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THERMODYNAMICS AND PHASE EQUILIBRIUM STUDIES OF SILVER HALIDE–COBALT(II) HALIDE SYSTEMS

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Phase diagrams for the systems AgCl–$CoCl_2$ and AgBr–$CoBr_2$ were determined by differential scanning calorimetry. The systems are of the eutectic type. Eutectic points are at 271±2 K, 19.5 mol% $CoCl_2$ and 653±2 K, 17.0 mol% $CoBr_2$, respectively. The solid solubility does not exceed 2 and 4 mol% in the systems AgCl–$CoCl_2$ and AgBr–$CoBr_2$, respectively. Thermodynamic activities of components in molten mixtures and molar free enthalpies of mixing were determined for both systems on the basis of liquidus curves. Deviations from ideality were not found to be considerable.

Keywords: *AgBr, AgCl, $CoBr_2$, $CoCl_2$, DSC, phase diagram*

Introduction

Studies of thermodynamics and phase equilibria are of primary importance in the search for new materials having interesting properties [1–6]. Knowledge of phase diagrams is necessary for many applications. For instance, in preparation of cobalt dichloride graphite compounds by intercalation of $CoCl_2$ from molten salts [7], the phase diagrams played a decisive role in the choice between the $CoCl_2$–NaCl and the $CoCl_2$–KCl systems. It is evident that the melt compositions and temperatures of the intercalation process were imposed by the phase diagram. Chemical reactions performed in molten salt mixtures, especially in low melting eutectics, allow to prepare some important materials like $CoAl_2O_4$ at a lower temperature than in solid-state reactions methods [8]. The study of the appropriate phase diagrams of the eutectic type is thus appreciable.

In this work, the phase diagrams for AgCl–$CoCl_2$ and AgBr–$CoBr_2$ systems have been completed and thermodynamic properties, based on the measured liquidus temperatures have been calculated. Literature data on these systems are very limited. Admittedly, both systems were supposed to be of the eutectic type [9] but no data besides the values of temperature and composition of the eutectic points were given.

Experimental

Anhydrous cobalt(II) chloride and anhydrous cobalt(II) bromide were obtained from the respective hexahydrates: $CoCl_2{\cdot}6H_2O$ (98%, Aldrich) and $CoBr_2{\cdot}6H_2O$ (99%, Aldrich). Silver chloride and silver bromide were precipitated from a dilute aqueous solution of $AgNO_3$ (reagent grade) with a solution of HCl or HBr, respectively. Then the product obtained was carefully washed, dried under vacuum and melted. Details of the preparation technique were reported in our previous works [10, 11].

Phase equilibria in the AgCl–$CoCl_2$ and AgBr–$CoBr_2$ systems were investigated by differential scanning calorimetry performed with a Mettler Toledo DSC 25 measuring cell with TC15 TA Controller. Basic software STAR^e Version 6.0 complemented by a few optional Mettler Toledo programs were used to carry out the measurements and to read the results. The calorimeter was calibrated with melting points of indium, tin, lead, zinc and aluminium.

Appropriate quantities of the components for DSC experiments were weighed on Mettler Toledo AT 261 balance (0.01 mg). The composition of samples was taken at intervals of around 2–3 mol% or less. Mixtures of salts were prepared under argon and red light, directly in small silica ampoules (6 mm in outer diameter and 14 mm in height), next used for DSC measurements. The total mass of a mixture was between about 20 and 145 mg. Ampoules were sealed under vacuum and heated in an electric furnace above the melting point of the respective cobalt dihalide. Then they were cooled slowly to 400 K and annealed during 24 h. The equilibrated samples were then cooled to room temperature.

DSC runs for all the samples were carried out with a heating rate of 2 and 5 K min^{-1} from room tem-

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perature to the liquidus temperature and with the same rate in the opposite direction. In some cases, heating and cooling curves were also taken with the rate of 20, 15, 1 or 0.4 K min^{-1}.

