The Electrical Conductivity of Molten (Ag, $Cd_{1/2}$)Br

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Z. Naturforsch. **56 a,** 751–753 (2001); received August 20, 2001

Presented at the NATO Advanced Study Institute, Kas, Turkey, May 4 - 14, 2001.

The electrical conductivity of molten (Ag, $Cd_{1/2}$)Br has been determined as a function of temperature in the whole range of compositions. The resulting activation energy values and the conductivity isotherm at 850 K are compared with those of the system (Ag, $Cd_{1/2}$)Cl.

Key words: AgBr; $CdBr_2$; Molten Salts; Electrical Conductivity.

1. Introduction

Solid silver chloride and silver bromide, like most of the alkali metal halides, have rocksalt-type structure with regular octahedral coordination between unlike ions. However, at elevated temperature silver halides exhibit an increasing disorder in the solid state, which results in a rapid increase of the ionic conductivity at about 150 K [1] and 100 K [2] below the melting point in AgCl and AgBr, respectively. Neutron diffraction measurements of AgBr [3, 4] show an increasing number of Ag^+ ions occupying interstitial tetrahedrally coordinated positions as the melting point is approached. In liquid AgCl and AgBr [3 - 5] the average coordination number between unlike ions falls to around four from the rocksalt-type structure value of six, while six is retained by the alkali metal halides on melting. A recent investigation of molten AgBr by anomalous X-ray scattering coupled with neutron diffraction [6] has confirmed that the average local symmetry of Br^- remains octahedral [3, 4], while Ag^+ ions occupy both octahedral and tetrahedral positions.

Solid cadmium chloride and cadmium bromide have a layer structure containing octahedrally coordinated Cd^{2+} and triply coordinated halide anion. According to Raman spectroscopic studies of pure molten $CdCl_2$ and $CdBr_2$ [7] the octahedral coordination of Cd^{2+} is retained in the liquid state, although in the case of the bromide also lower coordination numbers are stable. In mixtures with alkali metal halides, Cd^{2+} ions have tetrahedral coordination. The conductivity of the molten cadmium halides increases with pressure [8], unlike that of fully ionised molten salts. This was attributed to an increase in the concentration of cadmium ions and halide ions caused by dissociation of complex ions or molecules present in the melts at atmospheric pressure.

The electrical conductivity of the pure molten silver halides is very high [9]. At the respective melting points the values for AgCl and AgBr are close to those for the typical ionic compounds NaCl and NaBr, respectively [10]. Similarly, the electrical conductivity of pure molten cadmium chloride or bromide is about as high as that of calcium, strontium or barium halides at the respective melting points [10].

In this paper we present the electrical conductivity of the molten system (Ag, $Cd_{1/2}$)Br and compare it with that of (Ag, $Cd_{1/2}$)Cl [11, 12].

2. Experimental

AgBr was precipitated from a dilute aqueous solution of $AgNO_3$ with a 1 M solution of KBr and then carefully washed, dried and melted in an electric furnace. Anhydrous $CdBr_2$ was obtained from $CdBr_2 \cdot 4\,H_2O$, using NH_4Br as a water removing carrier, and purified by vacuum distillation. For details of the preparation of the salts see [13].

The mixtures were melted in silica ampoules sealed under vacuum. Weighing, handling and transfer of

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Table 1. Least squares regression analysis of electrical conductivity data for molten $CdBr_2$-AgBr mixtures.

Composition x_{AgBr}	Temp. range K	$\ln \sigma^\circ$ $\ln(\Omega^{-1}m^{-1})$	E_a/R K	s $\ln(\Omega^{-1}m^{-1})$
0.020	839 - 998	6.1982	1336.10	0.0016
0.050	840 - 930	6.2196	1328.01	0.0019
0.070	814 - 990	6.2475	1230.68	0.0020
0.200	812 - 978	6.1729	1088.75	0.0014
0.400	794 - 933	6.2872	1086.05	0.0035
0.600	720 - 921	6.1961	767.71	0.0028
0.750	723 - 922	6.2415	656.87	0.0029
0.850	724 - 894	6.2902	574.38	0.0018
0.920	732 - 968	6.1902	460.57	0.0031
0.960	712 - 930	6.1571	429.65	0.0028

all samples containing AgBr were conducted under safelight.

The conductivity measurements were performed using AC techniques. Capillary-type conductance cells, made of silica glass, with platinum electrodes were used [14]. They were calibrated with a standard aqueous solution of potassium chloride (71.1352 g KCl/1000 g of the solution [15, 16]). The cell constants were between 22784 and 54698 m^{-1}. A new cell was used for every sample.

About 20 g of the salt mixtures were heated in the conductivity cell in an electric furnace in argon atmosphere. The temperature was gradually raised above the melting point of the salts. Conductivity measurements began as soon as the electric contact was obtained. They were carried out during several cycles of heating and cooling. The heating and the cooling rates did not exceed 1 K per minute. Due to the large values of the cell constants, the electrical resistance of the fused mixtures was high, between 130 Ω and 240 kΩ.

The conductance was measured with a Taccusel CD 810 conductometer. The frequency dependence was checked in the range from 62.5 Hz to 16 000 Hz and was found to be negligible. Measurements were thus taken at 1000 Hz. The temperature was measured with an accuracy of ±1 K by means of a platinum / platinum rhodium thermocouple. Data acquisition and analysis were controlled with a computer, the software of which developed expressly for this type investigation.

