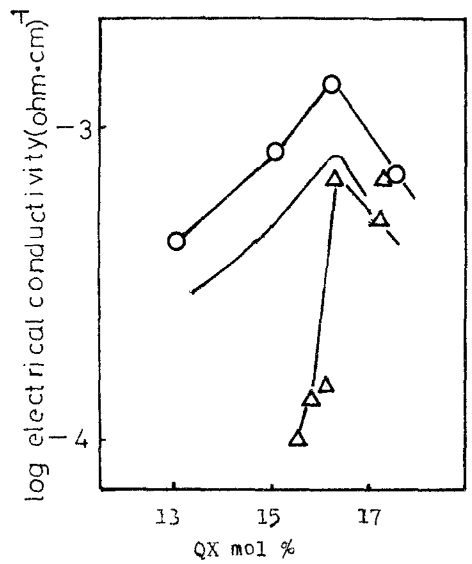
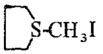
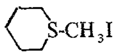
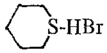
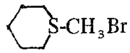
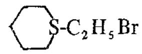
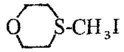
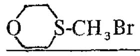


Fig. 1. The composition dependence of the electrical conductivities of the CuI-$C_5H_{10}SCH_3I$ (○); CuI-$C_4H_8OSCH_3I$ (△) and CuI-$C_5H_{11}NCH_3I$ (——) [4] systems.

The decomposition temperatures of these new copper ion conductivity compounds were

Table 2. The electrical conductivities of the copper (I) halide-sulphonium halide systems at room temperature

Electrolyte	*Conductivity* $(\Omega\ cm)^{-1}$
Trimethylsulphonium iodide-CuI (84 mol%) $(CH_3)_3SI$	$\sigma_i^* \ll \sigma_e^*$
Dimethylethylsulphonium iodide-CuI (84 mol%) $(CH_3)_2C_2H_5SI$	$\sigma_i \ll \sigma_e$
1-Methyl-1-thioniacyclopentane iodide-CuI (84 mol%) 	$\sigma_i \ll \sigma_e$
1-Methyl-1-thioniacyclohexane iodide-CuI (83·4 mol%) 	$1{\cdot}4 \times 10^{-3}$
1-Hydro-1-thioniacyclohexane bromide-CuBr (85 mol%) 	$8{\cdot}4 \times 10^{-6}$
1-Methyl-1-thioniacyclohexane bromide-CuBr (84 mol%) 	$< 10^{-7}$
1-Ethyl-1-thioniacyclohexane bromide-CuBr (88 mol%) 	$2{\cdot}0 \times 10^{-6}$
4-Methyl-1-oxa-4-thionacyclohexane iodide (or 4-methyl-1, 4-oxathianium iodide)-CuI (83·4 mol%) 	$7{\cdot}2 \times 10^{-4}$
4-Methyl-1, 4-oxathianium bromide-CuBr (85 mol%) 	$5{\cdot}0 \times 10^{-5}$

* σ_i is the ionic conductivity and σ_e is the electronic conductivity.

measured by TGA; CuI 83·4 mol%-$C_5H_{10}SCH_3I$ 16·6 mol% and CuI 83·4 mol%-$C_4H_8OSCH_3I$ 16·6 mol% were found to be stable up to 177 and 170° C, respectively. The electrical conductivity for the CuBr-$C_5H_{10}SCH_3Br$ system was measured at temperatures ranging from 20 to 170° C and at CuBr compositions ranging between 91 and 79 mol%. The conductivity versus the reciprocal of the absolute temperature curve of CuBr 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol% is shown in Fig. 2.

Fig. 2 consists of three parts. At temperatures below 117° C, the conductivity was almost the same order of magnitude as that of CuBr, and the X-ray diffraction patterns of this system give only the strong peaks due to CuBr. A sharp jump in the conductivity was observed in the vicinity of 117–124° C. At temperatures above 124° C, the conductivity was higher than 10^{-1} $(\Omega\ cm)^{-1}$. The conductivities of the CuBr-$C_5H_{10}SCH_3Br$ system at 124° C are shown in Fig. 3 as a function of $C_5H_{10}SCH_3Br$ mol%. The highest conductivity of $1{\cdot}9 \times 10^{-1}$ $(\Omega\ cm)^{-1}$ was found at 124° C and at the composition of about 16 mol% $C_5H_{10}SCH_3Br$. For CuBr 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol%, which was annealed in a sealed evacuated Pyrex vessel at temperatures above 124° C, before being quenched to room temperature, X-ray analysis showed no peaks due to CuBr. Peaks which may be considered to be due to a new compound were observed. The electronic conductivity of this compound at temperatures above 124° C was measured by the Wagner method; it was found to be negligibly small.