Results and discussion

Phase diagrams

The phase diagrams for the AgCl–$CoCl_2$ and AgBr–$CoBr_2$ systems determined in this study are presented in Figs 1 and 2.

Both systems are of the eutectic type. The temperature of the eutectic reaction was found to be 671.0±0.5 and 652.8±0.3 K in the AgCl–$CoCl_2$ and AgBr–$CoBr_2$ systems, respectively. The mole fraction of the cobalt dihalide corresponding to the eutectic point was found to be $x(CoCl_2)=0.195$ and $x(CoBr_2)=0.170$ for AgCl–$CoCl_2$ and AgBr–$CoBr_2$, respectively.

It should be noted that additional invariant equilibria appear on the phase diagrams: at 979 K (AgCl–$CoCl_2$) and at 637 K (AgBr–$CoBr_2$). They result from the polymorphic transitions of the pure components: $CoCl_2$ at 979 K [11] and $CoBr_2$ at 650 K [11–13]. The former is not far from the melting point of $CoCl_2$ (999 K [11]). The latter is quite close to the eutectic temperature in the AgBr–$CoBr_2$ system. That is why the thermal effects corresponding to the eutectic reaction and these involving the polymorphic transition of $CoBr_2$ are superimposed. This last was observed for samples containing more than 70 mol% $CoBr_2$. A few examples of DSC runs for mixtures rich in cobalt dibromide are shown in Fig. 3. Similar invariant equilibria: eutectic and metaeutectic, one close to another, were observed for instance in the $GeSe_2$–SnSe system [14].

In the range of composition between $x(CoBr_2)=0.715$ and $x(CoBr_2)=0.985$, the onset of overlapping peaks gives a rather constant value of 637.1±1.1 K, which has been ascribed to the invariant equilibrium involving polymorphic transition of $CoBr_2$. This effect being negligible below 70 mol% $CoBr_2$, the range of composition between $x(CoBr_2)=0.043$ and $x(CoBr_2)=0.703$ was considered for determining the eutectic temperature 652.8±0.3 K.

The compositions of the eutectic points were determined by two methods: extrapolation of two liquidus curves in each system to the appropriate eutectic invariance and plotting values of thermal effects of the eutectic reaction *vs.* mole fraction of one salt (the Tamman method [15, 16]). The maximal value of the thermal effect should appear at the

