Electrical Conductivity of Molten Cobalt Dibromide + Potassium Bromide Mixtures

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Electrical conductivities of $CoBr_2$ and $CoBr_2$ (1) + KBr (2) mixtures in the whole range of compositions were measured as a function of the temperature by the conductometric method. Parameters of an Arrhenius-type equation, preexponential factors and activation energies for conduction of molten salts, calculated with the least-squares method are given. The electrical conductivity of the molten $CoBr_2$, reported here for the first time, shows a high value of activation energy of (30.90 ± 0.52) $kJ\cdot mol^{-1}$, decreasing on addition of KBr, probably due to disruption of a network structure of the pure molten cobalt dibromide. Comparing the conductivity isotherms at 1100 K for the molten systems $CoCl_2$ (1) + KCl (2) and $CoBr_2$ (1) + KBr (2), one notes that that of the $CoCl_2$ (1) + KCl (2) system is rather regular, whereas in the $CoBr_2$ (1) + KBr (2) system a significant drop of conductivity is observed at $x_1 = 0.333$. This last may indicate the formation of the complex ions $CoBr_4^{2-}$ in the liquid mixture in the course of melting of the compound K_2CoBr_4.

Introduction

Molten cobalt(II) halides and their solutions in molten salts were in the past a subject of a number of works. However, for the most part, studies have focused on the chloride systems (e.g., refs 1−12). Works involving cobalt(II) bromide are rather rare.[13−17] To our knowledge, neither the electrical conductivity of the pure $CoBr_2$ nor those of the $CoBr_2$ (1) + KBr (2) mixtures have been reported. In this work, we measured electrical conductivity of $CoBr_2$ and of $CoBr_2$ (1) + KBr (2) mixtures at high temperature with the purpose to obtain data concerning phase transitions and transport properties in this system.

It is generally accepted that electrical conductivity of molten salt systems is often influenced by the formation of complexes (e.g., ref 18). Inman et al.[19] showed that in an electric field Co^{2+} migrates toward the anode, indicating the presence of a strong, negatively charged chlorocobalt complex ion in molten salts. The existence of a tetrahedral unit $CoCl_4^{2-}$ in molten pure cobalt(II) chloride was shown by X-ray difraction analysis by Takagi and Nakamura.[20]

On the other hand, it is well-known that cobalt(II) halides crystallize with the $CdCl_2$ or CdI_2 layer structures, in which cobalt(II) ions are octahedrally coordinated.[21] The change in the coordination symmetry around the Co(II) ion, from octahedral in the solid state to tetrahedral in the molten state, was observed by Trutia and Musa[14] in the pure cobalt(II) chloride and cobalt(II) bromide on the basis of absorption spectra (visible) as well as by Mulak[22] on the basis of measurements of the magnetic susceptibility.

In liquid mixtures of cobalt(II) chloride or cobalt(II) bromide with alkali halides, the existence of four-coordinated complexes $CoCl_4^{2-}$ or $CoBr_4^{2-}$ has been revealed based on thermodynamic[3−5,8,10,23−25] and spectroscopic investigations.[1,2,13,26,27] These kinds of complexes are usually stabilized in the alkali halide-rich melts while a network-like structure of the pure molten cobalt(II) halide dominates the structure of liquid mixtures rich in cobalt(II) halides.[28]

Our previous investigations[29] involved the $CoCl_2$ (1) + KCl (2) system, of a similar type. In this system, we observed on the plot of the activation energy for conduction a distinct local minimum at about $x_1 \approx 0.75$ and a clear local maximum at about $x_1 \approx 0.60$. The decrease of activation energy was probably due to a process of destruction of the primary $CoCl_2$ structure induced by the addition of another salt. The maximum of activation energy might arise from formation of chlorocobaltate complexes. Occurrence of similar effects could be expected in the $CoBr_2$ (1) + KBr (2) system.

Experimental Section

Conductivity measurements of salt mixtures were performed in capillary-type conductivity cells[30,31] with platinum electrodes. The temperature was measured using a Pt/Pt,Rh thermocouple, fixed close to the capillary. The cells were calibrated with a standard aqueous solution of potassium chloride (71.1352 g of KCl/kg of the solution).[32,33] The cell constants were between 18737 m^{-1} and 60765 m^{-1}.

