The Electric Conductivity of Molten HgI_2-$HgBr_2$ and HgI_2-SbI_3 Binary Mixtures

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The specific electric conductivity of molten HgI_2-$HgBr_2$ and HgI_2-SbI_3 binary mixtures was measured as a function of composition and temperature in the ranges $220-540\,^{\circ}C$ and 180 to $540\,^{\circ}C$, respectively. In the HgI_2-$HgBr_2$ system negative deviations from additivity are found in mixtures rich in $HgBr_2$, and positive ones in those rich in HgI_2. The positive deviations are more pronounced at higher temperatures. In the HgI_2-SbI_3 system the deviations from additivity are negative throughout.

Introduction

The electric conductivity of pure molten mercury (II) iodide [1-3] and mercury (II) bromide [2] has been studied earlier. Molten HgI_2 (m. p. $257\,^{\circ}C$) has a negative temperature coefficient of conductivity, while molten $HgBr_2$ (m. p. $237\,^{\circ}C$) shows a maximum of conductivity at about $460\,^{\circ}C$. Grantham and Yosim [2] have shown that the negative temperature coefficient of electric conductivity in the melts is a consequence of the decrease in density and increase in covalent character of the melt as the temperature increases. Such an explanation is satisfactory in view of the work of Darnell and McCollum [4], who achieved a large increase in ionicity of molten HgI_2 by subjecting it to a high pressure.

The electric conductivity of pure SbI_3 has been investigated earlier [5] as a function of temperature in the narrow temperature range $208 - 270\,^{\circ}C$.

Grantham [6] studied the electric conductivity of molten $HgCl_2$-Hg_2Cl_2 and HgI_2-Hg_2I_2 mixtures. Deviations from additivity are markedly positive in mixtures rich in monovalent component, and negative in those rich in bivalent component.

Wholly negative deviations from additivity of electric conductivity is often encountered in markedly ionic melts such as KCl-LiCl, NaCl-KCl, KCl-Ki [7] or KBr-$BaBr_2$, KCl-NaI, KNO_3-KBr [8] mixtures, whereas positive deviations are frequent in mixtures of molten covalent salts such as AlI_3-SbI_3 [9], because each component behaves as a solvent in which the other component electrolytically dissociates. Plotnikov [10] has found that mixtures of the covalent compounds PCl_5 and Br_2 are good conductors, although the pure components are insulators.

In systems of mixed character, such as $ZnCl_2$-KCl [11] or $AlCl_3$-KCl [12], both positive and negative deviations from additivity are encountered.

It is of interest to study from this point of view HgI_2-$HgBr_2$ and HgI_2-SbI_3, since the components of these systems are similar in their predominantly covalent character and low electric conductivity. The melting and boiling points of these salts are close to each other. Gäumann [13] has found that the melting-solidification phase diagram of the HgI_2-SbI_3 system is simple, with one eutectic point.

Experimental

Since the work was to be done also above the boiling point of the salts investigated the electric conductivity was measured in a heavy-walled sealed cell shown in Figure 1. The cell was made of Pyrex glass with platinum electrodes. The level of the melt was maintained above the narrow channel, so that its change due to a change in temperature or to addition of one of the components did not affect the cell constant.

By measurement of the conductivity of HgI_2 on the basis of the Grantham-Yosim [2] procedure the cell constant was determined to be $6.60 \pm 0.06\ cm^{-1}$ in the temperature range observed.