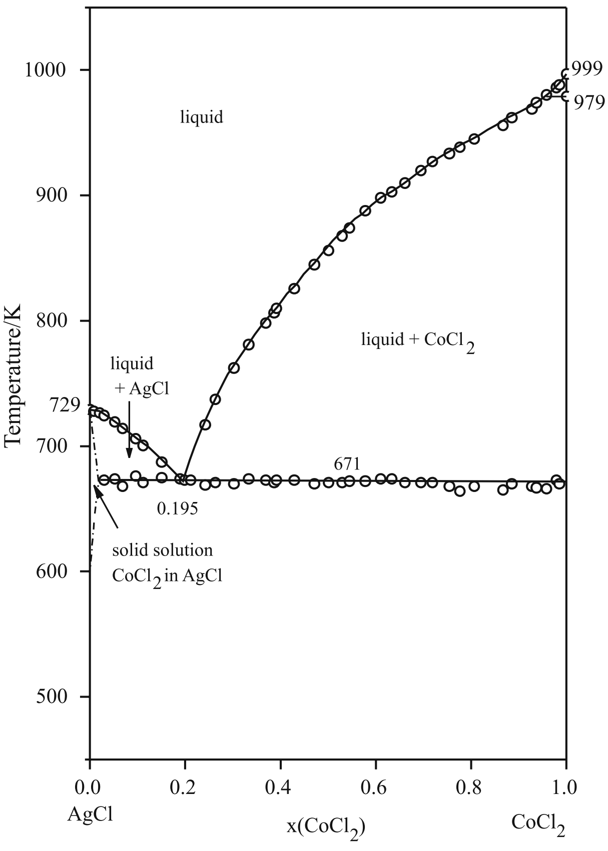

Fig. 1 Phase diagram of the AgCl–$CoCl_2$ system

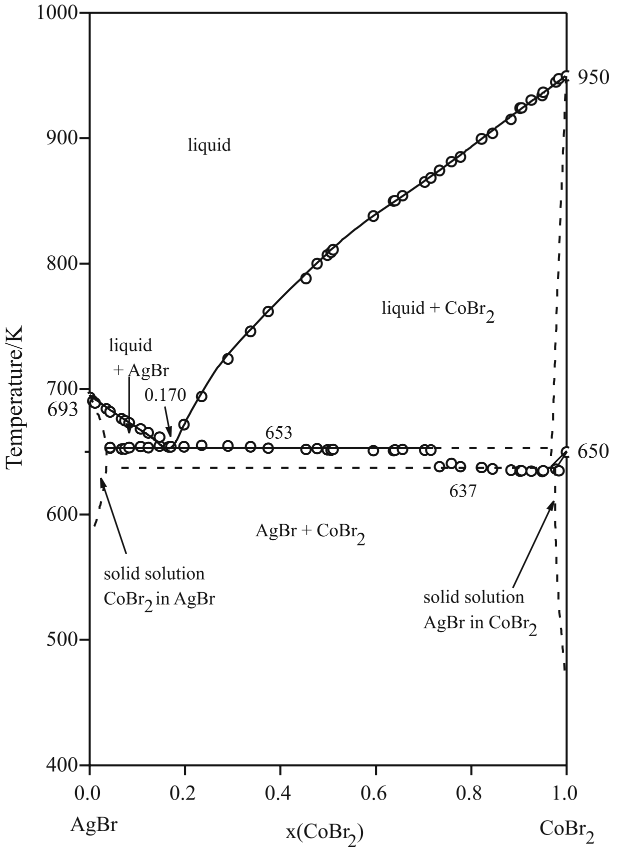

Fig. 2 Phase diagram of the AgBr–$CoBr_2$ system

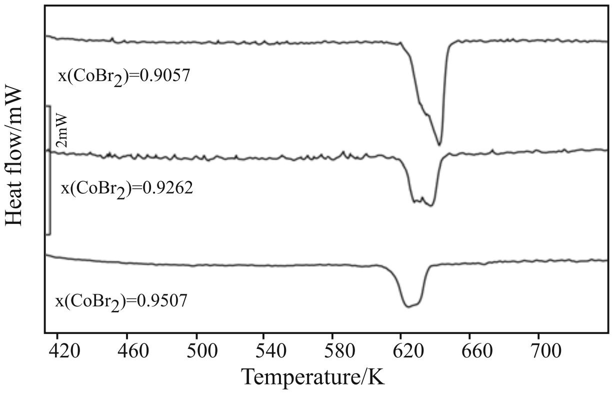

Fig. 3 Examples of DSC curves on the $CoBr_2$ rich side (heating rate of 5 K min^{-1}), showing overlapping peaks corresponding to the eutectic and solid-state transition

