A Conductometric Study of the Bi-HgI_2 System

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The electric conductivity of the homogeneous liquid Bi-HgI_2 system was measured in the temperature range 260–540 °C for several Bi mole fractions ranging from 0.00 to 0.38. The specific conductivity-composition isotherms are indicative of the occurrence of electronic conductivity also before reaching a bismuth concentration sufficient for a complete conversion of HgI_2 into Hg_2I_2. As the temperature rises the share of electronic conductivity in the total conductivity abruptly increases. Comparing the properties of this system with those of the BiI_3-Bi system the conclusion is drawn that electronic conductivity in liquids is due to free metal atoms.

Introduction

Metal-molten salt systems are of great theoretical and practical interest because both ionic and electronic conductivities occur in them. In view of technical difficulties encountered in quantitative investigations associated with high temperatures and corrosion of the systems under consideration, reliable measurements of this type have only recently been available. Bronstein and Bredig[1, 2] have carried out extensive investigations of sodium and potassium solutions in the melts of their halides. The specific conductivity isotherms of these systems exhibit an abrupt increase with increasing metal mole fraction. Also the Ce-$CeCl_3$[3] and La-$LaCl_3$[4] systems behave in the same manner. In contrast to these systems wherein the metals do not readily form lower-valent states, the liquid Cd-CdX_2 systems (where X is a halogen element) show constant values of isothermal specific conductivity which are independent of the metal mole fraction. This phenomenon has been explained[5] by the formation of the complex Cd_2^{2+} ions. At temperatures below the critical temperature of mixing, the Bi-$BiCl_3$[6], Bi-$BiBr_3$[6] and Bi-BiI_3[7] systems display a similar isothermal specific conductivity which is only slightly dependent on the metal mole fraction. Above the critical temperature of mixing the conductivity increases abruptly with increasing metal mole fraction, as in systems consisting of an alkali metal and of its halide. The behaviour of the former systems has been explained by the reduction of the Bi^{3+} ion to the monovalent Bi^+ ion with increasing addition of bismuth metal.

Releigh[8] has tried to interprete the electronic conduction mechanism in the BiI_3-rich composition region of the Bi-BiI_3 system in terms of oriented motion of electrons which are exchanged between the Bi^+ and Bi^{3+} ions. Such an interpretation of the mechanism, however, is disputable, since the former results[1–7] as well as the measurement of the supercritical mercury vapour conductivity in relation to density[9] show that the electronic conductivity is associated with the presence of free metal atoms. Namely, in systems wherein the metal atoms are most likely bound as ions of lower-valent states the order of magnitude of conductivity remains within the limits of ionic conductivity. In this work the electric conductivity of the Bi-HgI_2 systems was measured in order to find out which of the above proposed mechanisms of electronic conduction in metal-molten salt system is to be preferred.

Experimental

Merck analytical grade HgI_2 and Bi were used without further purification. Mixtures of various mole composition were prepared by successive addition of powdered bismuth to a conductometric cell which in the beginning contained pure HgI_2. The addition of bismuth was carried out at room temperature, when the components are in solid state. After each addition of bismuth the cuvette was sealed in vacuum. This is necessary in order to prevent the melt from coming into contact and reacting chemically with air as well as to hinder volatilization of the melt. The cell is shown in Figure 1. The cell constant was determined by measuring at several temperatures the resistance of the pure HgI_2

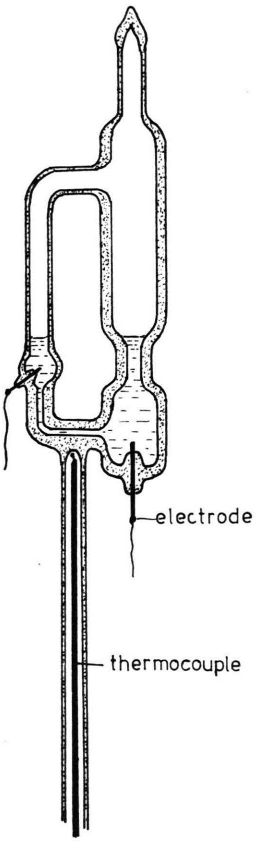

Fig. 1. The Pyrex conductometric cell with tungsten electrodes used for measurement of electric conductivity of the Bi-HgI$_2$ system.