Owing to the small volume of the cell (the diameter being about 0.8 cm) the temperature gradient between the outer walls of the cell and the thermocouple did not introduce a considerable error. Measurements with a definite mole composition were made during continuous slow heating and cooling. The time of one heating-cooling cycle was about 4 hours. A cylindric furnace 50 cm in height and 6 cm in inner diameter was used. No difference in conductivity was observed at a definite temperature during heating and cooling of the melt.
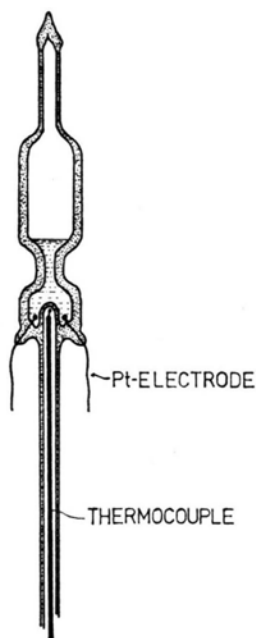
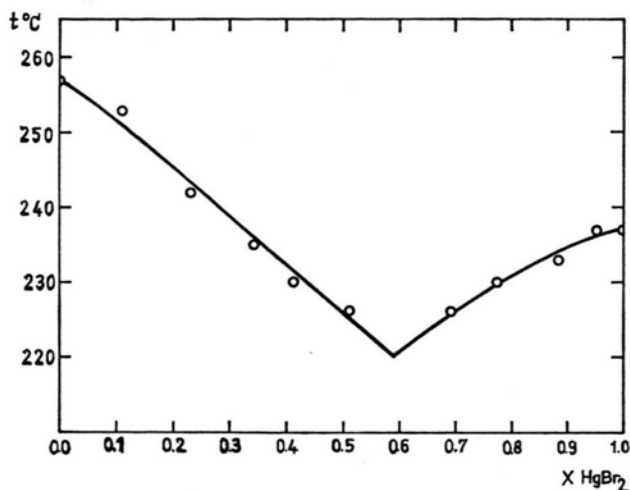Fig. 1. The view of the cell used in the present experiment for measurement of conductivity.

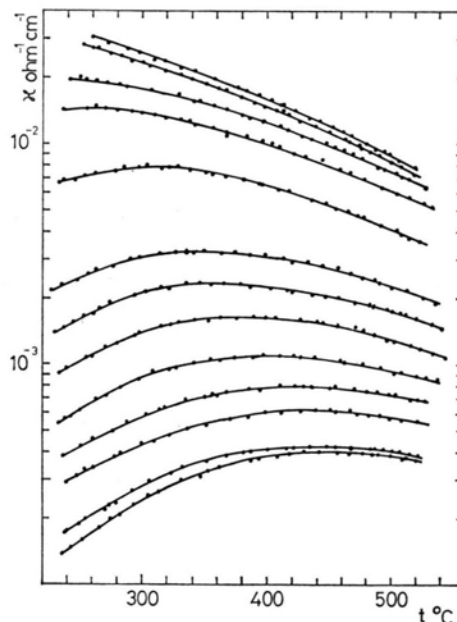Fig. 2. The phase diagram of the HgI_2-$HgBr_2$ system, determined conductometrically.

Fig. 3. The specific electric conductivity of molten HgI_2-$HgBr_2$ mixtures as a function of temperature for the following mole fractions of HgI_2 (from top to bottom): 1,00; 0,89; 0,77; 0,66; 0,49; 0,31; 0,23; 0,17; 0,12; 0,08; 0,05; 0,01 and 0.00.

The temperature was measured, to an accuracy of ± 1 °C, with a calibrated chromel-alumel thermocouple placed in the central part of the cell (Figure 1).

A Wheatstone bridge was used as provided by the VEB Mellenbach, with an audio-frequency oscillator and a cathode tube as null-point detector connected through a home made amplifier.

Merck HgI_2 of 99.0% purity was distilled under partial pressure of O_2 and then sublimed off in vacuum [6]. Merck $HgBr_2$ of 99.5% purity was triply distilled in a stream of $N_2 + HBr$ and then sublimed off in vacuum. SbI_3 was prepared from the elements Sb (BDH powder) and I (BDH, resublimed), crystallized from CS_2 and twice distilled in a stream of CO_2.

Results

On the basis of the abrupt change in conductivity of the mixture at the beginning of separation of solid component [6] the melting-solidification phase diagram was constructed for the HgI_2-$HgBr_2$ system. This is a system with one eutectic point (Figure 2).