Mixtures of salts were obtained beforehand from suitable amounts of anhydrous KBr and $CoBr_2$ (analytical grade). The components were placed in quartz tubes, heated under vacuum until they melted, and next kept at high temperature about 24 h in order to get homogenized.

Solidified mixture was put into the conductivity cell, which was then evacuated, filled with argon, and heated. Every mixture was put into a new conductivity cell. The measurements were begun after melting when the investigated mixture filled up the capillary and made an electrical contact between the platinum electrodes. Several cycles of heating and cooling were performed for each mixture in the range of temperature generally between 550 K and 1130 K. Heating and cooling rates used did not exceed 1 $K\cdot min^{-1}$.

Electrical conductivity was measured using a conductometer CDM 230 radiometer. The applied ac frequency was set automatically between (94 and 46 900) Hz, depending on the value of the resistance measured. Conductivity and temperature were simultaneously registered by a computer every 10 s. A

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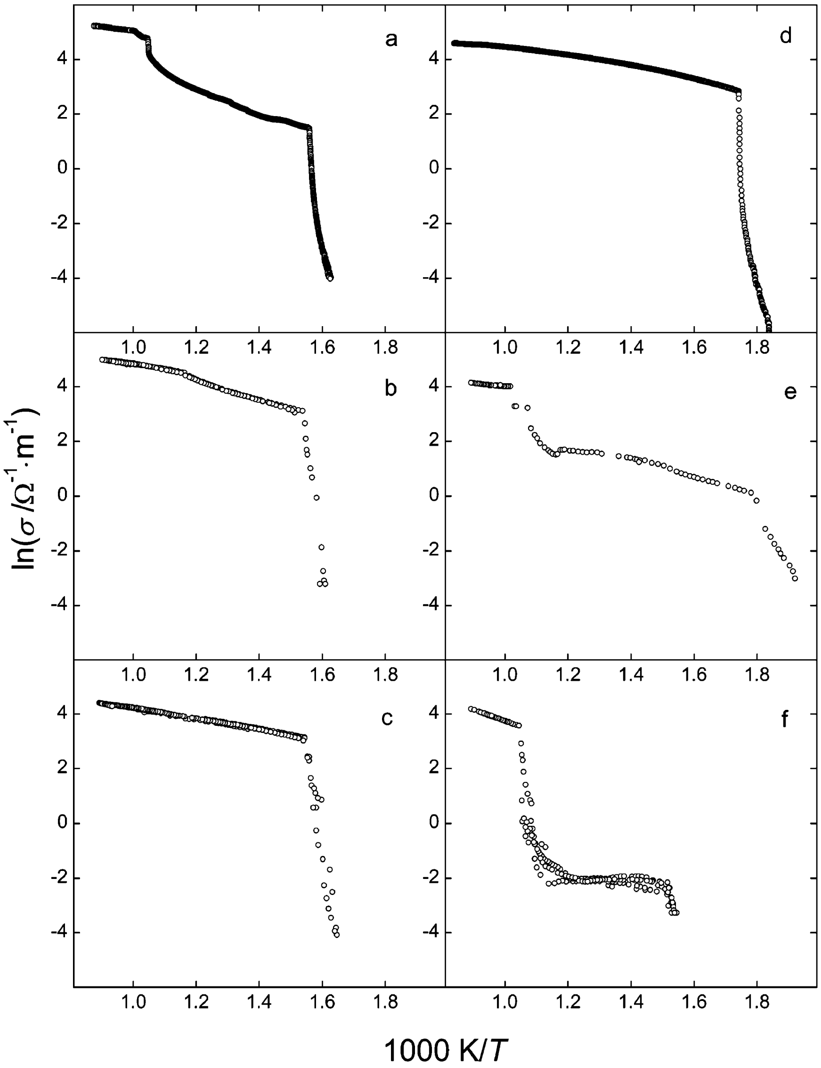

Figure 1. (a−f) Examples of conductivity curves for $CoBr_2$ (1) + KBr (2) mixtures; mole fraction of cobalt dibromide: $x_1 = 0.100$ (a), $x_1 = 0.272$ (b), $x_1 = 0.333$ (c), $x_1 = 0.445$ (d), $x_1 = 0.931$ (e), $x_1 = 1.000$ (f).

part of runs of the electrical conductivity measurements were performed using an ac bridge at 5000 Hz.[31,34] In this case, the dependence of the conductance on frequency in the range from (1 to 30) kHz was checked during each run and was found to be negligible. The electrical conductivities of molten $CoBr_2$ (1) + KBr (2) mixtures of a given composition are recorded in Table S1 (Supporting Information) as a function of temperature. The standard uncertainty in conductivity and temperature measurements was 1 % and 0.5 K, respectively; the standard uncertainty in composition was $u_c(x_i) = 0.0005$.