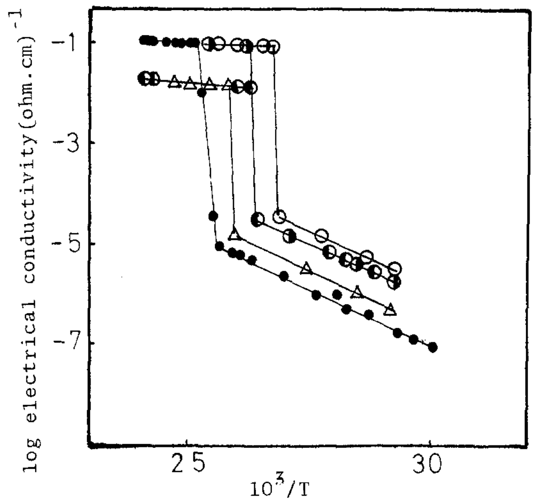


Fig. 2. The temperature dependence of the electrical conductivities of CuI_xBr_{1-x} 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol%: at $x = 0{\cdot}00$ (●), $x = 0{\cdot}12$ (◑); $x = 0{\cdot}30$ (○); $x = 0{\cdot}62$ (◐) and $x = 1{\cdot}00$ (△).

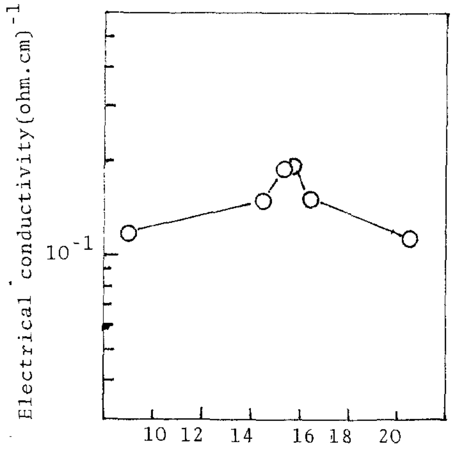


Fig. 3. The composition dependence of the electrical conductivities of the CuBr-$C_5H_{10}SCH_3Br$ system at 124° C.

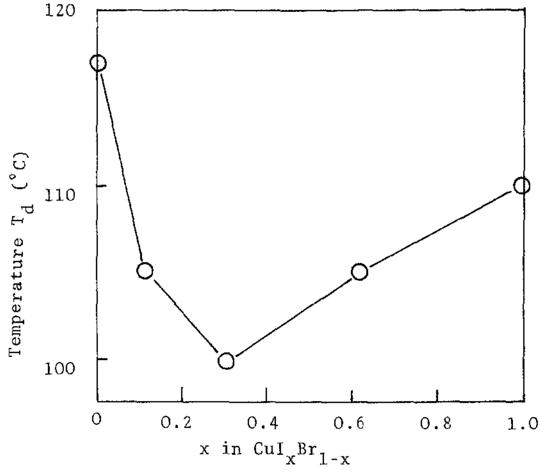


Fig. 4. Temperatures T_d as a function of x in CuI_xBr_{1-x} 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol%.

In order to stabilize the high ionic conductivity phase in CuBr 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol% at lower temperatures, we attempted to substitute bromine with iodine in this compound. The temperature dependence of the conductivity of CuI_xBr_{1-x} 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol% was measured over the temperature range 20 to 160° C and the results are shown in Fig. 2. Each curve consists of three parts and the conductivities of these compounds increase suddenly at a certain temperature T_d. At temperatures above T_d, conductivity behaviours of CuI_xBr_{1-x} 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol% were almost the same in the range of 0·00 to 0·30 for x, but the conductivity values in the range of 0·00 to 0·30 for x were higher than those in the range of 0·30 to 1·00. The electronic conductivities of CuI_xBr_{1-x} 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol%, measured by Wagner's polarization method, were negligible.

Temperatures T_d are shown as a function of x in Fig. 4, which become lower with the increase of x in the range of 0·00 to 0·30 for x, but become higher with increasing values of x in the range of 0·30 to 1·00. These facts indicate that high ionic conductivity phases can be stabilized by substituting bromine with iodine in CuBr 84 mol%-$C_5H_{10}SCH_3Br$ 16 mol%. The iodine substitution limit is reached at $x = 0{\cdot}30$ in CuI_xBr_{1-x}, at which point $T_d = 100°$ C. The reason why the high-conductivity phases are stabilized by this substitution however, is not clear.

References

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