The Electric Conductivity of the Molten Systems $BiBr_3$-$HgBr_2$ and $BiBr_3$-$CdBr_2$

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The electric conductivity of the molten binary mixtures $BiBr_3$-$HgBr_2$ and $BiBr_3$-$CdBr_2$ was measured for different molar compositions of the mixtures over the temperature ranges 500—770 K and 720—870 K, respectively. The curves of the specific conductivity as a function of composition show in the $BiBr_3$-$HgBr_2$ system negative and positive deviations from additivity in the $HgBr_2$-rich and $BiBr_3$-rich composition regions, respectively. In the $BiBr_3$-$CdBr_2$ system the isotherms of specific conductivity deviate positively from additivity over the entire composition range.

Introduction

The mechanism of conduction of current in molten salts has not yet been explained theoretically with certainty. Spedding [1] assumes that current is conducted simultaneously by ions and ionic agglomerates. Cases of mixtures of incompletely dissociated salts are especially complicated, since beside incompletely dissociated molecular species they contain complex ionic species the number of which varies with composition and temperature. The effect of temperature is particularly pronounced in systems in which the maximum of specific conductivity is easily attained [2—6].

Janz [6] has shown that in molten mercury halides current carriers arise mostly according to the equation

$$2\,HgX_2 = HgX^+ + HgX_3^- \quad \text{(X is a symbol for halogen).}$$

The conductometric properties of the systems HgI_2-SbI_3, HgI_2-$HgBr_2$ [7], and HgI_2-BiI_3 and BiI_3-CdI_2 [8] are explained by a reaction of this type.

Attempts to relate the deviations of electric conductivity from additivity in binary mixtures of molten salts to those of molar volume have not led to significant results [9—11].

This investigation of the electric conductivity of the systems $BiBr_3$-$HgBr_2$ and $BiBr_3$-$CdBr_2$ was undertaken with the purpose of comparing the results with corresponding measurements in systems of iodides of the same metals [8].

Experimental

Use was made of Merck P.A. $CdBr_2$ and $HgBr_2$, while $BiBr_3$ was synthetized from analytical grade powdered bismuth and analytical grade bromine dried over concentrated sulphuric acid. Bromine vapour was carried in a stream of argon over heated bismuth powder, and bismuth bromide vapour was condensed in a cool part of the apparatus. Thereupon the cool part was separated and sealed, so that $BiBr_3$ was stored prior to experiment without contact with air.

The cell for conductometry [8] was made of Pyrex glass with platinum electrodes for the $BiBr_3$-$HgBr_2$ system (which is more easy to melt) and tungsten electrodes for the $BiBr_3$-$CdBr_2$ system (which is more difficult to melt). The cell was filled with solid powdered salts in definite molar ratio at room temperature and was sealed in vacuum. Thereupon the cell was fixed to a heater of a rather large working volume. The resistance of the system was measured during several cycles of heating and cooling with a RCL Wayne-Kerr bridge B 224.

The cell constant was determined by measurements of the resistence of molten bismuth bromide, the conductivity of which is known from tables [12], at several temperatures. The constants of the cells used were about 5 cm^{-1} for both systems.

Results

The results of measurement of the specific conductivity of the $BiBr_3$-$HgBr_2$ and $BiBr_3$-$CdBr_2$ systems are presented in Tables 1 and 2 and in Figures 1 and 2. Figures 1 and 2 show that in the $BiBr_3$-$HgBr_2$ system there are both positive and negative deviations of conductivity from additivity, whereas in the $BiBr_3$-$CdBr_2$ system the deviations are only positive, irrespective of the composition.

Table 1. Values of the specific conductivity (10^2 ohm^{-1} cm^{-1}) interpolated at the identical temperatures, of molten $BiBr_3$-$HgBr_2$ mixtures.