Results

The results of the experiments were processed by a computer program and presented as a natural logarithm of specific conductivity σ versus reciprocal of absolute temperature T. Examples of conductivity curves are presented in Figure 1, panels a to f. The discontinuities and kinks on the conductivity curves appear at solid/liquid-phase transitions and are discussed later.

For molten mixtures, the parts of conductivity curves that follow an Arrhenius temperature dependence:

$$\sigma = \sigma^0 \cdot e^{-E_a/RT} \tag{1}$$

were approximated with a linear function:

$$\ln \sigma = a - b \cdot 1/T \tag{2}$$

The parameters $a = \ln \sigma^0$ and $b = E_a/R$ and the standard deviation s of the function $\ln \sigma$, calculated with the least-squares method, are gathered in Table 1 where compositions of the mixtures, temperature ranges, and activation energy E_a are given. Parameters for molten KBr were calculated with the least-squares method based on the results of original conductivity measurements of Yaffe and Van Artsdalen[35] and recommended by Janz et al.[33]

Specific conductivity of the molten system $CoBr_2$ (1) + KBr (2) with the eutectic composition ($x_1 = 0.445$, according to Seifert and Al-Khudair[36]) does not satisfy the Arrhenius formula in the whole measured range of temperature. The activation energy strongly decreases with temperature (Table 1). In this case, to the results of the measurements in the range of (580 to 1180) K a quadratic function of temperature was fitted as well:

$$\sigma/\Omega^{-1}\cdot m^{-1} = -166.84 + 0.4061T/K - 1.535\cdot 10^{-4}(T/K)^2 \tag{3}$$

Original experimental data for molten $CoBr_2$ (1) + KBr (2) mixtures are provided in Table 1S (Supporting Information). For the pure molten cobalt(II) bromide, two independent sets of data (run 1 and run 2) giving similar results have been given. Results of calculations based on the run 1 have been included in Table 1 because of a larger temperature range involved.

Table 1. Parameters of Arrhenius Formula (ln $\sigma = \ln \sigma^0 - E_a/RT$) for Molten Mixtures $CoBr_2$ (1) + KBr (2)

x_1	ΔT K	$a = \ln(\sigma^0/\Omega^{-1}\cdot m^{-1})$	$\ln(s/\Omega^{-1}\cdot m^{-1})$	$b = E_a/R$ K	E_a kJ·mol^{-1}
0.000[a]	1010−1233	6.4383 ± 0.0985	0.0096	1354 ± 39	11.25 ± 0.32
0.100	1030−1135	6.6073 ± 0.0422	0.0034	1567 ± 10	13.03 ± 0.08
0.200	920−1155	6.4175 ± 0.0173	0.0056	1551 ± 4	12.89 ± 0.03
0.272	860−1100	6.6439 ± 0.0260	0.0160	1819 ± 26	15.12 ± 0.22
0.300	750−1140	6.6440 ± 0.0050	0.0287	1932 ± 5	16.06 ± 0.04
0.333	647−1122	6.1534 ± 0.0120	0.0279	1940 ± 10	16.13 ± 0.08
0.400	800−1110	7.1468 ± 0.0569	0.0272	2106 ± 54	17.51 ± 0.45
0.445	575−790	7.2526 ± 0.0134	0.0329	2482 ± 9	20.64 ± 0.07
	790−1150	5.7752 ± 0.0048	0.0182	1334 ± 5	11.08 ± 0.04
0.599	888−1120	6.2670 ± 0.0357	0.0241	1997 ± 35	16.60 ± 0.29
0.680	860−1130	6.0184 ± 0.0010	0.0051	1692 ± 1	14.06 ± 0.01
0.777	877−1121	6.8925 ± 0.0856	0.0751	2533 ± 86	21.06 ± 0.72
0.857	921−1120	6.5548 ± 0.0298	0.0205	2478 ± 31	21.62 ± 0.26
0.931	953−1121	7.2131 ± 0.0789	0.0282	3319 ± 81	27.60 ± 0.67
1.000	975−1121	7.4904 ± 0.0817	0.0183	3717 ± 63	30.90 ±0.52

[a] For KBr: according to ref 35.