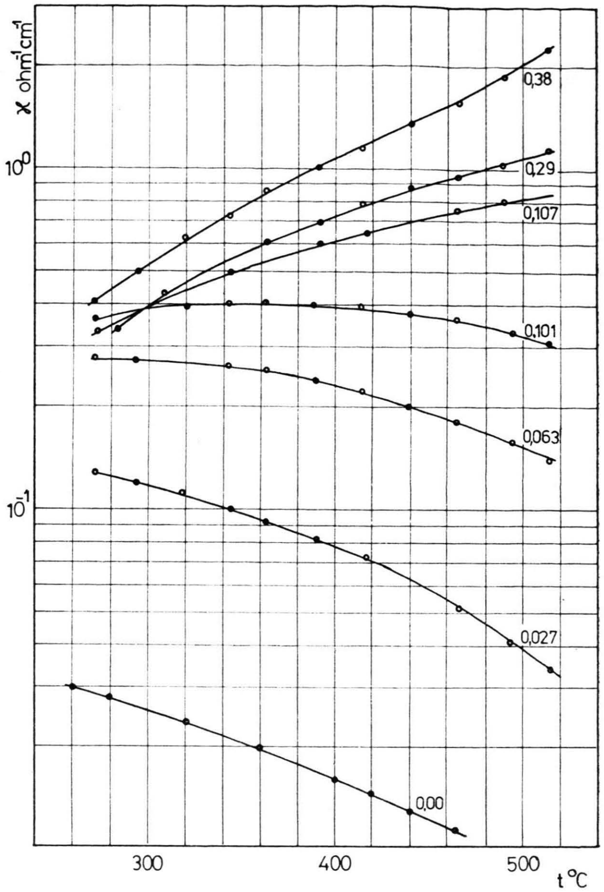

Fig. 2. Temperature dependence of the specific electric conductivity of the Bi-HgI$_2$ system. Bismuth mole fractions are indicated for each curve.

melt the conductivity of which has previously been reported in the literature [10]. The cell constant, which was found to be 147 ± 2 cm^{-1}, remained invariable within the limits of experimental error over the temperature range investigated.

The conductivity was measured with an IEV 5960 conductometer.

The results are presented in Figure 2. It is seen that the conductivity increases nearly monotonously with increasing Bi mole fraction and that the negative temperature coefficient of conductivity of molecular HgI$_2$ melt gradually turns over into a positive one characteristic of ionic melts.

Discussion

The isothermal specific conductivity of the Bi-HgI$_2$ system as a function of Bi mole fraction at several temperatures is shown in Figure 3. Dashed lines in the figure represent additivity lines calculated by summing up the specific conductivities of HgI$_2$, Hg$_2$I$_2$ and BiI$_3$ in mole amounts formed according to the equation

$$3\,\mathrm{HgJ_2} + \mathrm{Bi} = 3/2\,\mathrm{Hg_2J_2} + \mathrm{BiJ_3}\,.$$

The conductivity of Hg$_2$I$_2$ is known from the literature [11]. Stoichiometrically all the mercuric iodide is converted into mercurous iodide at a bismuth mole fraction of 0.25. This is manifested as inflection point on the experimental curves shown in Figure 3. Up to a bismuth mole fraction of 0.25 the experimental specific conductivity-versus-composition curves are of the S-form characteristic of mixtures of a weak and a strong electrolyte (HgCl$_2$-Hg$_2$Cl$_2$, HgI$_2$-Hg$_2$I$_2$ [11], HgI$_2$-BiI$_3$ [12]), while above this value the conductivity increases abruptly with mole fraction and temperature. The effect of temperature is interesting. In all the cases of mixtures of salt melts studied previously the temperature was found to improve the additivity of conductivity[12]. In the system observed in the present work, additivity of conductivity at a Bi mole fraction of 0.25 (when the composition of the HgI$_2$-BiI$_3$ system is stoichiometric) was to be expected to become progressively better with increasing temperature, since some additivity exists already at a temperature of 392 °C. In Fig. 3, however, it is seen that the experimental curves increasingly depart from the additivity line as the temperature rises. Furthermore, the conductivity was found to increase abruptly with rising temperature at bismuth mole fractions larger than 0.25. This increase cannot be accounted for merely by formation of monovalent bismuth iodide according to the equation[13]

$$\mathrm{Bi} + 2\,\mathrm{BiI_3} = 3\,\mathrm{BiI}$$

since the extrapolation of the experimental curve at 515 °C to a bismuth mole fraction of 0.5 (when stoichiometrically there are only BiI and Hg$_2$I$_2$) would lead to a specific conductivity higher than 10 ohm^{-1} cm^{-1}, which is possessed by no ionic conductor[14] at this temperature. Therefore this increase should be ascribed to a share of electronic conductivity in the total conductivity of the system, which is manifested at bismuth mole fractions smaller than those in the case of the Bi-BiI$_3$ system. Namely, in the system observed the specific conductivity curve begins to depart abruptly from the additivity line at a bismuth mole fraction smaller than 0.15.