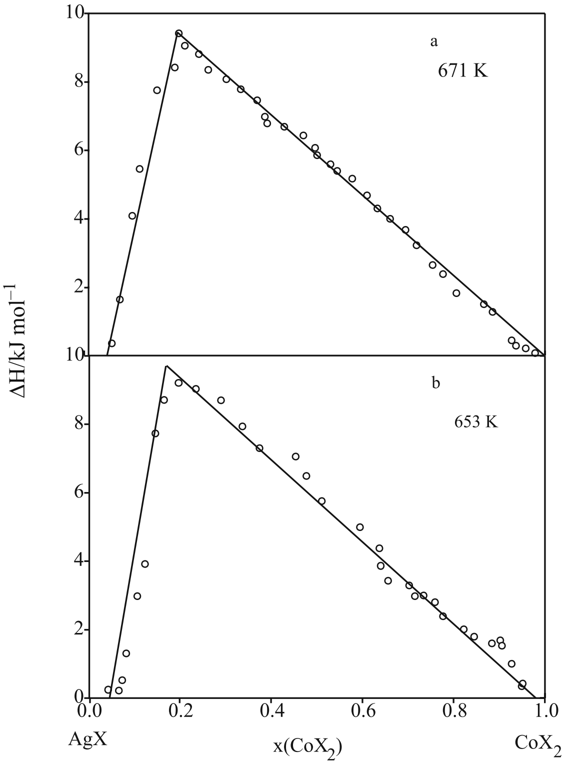

Fig. 4 Tamman triangles for the eutectic reactions: a – AgCl–$CoCl_2$ system; b – AgBr–$CoBr_2$ system

eutectic point. Tamman triangles obtained are presented in Fig. 4. Thermal effects used for construction of the Tamman triangle in the AgBr–$CoBr_2$ system (Fig. 4b) were considered as resulting merely from the eutectic event.

Limiting solid solutions in the AgCl–$CoCl_2$ and AgBr–$CoBr_2$ systems are not large. The thermal effect, corresponding to the eutectic reaction in the AgCl–$CoCl_2$ system, has been observed on DSC scans practically in the whole range of compositions, between $x(CoCl_2)=0.029$ and $x(CoCl_2)=0.985$ (Fig. 1). Hence limiting solid solution in this system do not exceed 2 mol% on either side. Limiting solid solutions in the AgBr–$CoBr_2$ system seem to be a little larger, but not exceeding 4 mol% (Fig. 2). These limits of solid solutions are also in agreement with values of intersection points of the respective edges of Tamman triangles with the abscissa (Fig. 4).

Thermodynamics of molten salt solutions

On the basis of liquidus curves, the thermodynamic activities of components in molten solutions of AgCl–$CoCl_2$ and AgBr–$CoBr_2$ systems have been calculated in the whole range of compositions. They are presented in Figs 5 and 6, respectively. The integral molar free enthalpies of mixing and the integral molar excess free enthalpies for both systems are shown in Fig. 7. Equations applied for the purposes of calculation of the thermodynamic properties were given in our previous papers [17–19]. Calculations were made assuming that limiting solid solutions are negligible.

Additional thermochemical data used in the calculations, i.e. values of the enthalpies of fusion and polymorphic transitions [11, 20, 21] as well as available heat capacity data for the respective phases as a function of temperature [20, 22, 23] are gathered in Table 1.

The knowledge of enthalpies of transition is more important than that of variation in heat capacity since the former have a relatively greater effect on the value of the free enthalpy of a substance. If nothing is known about the heat capacity of one or two phases involved in a liquid–solid or solid–solid phase transition, then the difference between respective molar heat capacities may be neglected without affecting most calculations too gravely [23].