Discussion

There are two forms of the phase diagram for the system $CoBr_2$ (1) + KBr (2) available in the literature.[36,37] The phase diagram of Saugier and Cohen-Adad[37] shows two compounds: K_3CoBr_5, melting incongruently at 652 K and K_2CoBr_4, decomposing in the solid state at 442 K. The phase diagram of Seifert and Al.-Khudair[36] shows only one compound, K_2CoBr_4, which undergoes a solid-state phase transition at (481 ± 10) K and melts, probably congruently, at 649 K. The solid compound K_2CoBr_4 was studied a number of times during the past decade (e.g., refs 38−40) mainly because of its ferroelectric properties.

Breaks on the conductivity curves presented in Figure 1 are generally consistent with phase equilibria.[36,37,41] For mixtures containing $x_1 = (0.100$ or $0.272)$ (Figure 1, panels a and b) the course of the conductivity changes at the liquidus temperature and decreases sharply at the eutectic temperature of 649 K. Only one drop is observed for a mixture having the stoichiometric composition (Figure 1c), corresponding to the compound K_2CoBr_4. This can be evidence that the compound melts congruently. However, its melting point is very close to the first eutectic point. The second eutectic point is at 581 K and $x_1 = 0.445$. One drop of the conductivity is observed for this eutectic mixture (Figure 1d) and two drops at the composition of $x_1 = 0.931$ (Figure 1e): the liquidus break which, in this case, corresponds to crystallization of cobalt dibromide, and the decrease at the eutectic temperature of 581 K. When we pass to the pure component, the conductivity of molten $CoBr_2$ decreases significantly when first crystals appear, but at a lower temperature, beginning from around 840 K it takes a practically constant value (about 10^{-1} $\Omega^{-1}\cdot m^{-1}$) and after that drops strongly below about 660 K (Figure 1f).

This last effect appears at the temperature of transformation reported by Wydeven and Gregory.[41] They observed an anomaly of the heat capacity of cobalt(II) bromide at about 650 K and suggested a phase transition in $CoBr_2$ from the CdI_2-type structure to a high-temperature modification with the $CdCl_2$-type structure. The results of our conductometric measurements also give a reliable evidence for the high-temperature phase transition in cobalt(II) bromide and confirm the existence of a high-temperature polymorphic form of $CoBr_2$.

In Figure 2, we compare the conductivity isotherms at 1100 K for the molten system $CoBr_2$ (1) + KBr (2) investigated here and for the molten system $CoCl_2$ (1) + KCl (2) investigated by us previously.[29] As a rule, the chloride system has higher conductivity than the bromide system, mainly due to a smaller size and a higher mobility of the Cl^- ion as compared with the Br^- ion.

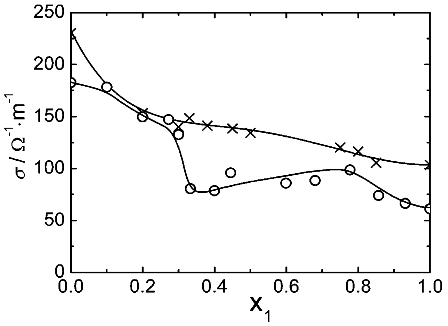

Figure 2. Comparison of conductivity isotherms of molten mixtures at 1100 K: ○, $CoBr_2$ (1) + KBr (2), this work; ×, $CoCl_2$ (1) + KCl (2), Wojakowska et al.[29]

Both isotherms show negative deviations from additivity, of about 20 % at the most. However, the isotherm is rather regular for the $CoCl_2$ (1) + KCl (2) system, whereas in the $CoBr_2$ (1) + KBr (2) an abrupt drop of conductivity is observed at about $x_1 = 0.333$. This last may indicate the formation of the complex ions $CoBr_4^{2-}$ in the liquid mixture in the course of melting of the compound K_2CoBr_4.[36] It seems that this might confirm the stability of the 4-fold coordination of divalent cobalt in the molten solution $CoBr_2$ (1) + KBr (2).