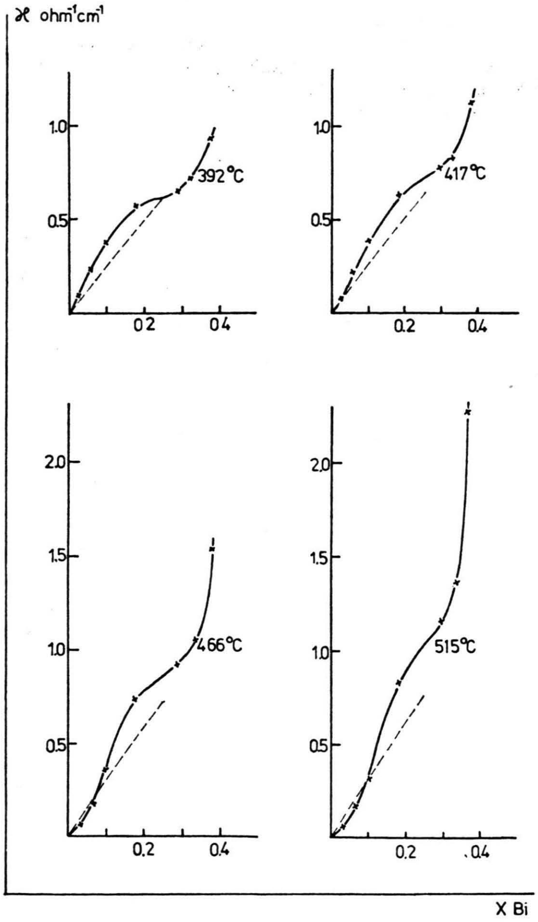

Fig. 3. Dependence of the specific electric conductivity of the Bi-HgI$_2$ system on Bi mole fractions at four constant temperatures.

At a temperature of 515 °C bismuth is soluble in HgI$_2$ up to a mole fraction of 0.38. It it is taken into consideration that above 458 °C bismuth is soluble in BiI$_3$ in any molar ratio, owing to the formation of a BiI$_3$-BiI mixture which is a good bismuth solvent, it may be concluded that the presence of Hg iodides lowers the bismuth solubility, most likely due to the reducing and salting-out actions of Hg$_2$I$_2$. As a result of this, bismuth appears in atomic state in the Bi-HgI$_2$ system at metal mole fractions smaller than those in the case of the Bi-BiI$_3$ system. If in the Bi-HgI$_2$ and Bi-BiI$_3$ systems the molar coefficients of conductivity are compared at 515 °C for a bismuth mole fraction of 0.35 ($d\varkappa/dx = 10$ and 2 ohm^{-1} cm^{-1} respectively), the effect of Hg iodides on prevention of metallic bismuth consumption and on speeding up the occurrence of electronic conductivity becomes apparent.

These considerations support the assumption that the phenomenon of electronic conductivity in metal-molten salt systems is due to free metal atoms, which does not favour the interpretation of the electronic conduction mechanism by oxidoreduction of ions of different valent states. From this point of view the effect of temperature on the increase of electronic conductivity share in the total conductivity of Bi-BiX$_3$ systems[6, 7] may be explained by the temperature displacement of the equilibrium

$$2\,\mathrm{Bi} + \mathrm{BiX_3} \rightleftharpoons 3\,\mathrm{BiX}$$

to the left-hand side rather than by an increase in frequency of electron jumps between Bi$^+$ and Bi^{3+}. Besides, free trivalent metal ions cannot be expected to be present in molten salts, i. e. if halogen ions happen to be in their close proximity, then the states BiX_2^+ and BiX^{2+} (see [12]) are much more likely to occur. Hence the equivalence of states of the electron donor and acceptor at the instant of the electron jump vanishes, which, according to the criteria of Franck-Condon and of other authors [15], reduces the probability of electron jumps to zero.

From the available experimental results it cannot be established whether electrons in the process of electronic conduction are transferred from a metal atom to its ion, or from an atom to another. An experiment in which the mercury electric conductivity was measured under supercritical conditions [9] demonstrates that the electric conductivity, which in that instance is electronic, changes in order of magnitude from metal into insulator conductivity if the density is lowered from the value corresponding to vapour to that corresponding to liquid under normal conditions. This enables a metal solution in a molten salt to be considered as metal vapour of various concentration, where electron transport is the easier to carry out, the higher the metal concentration, but the validity of this assumption is to be checked by further experimental investigations.

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