Figure 3 shows the change of specific conductivity of molten HgI_2-$HgBr_2$ mixtures as a function of temperature for several mole compositions from one pure component to the other.

Figure 4 shows the specific conductivity of the same system as a function of mole fraction at three constant temperatures of 260, 400 and 520 °C.

Figure 5 presents the electric conductivity of the HgI_2-SbI_3 system as a function of temperature when the composition varies from one pure component to
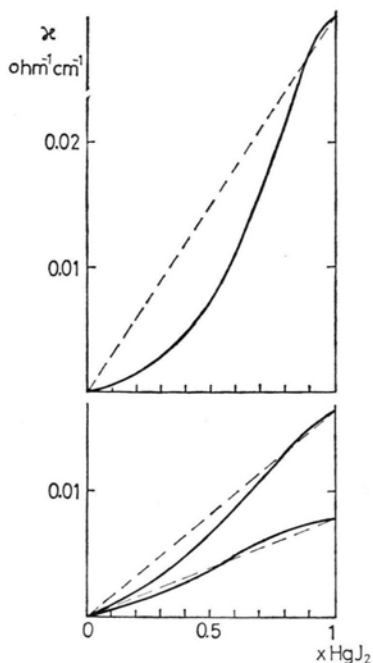
Fig. 4. The specific electric conductivity of molten HgI$_2$-HgBr$_2$ mixtures as a function of mole fraction of HgI$_2$ at temperatures of (from top to bottom) 260, 400 and 520 °C. The additivity lines are represented by dashed lines.
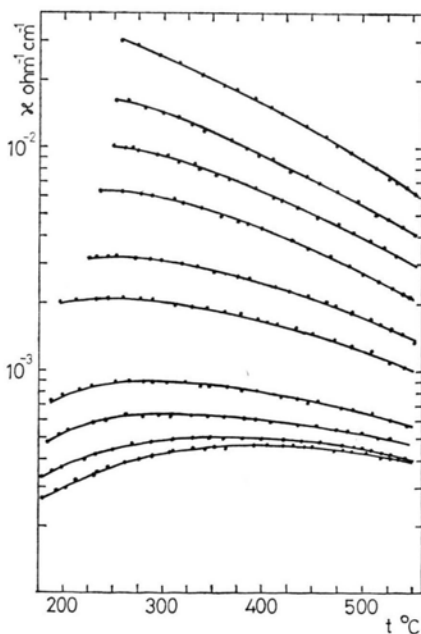

Fig. 5. The specific electric conductivity of molten HgI$_2$-SbI$_3$ mixtures as a function of temperature for the following mole fractions of HgJ$_2$ (from top to bottom): 1,00; 0,91; 0,83; 0,74; 0,58; 0,42; 0,27; 0,16; 0,09; 0,00.

the other. If the conductivity curve of pure SbI$_3$ is compared with that presented in Ref. [5], it is seen that our values are lower by about 20%, which is probably due to the higher purity of our sample.

Figure 6 shows the specific conductivity as a function of mole fraction of HgI$_2$-SbI$_3$ mixtures at the temperatures of 350, 450 and 550 °C. A large negative deviation from the additivity line is seen at all the three temperatures.
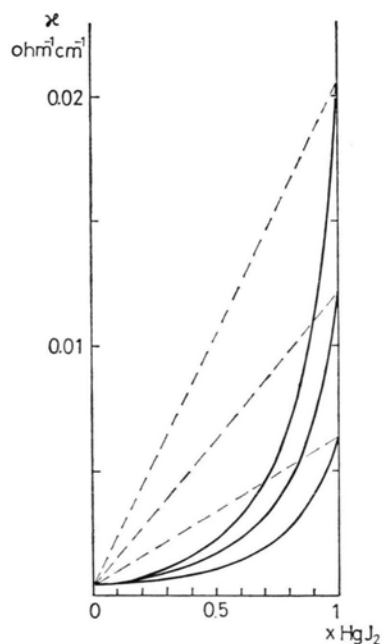

Fig. 6. The specific electric conductivity of molten HgI$_2$-SbI$_3$ mixtures as a function of the mole fraction of HgI$_2$ at temperatures of (from top to bottom) 350, 450 and 550 °C. The additivity lines are represented by dashed lines.