The isotherm for the $CoCl_2$ (1) + KCl (2) system is typical for molten salt solutions where faster ions (K^+) are hampered by slower ions (Co^{2+}) and slower ions are accelerated by faster ions (drag effect, according to Klemm[42]). Usually, the first effect is more visible. The drag effect is also observed in the $CoBr_2$ (1) + KBr (2) system, but the drop of conductivity after adding $CoBr_2$ to KBr is relatively small, while the rise of conductivity after adding KBr to $CoBr_2$ is quite significant. Thus in the ranges of composition between the pure KBr and $x_1 \approx 0.3$ as well as between $x_1 \approx 0.7$ and the pure $CoBr_2$, the run of the conductivity isotherm is not far from additivity.

In Figure 3 activation energies versus composition for the molten mixtures $CoBr_2$ (1) + KBr (2) and $CoCl_2$ (1) + KCl (2)[29] are compared. Molten $CoBr_2$, like molten $CoCl_2$, shows a high value of the activation energy for conduction. It may be related to a partial "network structure" of the melt[28] consisting of bridged $CoBr_4$ or $CoCl_4$ tetrahedra, respectively. We can expect a similar structure of both $CoBr_2$ and $CoCl_2$ in the molten state, if they have the same type of structure in the solid-state just before melting[43] (i.e., if we admit that a high-temperature modification of $CoBr_2$ has the $CdCl_2$-type structure).[41]

In the region rich in cobalt(II) halide, a strong drop of the activation energy is observed on addition of corresponding

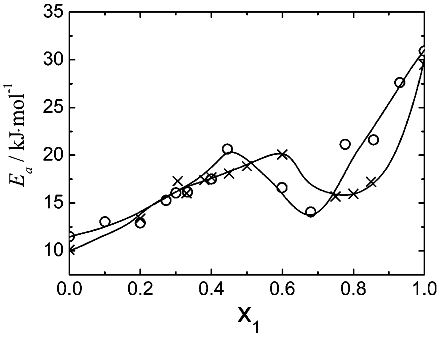

Figure 3. Comparison of activation energies for conduction of molten mixtures: ○, $CoBr_2$ (1) + KBr (2), this work; ×, $CoCl_2$ (1) + KCl (2), Wojakowska et al.[29]

potassium halides, probably due to the disruption of the network structure of the melt.[16] This effect is similar in both systems.

In the region rich in potassium halide, we observe a moderate increase of activation energy on addition of corresponding cobalt(II) halides, also similar in both system and among others probably related to formation of complexes. In the $CoBr_2$ (1) + KBr (2) system, at the eutectic composition of $x_1 = 0.445$ we observe a significant decrease of the activation energy with temperature (Table 1). This can indicate decomposition of complexes when temperature rises. However, the activation energy remains relatively high until about 200 K above the eutectic point. For mixtures richer in $CoBr_2$ than the eutectic composition, the activation energy begins to fall. Similarly, in the $CoCl_2$ (1) + KCl (2) system the activation energy decreases, but only for x_1 larger than about 0.6. Above these limits, stability of complexes probably becomes lower.

Phase equilibrium diagrams indicate one compound, K_2CoBr_4 in the $CoBr_2$ (1) + KBr (2) system,[36] and two compounds, K_2CoCl_4 and $KCoCl_3$ in the $CoCl_2$ (1) + KCl (2) system.[44] Therefore, we can expect that in the respective molten mixtures, the appropriate chloride complexes will be stable at higher concentrations of cobalt dihalide than bromide complexes. On the other hand, in molten salt mixtures we cannot expect drastic changes in the electrical conductivity or activation energy versus composition because generally several complex ion forms may exist in equilibrium.

Conclusions

Electrical conductivity of $CoBr_2$ (1) + KBr (2) molten mixtures shows negative deviation from additivity, especially around $x_1 = 0.333$ where formation of the complex $CoBr_4^{2-}$ can be expected on the basis of the phase diagram. At higher concentration of divalent cobalt the complex becomes less stable, especially at higher temperature.

A drag effect in solutions rich in KBr is surprisingly low, in contrast to solutions rich in $CoBr_2$, where an increase of the electrical conductivity as well as an important decrease of activation energy are observed on addition of potassium ions. Arrhenius parameters for the conductivity of the pure molten cobalt(II) bromide are similar to those for the pure molten cobalt(II) chloride, although the activation energy for conduction is a little higher for the bromide. Electrical conductivity measurements in the solid state give proof of existence of a high-temperature polymorphic modification of the solid $CoBr_2$.

Supporting Information Available:

Measured electrical conductivities of molten $CoBr_2$ (1) + KBr (2) mixtures of a given composition as a function of temperature (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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