X_{HgBr_2}	0,00	0,10	0,25	0,38	0,48	0,55	0,64	0,75	0,86	0,93
T K										
510		21,4	20,0	16,0	13,3	9,60	8,61	4,73	1,40	0,232
524	24,5	23,4	21,8	17,8	14,4	11,0	8,80	5,14	1,42	0,261
539	26,2	25,6	23,8	19,4	15,4	11,3	9,72	5,41	1,50	0,292
553	27,9	27,4	25,7	20,7	16,1	12,0	10,2	6,01	1,52	0,319
568	29,6	28,9	26,3	21,6	16,9	13,0	11,1	6,80	1,58	0,340
583	31,0	30,3	28,2	22,6	17,6	13,8	11,6	7,11	1,62	0,358
598	32,5	31,4	28,5	23,3	18,3	14,5	12,5	7,39	1,70	0,387
612	33,8	32,7	30,0	24,0	19,0	14,9	13,1	7,67	1,82	0,418
627	34,8	33,6	30,6	24,5	19,6	15,3	14,0	7,90	1,83	0,430
642	36,2	34,3	30,9	24,9	19,9	15,8	14,2	8,01	1,83	0,431
656	36,9	35,1	31,7	25,2	20,3	15,8	14,4	8,11	1,85	0,440
672	37,2	35,8	32,0	25,3	20,6	16,0	14,6	8,11	1,90	0,442
686	37,2	36,1	32,3	25,4	20,6	16,1	14,6	8,13	1,84	0,441
701	37,2	36,1	32,3	25,4	20,7	16,0	14,6	8,06	1,80	0,434
716	37,8	35,9	32,3	25,3	20,6	15,8	14,5	7,92	1,79	0,422
730	37,8	35,7	32,3	25,1	20,3	15,6	14,4	7,90	1,70	0,414
745	37,6	35,2	31,9	24,6	19,9	15,4	14,3	7,66	1,68	0,390

Table 2. Values of the specific conductivity (ohm^{-1} cm^{-1}) interpolated at the identical temperatures, of molten $BiBr_3$-$CdBr_2$ mixtures.

X_{CdBr2}	0,14	0,29	0,38	0,50	0,61	0,68	0,79	0,89
T K								
750	0,528							
755	0,540	0,726						
765	0,544	0,734						
770	0,544	0,736	0,766					
775	0,546	0,740	0,770					
785	0,546	0,750	0,774	0,844				
790	0,547	0,751	0,776	0,848				
799	0,546	0,748	0,786	0,858				
809	0,545	0,750	0,790	0,868	1,01			
814	0,542	0,746	0,791	0,870	1,02			
824	0,536	0,741	0,796	0,876	1,04	1,06	1,11	1,08
834	0,528	0,738	0,798	0,886	1,05	1,08	1,13	1,10
839	0,524	0,736	0,799	0,890	1,06	1,08	1,13	1,12
849	0,519	0,733	0,800	0,900	1,07	1,09	1,15	1,13
859	0,512	0,728	0,800	0,910	1,09	1,11	1,17	1,15
869	0,509	0,726	0,799	0,917	1,10	1,12	1,19	1,17

Discussion

Experiments on binary mixtures in which at least one component undergoes a change in sign of the temperature coefficient of conductivity show that the conductivity as a function of composition does not differ substantially in the regions of negative and positive signs of the temperature coefficient of conductivity. One encounters here usual positive, negative or mixed deviations of the specific electric conductivity form additivity.

In mercuric bromide the equilibrium

$$2\,HgBr_2 = HgBr_3^- + HgBr^+$$

is considerably shifted to the left in view of the order of magnitude of the specific electric conductivity of $HgBr_2$ (10^{-4} Ω^{-1} cm^{-1}). This and the relative closeness of the maximum of conductivity 733 K to the melting point 491 K show that $HgBr_2$ is of molecular character.

In contrast to this, $CdBr_2$ has ionic properties. This is pointed out by the order of magnitude of its

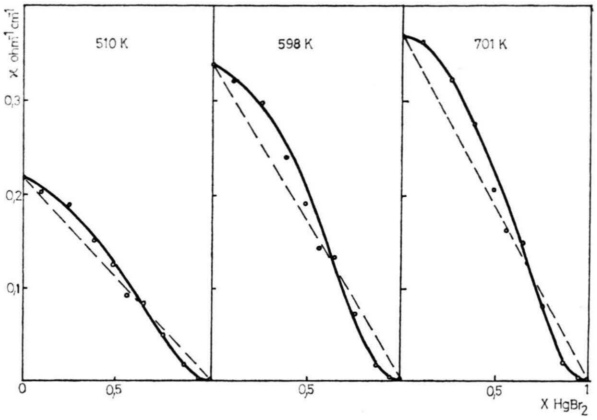

Fig. 1. Dependence of the specific conductivity on the composition of the molten $BiBr_3$-$HgBr_2$ system.