3. Results

The electrical conductivity σ / (S m^{-1}) of ten $CdBr_2$-AgBr molten mixtures has been determined as a function of temperature T/K in the range from a few degrees above the liquidus temperature [13] to about 900 K or higher (Table 1). An Arrhenius-type equation

$$\sigma = \sigma^\circ \exp(-E_a/RT)$$

was fitted to the results of the measurements. σ°/(S m^{-1}) and E_a/(kJ mol^{-1}) were calculated by the method of least squares. Respective values of $\ln \sigma^\circ$ and E_a/R, as well as s, the standard error of estimate of $\ln \sigma$ are listed in the Table 1.

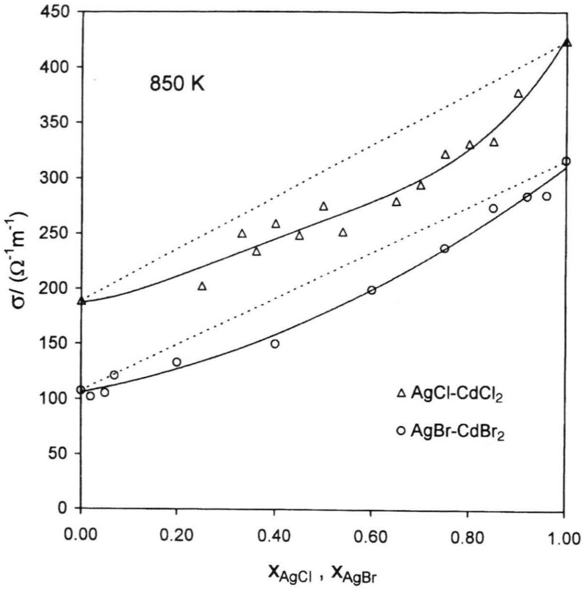

Fig. 1. Conductivity isotherms at 850 K for molten $CdBr_2$-AgBr (this work) and $CdCl_2$-AgCl [12]; data for pure molten AgBr, $CdBr_2$ and $CdCl_2$ from [9] and those for pure molten AgCl from [11].

4. Discussion

The electric conductivity at 850 K versus composition for AgBr-$CdBr_2$ [this work] and AgCl-$CdCl_2$ [12] is presented in Figure 1. Data for the pure molten AgBr, $CdBr_2$ and $CdCl_2$ were taken from the NIST Molten Salts Database [9] and those for the pure molten AgCl from [11].

The conductivity values at 850 K for the system (Ag, $Cd_{1/2}$)Br are lower than those for the system (Ag, $Cd_{1/2}$)Cl [12] as it could be expected from the lower mobility of the heavier bromide anion [10].

Both isotherms are typical for binary molten salt solutions showing negative deviations from additivity.

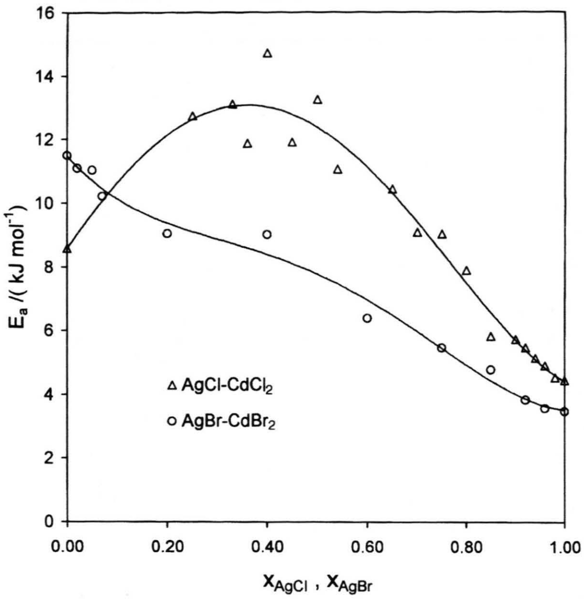

Fig. 2. Activation energy of conduction for molten $CdBr_2$-AgBr (this work) and $CdCl_2$-AgCl [11, 12]; data for pure molten AgBr, $CdBr_2$ and $CdCl_2$ from [9], and those for pure molten AgCl from [11].

The decrease in conductivity on addition of cadmium ions is sharper in the case of AgCl than in the case of AgBr.

If we adopt the dynamic dissociation model presented by Okada and his co-workers [17, 18] we find that Cd^{2+} will slow down the motion of Ag^+ because the cadmium ion interacts stronger with the halide ion than the silver ion. It is known from a neutron diffraction study [5] that with increasing temperature the relative motion between the neighbouring cation and anion becomes much larger in liquid AgCl than in liquid AgBr. Hence, the conductivity of silver bromide is less affected by addition of Cd^{2+} ions than that of silver chloride.

The activation energy for the conduction of the molten (Ag, $Cd_{1/2}$)Br system (Fig. 2) is rising regularly with the $CdBr_2$ content and does not show a maximum like in the (Ag, $Cd_{1/2}$)Cl system, where the tendency to form complexes seems to be stronger.

The activation energy for conduction of molten chlorides is usually lower than that of molten bromides [9] whereas in the case of AgCl and AgBr it is heigher. Therefore the activation energy curves for (Ag, $Cd_{1/2}$)Br and (Ag, $Cd_{1/2}$)Cl cross each other. This peculiar behaviour of AgBr and AgCl is consistent with the faster increase of the defect concentration in AgBr than in AgCl below the melting point where the silver bromide is close to transforming to the superionic state [4]. It would be interesting to study the mobility isotherms of these two binary systems.

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