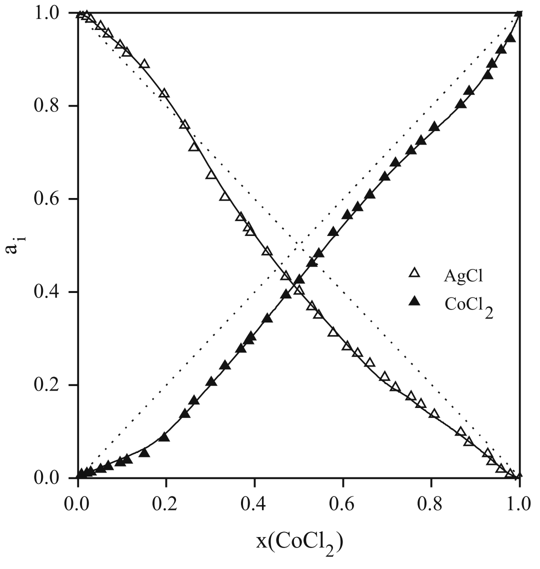

Fig. 5 Thermodynamic activities in the AgCl+$CoCl_2$ molten solutions

Table 1 Thermochemical data of the pure components

Component	Enthalpy of fusion or solid-state transition/kJ mol^{-1}	Ref.	$C_p=A+BT+CT^{-1}$/J mol^{-1} K^{-1}				Ref.
			Phase	A	B	C	
AgCl	$\Delta_{fus}H$=13.22	[20]	Liquid	57.30			[20]
			Solid	41.30	0.03323		
AgBr	$\Delta_{fus}H$=9.1365	[21]	Liquid	67.722			[22]
			Solid	–63.839	0.21402	5896762	
$CoCl_2$	$\Delta_{fus}H$=36.4 $\Delta_{tr}H$=9.6	[11]	Liquid	99.1610			[23]
			Solid				
			Solid	82.09	0.00674	–498000	
$CoBr_2$	$\Delta_{fus}H$=27.2 $\Delta_{tr}H$=0.18	[11,13]	Liquid				[23]
			Solid	92.05			
			Solid	73.39	0.02092		

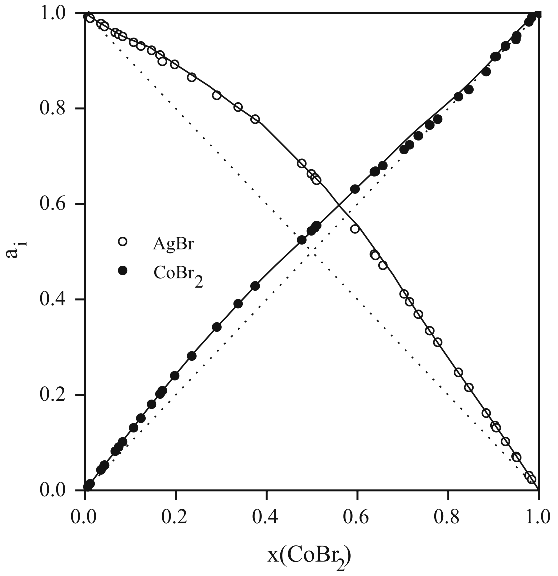

Fig. 6 Thermodynamic activities in the AgBr+$CoBr_2$ molten solutions

When the AgCl–$CoCl_2$ and AgBr–$CoBr_2$ systems are concerned, information on the heat capacity of the high-temperature solid form of $CoCl_2$ as well as that of liquid $CoBr_2$ is lacking (Table 1). Accordingly, in this work, the following assumptions have been made:

- the difference between the heat capacity of liquid $CoCl_2$ and that of the high-temperature solid form of $CoCl_2$ was assumed to be zero
- below the transition temperature of 979 K, the difference between the heat capacity of supercooled liquid $CoCl_2$ and that of the low-temperature solid form of $CoCl_2$ was used
- the difference between the heat capacity of liquid $CoBr_2$ and that of the high-temperature solid form of $CoBr_2$ was assumed to be zero

The polymorphic transition in $CoBr_2$ was not considered in the thermodynamic calculations for molten mixtures because, according to the phase diagram (Fig. 2), the low-temperature modification of $CoBr_2$ has no influence on liquid-solid equilibria in the AgBr–$CoBr_2$ system.