Discussion

HgI$_2$, HgBr$_2$ and SbI$_3$ are salts of the covalent type, of which HgI$_2$ is the better electric conductor by one or two orders of magnitude.

No relationship between the position of the eutecticum and the electric conductivity isotherm can be observed, contrary to some systems in which chemical compounds are formed [8, 11].

Figures 3 and 5 show that the conductance of the melts gradually changes with composition. From the shift of the maximum of the conductivity with composition it is seen that molten HgI$_2$ should have a maximum of its conductivity at $50 - 100$ °C below the melting point, a conclusion similar to the one drawn in [6].

Figures 4 and 6 show that there is no strict additivity of electric conductivity. The studies [6-10] as well as the present work suggest that one component of a binary mixture should be considered as a solvent of the other component. In such a case two opposing effects occur: the molecules or ions of one component represent "traps" for the carriers of electric current of the other component, which causes a negative deviation, or one component causes by its dielectric and polarization properties the electrolytic dissociation of the other component, hence an excess of carriers of electric current arises and a positive deviation from additivity appears. The effect that is predominant determines the positive or negative deviation from additivity of electric conductivity.

According to McIntyre and Janz [4], the carriers of electric current in a HgI_2-$HgBr_2$ mixture should be considered to be the HgI^+, HgI_3, $HgBr^+$ and $HgBr_3$ ions. With this assumption and using the significant structure theory of liquids proposed by Eyring et al. [15], Mu Shik Jhon et al. [16] have calculated some physical properties of mercury halides in good agreement with experiment. Negative deviations in this system may be explained by the interactions between ions of opposite sign:

$$HgI^+ + HgBr_3^- \rightleftharpoons [HgI \cdot HgBr_3] , \qquad (1)$$

$$HgBr^+ + HgI_3^- \rightleftharpoons [HgBr \cdot HgI_3] . \qquad (2)$$
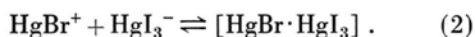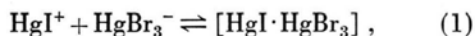
The mixed compounds thus formed are not so stable to complicate the phase diagram of this system, and an increase in temperature shifts the equilibrium to the left, which is seen in Fig. 5 from the enlargement of the range of positive deviations as the temperature rises.

Positive deviations in this system can be accounted for by dissociation of the weaker electrolyte $HgBr_2$ in the stronger electrolyte HgI_2. Such deviations are especially pronounced in HgI_2-Hg_2I_2 and $HgCl_2$-Hg_2Cl_2 mixtures [6], in which the monovalent components are very strong electrolytes in those composition ranges where monovalent components are predominant. It seems that a solvent in which there is already a sufficient quantity of ions favours the increase of the number of ions of the dissolved component.

Because of the similarity in the physical properties of SbI_3 and the mercury halides it is natural to assume that the carriers of electric current in molten SbI_3 are SbI_2^+ and SbI_4^- ions. Thus the negative deviations from additivity of electric conductivity in the HgI_2-SbI_3 system can be explained by the interactions between the two components:

$$HgI^+ + SbI_4^- \rightleftharpoons [HgI \cdot SbI_4] , \qquad (3)$$

$$HgI_3^- + SbI_2^+ \rightleftharpoons [HgI_3 \cdot SbI_2] . \qquad (4)$$
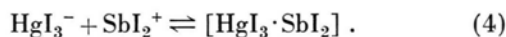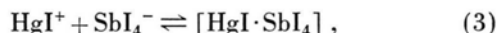
Because of the very large negative deviation from additivity the dissociation of one component in the other is not manifested in this system (Figure 6).

New useful data on the molecule-ion interactions in these systems might be obtained by measurement of their densities and dielectric properties.

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