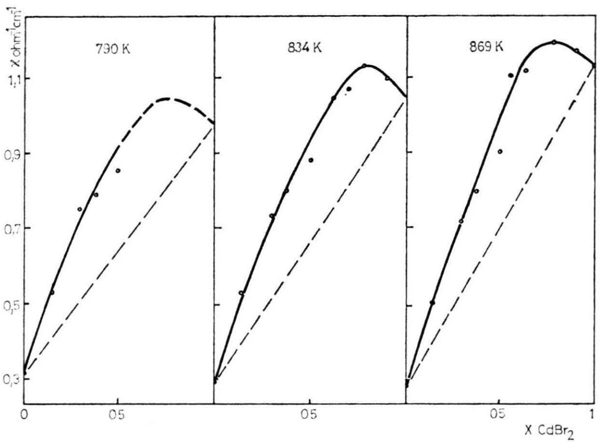

Fig. 2. Dependence of the specific conductivity on the composition of the molten $BiBr_3$-$CdBr_2$ system.

conductivity ($1\ \Omega^{-1}\ cm^{-1}$) as well as by the large distance of the temperature maximum of conductivity from the melting point. Therefore it may be assumed that the degree of dissociation according to the equation

$$CdBr_2 = CdBr^+ + Br^-$$

has a value close to unity. In addition, the heats of evaporation ($Q_{CdBr_2} = 102{,}9$ kJ/mole and $Q_{HgBr_2} = 69{,}6$ kJ/mole) [13] indicate the ionic character of $CdBr_2$.

As regards $BiBr_3$, it is of transitional character. Its low melting point (491 K) and boiling point (726 K) speak in favour of it's molecular character. However the relatively high conductivity (lower by only one order of magnitude than that of purely ionic salts) indicates a considerable dissociation according to

$$BiBr_3 = BiBr_2^+ + Br^- .$$

The subsequent dissociations

$$BiBr_2^+ = BiBr^{2+} + Br^-$$

and

$$BiBr^{2+} = Bi^{3+} + Br^-$$

are less probable, as are dissociations into polybasic acids and bases in general.

The behaviour of the systems investigated can be explained on the basis of the above considerations of the properties of the components.

In the $BiBr_3$-$HgBr_2$ system (Fig. 1), the negative deviations of conductivity in the $HgBr_2$-rich region may be explained by a suppression of dissociation of the electrolyte which is added in small quantities to the electrolyte where the existence of a large number of ions is not permitted. Namely, the added $BiBr_3$ would increase the degree of dissociation of $HgBr_2$ because of the possibility of ion exchanges

$$BiBr_2^+ + HgBr_2 = BiBr_3 + HgBr^+ \quad \text{and}$$
$$BiBr_4^- + HgBr_2 = BiBr_3 + HgBr_3^- .$$

Because of the domination of the properties of $HgBr_2$, the excess of ions is removed according to the equations

$$HgBr^+ + HgBr_3^- = 2\,HgBr_2 ,$$
$$BiBr^{2+} + HgBr_3^- = BiBr_3 + HgBr_2 .$$

In the composition region rich in $BiBr_3$, which allows the existence of a relatively large number of ions, an increase occurs in the degree of dissociation of $HgBr_2$ in analogy with an increase in the degree of dissociation of a weak electrolyte due to dilution. This leads to a positive deviation from additivity. The increase of temperature does not change the type of deviation of the specific electric conductivity from additivity.

In the $BiBr_3$-$CdBr_2$ system (Fig. 2) there is no monotonous change in conductivity from the properties of one component to those of the other component as in the preceding system. Namely, in a certain composition region the specific electric conductivity is larger than that of the pure components. The positive deviations of conductivity from additivity might be explained by an increase of dissociation of the weaker electrolyte in the stronger one. However, as the temperature increases the tendency appears of negative deviations in the $BiBr_3$-rich composition region. This occurs because, as the temperature increases up to a certain limit, the conductivity of bismuth bromide begins to decrease, whereas the conductivity of cadmium bromide further increases, hence the system becomes qualitatively similar to the BiI_3-HgI_2 system [8] at lower temperatures. It has also been observed that the maximum of specific conductivity is shifted to larger mole fractions of cadmium bromide as the temperature increases. This may be explained by the fact that the internal pressure of cadmium bromide (which decreases more slowly with temperature than that of bismuth bromide) predominates in the mixture.

If we compare the dependencies of the specific conductivity on molar composition for the iodides [8] and bromides (the present work) of mercury, bismuth and cadmium, we see that positive deviations of conductivity from additivity considerable predominate in the systems of iodides. Also in a work of Grantham [3] it has been found that the positive deviation of conductivity from additivity is more pronounced in the HgI_2-Hg_2I_2 system than in the $HgCl_2$-Hg_2Cl_2 system. It is evident that an explanation of these differences should be sought in the magnitude of the ionic radii of the anions. It is interesting to consider in this respect the super ionic conductivity of crystalline silver iodide [14—17], $RbAg_4I_5$ [18—20] and KAg_4I_5 [21]. Super ionic conductivity has not been observed in analogous systems of chlorides and bromides in which the ratio of anionic to cationic radius is smaller than in the iodides.

Therefore the tendency toward positive deviations of conductivity of binary systems of iodides with respect to bromides and chlorides is to be attributed to the looser structure of molten iodides due to the large ratio of anionic to cationic radius.

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