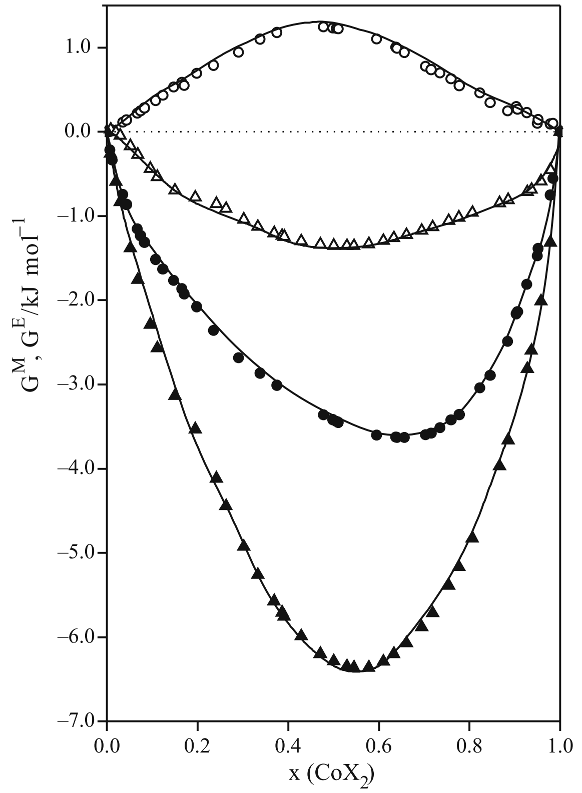

Fig. 7 Molar free enthalpy of mixing G^M for molten solutions: ▲ – AgCl+$CoCl_2$; ● – AgBr+$CoBr_2$. Excess molar free enthalpy G^E for molten solutions: Δ – AgCl+$CoCl_2$; ○ – AgBr+$CoBr_2$

Thermodynamic activities (Figs 5 and 6) and excess free enthalpies in the AgCl+$CoCl_2$ and AgBr+$CoBr_2$ molten mixtures (Fig. 7), calculated on the basis of the respective phase diagrams, do not indicate considerable deviations from ideality. The chloride system may be compared for instance with the alkali chloride – $CoCl_2$ systems [24, 25], where the above quantities reveal more pronounced negative deviations. They are only slightly different in the case of LiCl+$CoCl_2$ mixtures and rise with a higher ionic radius of the alkali cation.

It is rather common that for eutectic systems, thermodynamic properties of liquid mixtures do not show big deviations from the ideal solution behavior [26, 27]. The absolute value of the excess molar free enthalpy for molten solutions, observed in this work, is not higher than 1.4 kJ mol^{-1} (Fig. 7). However, despite a similarity of the phase diagrams (Figs 1 and 2), this excess free enthalpy was found negative for AgCl+$CoCl_2$ mixtures and positive for AgBr+$CoBr_2$ mixtures. Deviations from Raoult's law which can be seen on the activity plots (Figs 5 and 6) are for the most part negative in the chloride system (except for slightly positive deviations for AgCl activity in solution rich in AgCl), and positive for each component in the entire range of compositions in the bromide system.

Bromide systems generally reveal much tendency to positive deviations from ideal solutions, comparing with respective chloride systems, e.g. like in AgBr+$ZnBr_2$ and AgCl+$ZnCl_2$ [19]. It seems that this may be caused by easier formation of solid solutions owing to a bigger size of the bromide ion as compared with that of the chloride. In some cases, deviations from an ideal solution behavior in the bromide system may basically consist of entropy contributions whilst in the chloride system enthalpy contributions are dominating e.g. like in CuBr+NaBr and CuCl+NaCl [18].

Comparison of the free enthalpies with the corresponding enthalpy data can give information on the entropy of mixing. In contrast to the AgBr+$CoBr_2$ system, where enthalpy data are lacking, the molar enthalpies of mixing for the AgCl+$CoCl_2$ molten mixtures are available from calorimetric measurements of Papatheodorou and Kleppa [28]. They are presented in Fig. 8 together with the molar entropies of mixing, calculated from the enthalpy [28] and the free enthalpy data.

The absolute values of the molar enthalpies of mixing for the AgCl+$CoCl_2$ molten mixtures are small and similar to those found for weakly interacting molten salt mixtures e.g. LiCl+$CoCl_2$ [29]. They are negative on the silver chloride side and positive on the cobalt dichloride side.

Since negative excess enthalpies suggest formation of complexes in the mixture, existence of tetrahedral $CoCl_4^{2-}$ ions [30] might be expected in solutions rich in AgCl, but not as stable as in stronger interacting systems, for instance in NaCl+$CoCl_2$ or KCl+$CoCl_2$ [29]. Positive excess enthalpies on the $CoCl_2$ side may result from the breakdown of a partly covalent structure of molten $CoCl_2$ [30, 31].

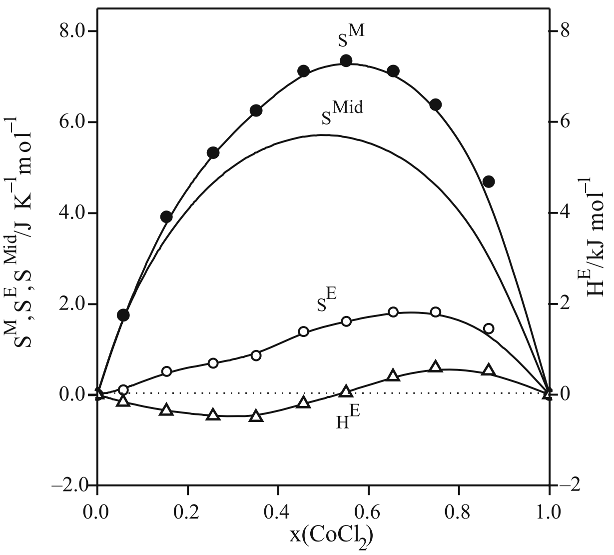

Fig. 8 Molar entropy of ● – mixing S^M and ○ – excess molar entropy S^E for molten solutions AgCl+$CoCl_2$ [this work]. Molar entropy of mixing for —– the ideal solution $S^{M,id}$. Molar enthalpy of mixing and Δ – excess molar enthalpy H^E for molten solutions AgCl+$CoCl_2$ [27]

The integral molar excess entropies S^E, plotted against mole fraction in Fig. 8, are compatible with the integral molar excess enthalpies H^E. Being positive in the entire range of compositions, they still follow the course of the enthalpy changes. A maximal value of 1.8 J K^{-1} mol^{-1} is situated on the $CoCl_2$ side.

It should be noted that this maximum of the molar excess entropy in the AgCl+$CoCl_2$ molten mixtures is about four times lower than that calculated in a similar way for the AgCl+$ZnCl_2$ molten mixtures [19]. This supports the results of Papatheodoru and Kleppa [31] that the covalent interactions are significantly larger in molten $ZnCl_2$ than in molten $CoCl_2$.

Conclusions

Thorough studies of phase equilibria have confirmed that both AgCl–$CoCl_2$ and AgBr–$CoBr_2$ systems are of the eutectic type [9] and, additionally, they corroborated the existence of high-temperature polymorphic modifications of $CoCl_2$ and $CoBr_2$, reported in [11, 13].

Limiting solid solutions have been estimated to be very narrow. However, some consistency with ionic sizes could be observed:

- because of a smaller ionic radius of Co^{2+} than of Ag^+, the solid solubility of the cobalt dihalide in the respective silver halide is a little higher than vice versa

- because of a higher ionic radius of Br^- than of Cl^-, limiting solid solutions in the $AgBr–CoBr_2$ system are a little larger than in the $AgCl-CoCl_2$ system.

Positive values of integral molar excess free enthalpy obtained for the $AgBr+CoBr_2$ molten mixtures in equilibrium with the solid phase may arise from entropy contributions whilst negative ones, obtained for the $AgCl+CoCl_2$ system probably result from enthalpy contributions. However, in view of relatively small deviations from ideal solution behavior, the $AgCl+CoCl_2$ and $AgBr+CoBr_2$ systems may be considered as rather weakly interacting systems.

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