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STUDIES OF PHASE EQUILIBRIA IN THE SYSTEMS $ZnCl_2$–AgCl AND $ZnBr_2$–AgBr

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Abstract

Phase equilibria in the systems zinc chloride – silver chloride and zinc bromide – silver bromide were investigated by differential scanning calorimetry, electric conductivity measurements and X-ray diffraction methods. No intermediate compounds were found. Solubility of components in the solid-state is negligible. Both systems are of the eutectic type. The eutectic temperatures in the $ZnCl_2$–AgCl system and in the $ZnBr_2$–AgBr system are 504 K and 551 K, respectively, and the compositions of the eutectic point are 53.5 mol% AgCl and 59.4 mol% AgBr, respectively.

Keywords: binary phase equilibrium diagram, silver bromide, silver chloride, zinc bromide, zinc chloride

Introduction

Zinc chloride and zinc bromide are very hygroscopic [1, 2] and reveal a glass-forming tendency [3–5]. For these reasons, investigation of phase equilibria in the systems involving zinc chloride and zinc bromide is very difficult. There is still a lack of reliable data, even in the case of some properties of the pure zinc halides. An example is existing of the polymorphism of zinc chloride and a value of its melting point.

At first, crystal structures of at least three modifications of zinc chloride were described [6]. However, they were next called into question [7, 8]. The explanation for formation of different structures was that zinc chloride was contaminated by water and a number of chloride ions was substituted by hydroxyl ions. Probably, the anhydrous zinc chloride has only one form. The structure can be regarded as orthorhombic, with tetrahedral zinc coordination in a close-packed chloride anion lattice.

For the melting point of zinc chloride given in literature, there are important differences even in recommended values, roughly between 548 K [1, 9] and 591 K

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[10, 11]. The disagreement may arise from easy supercooling of the liquid or from glass formation.

The aim of our work was to investigate the phase equilibria in the systems zinc chloride–silver chloride and zinc bromide–silver bromide by differential scanning calorimetry, electric conductivity measurements and X-ray diffraction methods, using high purity materials and a glove box for sample preparation.

To our knowledge, the phase diagram for the system AgBr–$ZnBr_2$ has not been reported. Liquid-solid phase equilibria in the $ZnCl_2$–AgCl system were studied only by the 'visual-polythermic' method by Glistenko and Artemova [12]. A possible eutectic reaction was indicated to be at 521 K. The reported value of the eutectic point composition (58% [12]) lacks consistency. The composition of the eutectic point after [12] was given later in [13] as 48 mol% $ZnCl_2$.

In the series Ternary Alloys [14] the only reference of the pseudobinary section $ZnCl_2$–AgCl of the ternary Ag–Cl–Zn system is the indirect reference to Glistenko and Artemova [12] as cited by Palkin and Shchirova [15]. Moreover, the phase diagram for the $ZnCl_2$–AgCl system in [14] shows a composition of the eutectic point to be 60 mol% $ZnCl_2$ while in [15] it is 60 equivalent % $ZnCl_2$ (43 mol% $ZnCl_2$). In the Ternary Alloys series [14] there is information about neither the ternary Ag–Br–Zn nor the binary $ZnBr_2$–AgBr systems.

Experimental

Preparation of salt mixtures

Mixtures were prepared from salts of high purity in a glove box Labmaster MBraun filled with dry helium gas and assuring less than 4 ppm H_2O and less than 1 ppm O_2.

Anhydrous zinc halides: $ZnCl_2$ (99.99%, Aldrich) and $ZnBr_2$ (99.99%, Aldrich) were commercial chemicals supplied as ball-shaped mass in sealed glass ampoules. After the ampoules were opened in the glove box, the salts were held therein it before further preparations of salt mixtures.

Silver halides were precipitated by dilute solution of hydrochloric or hydrobromic acid from dilute solution of silver nitrate (reagent grade). The preparation was performed under red light. The precipitate was washed with bi-distilled water and held in a vacuum dryer for a dozen of hours. Then it was heated in an electric furnace to melting, held about one hour at 770 K and cooled to room temperature. AgCl and AgBr thus obtained were stored in dark.

Mixtures were prepared by direct fusion of silver halide with the respective zinc halide in evacuated silica ampoules. The molar ratio of the mixtures was determined by accurately weighing their components in the glove box. The salts were introduced into fused silica ampoules, next sealed under vacuum. The mixtures of salts were then heated in an electric furnace to melting and homogenisation. After cooling to room temperature they were used for DSC examinations, electric conductivity measurements or X-ray diffraction experiments.

DSC measurements

Phase transitions studies were performed mainly with a Mettler Toledo differential scanning calorimeter: DSC 25 module with TC15 TA Controller. Basic software STARe Version 6.0 complemented by a few optional Mettler Toledo programs were used to carry out the measurements and to read the results.

Samples for DSC measurements were inserted, in the glove box, into small silica ampoules of 6 mm in outer diameter and 14 mm in height. The ampoules had a flat, polished bottom and were sealed under vacuum. An identical empty ampoule sealed under vacuum served as a reference. Sixty-one compositions were prepared for examination of phase equilibria.

At first, the DSC scans with a heating rate of 5 K min^{-1} for all compositions were made between 323 K and 773 K for the $ZnCl_2$–AgCl system and between 323 K and 723 K for the $ZnBr_2$–AgBr system. Then other heating or cooling cycles were carried out with rates of 0.5, 1, 2, 10 and 20 K min^{-1} in appropriate ranges of temperature.

Conductivity measurements

Conductivity measurements as a function of temperature were performed by AC techniques to check phase transitions in the systems under study. 14 samples were examined. Electrical conductivity was measured by a Radiometer Analytical conductivity meter CDM 230. The temperature was measured by means of a platinum/platinum rhodium thermocouple. Data acquisition and analysis were controlled with a computer.

Capillary-type conductance cells [16], made of silica glass, were loaded with a salt mixture, prepared beforehand and homogeneous. The cells were evacuated and filled with argon of high purity. They were next placed in an electric furnace and heated until the salt mixture melted and electric contact between the two fixed platinum electrodes was obtained. Conductivity measurements were then started and carried out during several cycles of heating and cooling within a suitable temperature range. The heating and cooling rates did not exceed 1 K min^{-1}. A new cell was used for every sample. They were calibrated with a standard aqueous solution of potassium chloride (71.1352 g KCl/1000 g of the solution [17]).

X-ray diffraction experiments

X-ray diffraction experiments were performed on a DRON type diffractometer with CoK_α radiation. Pure components and mixtures containing 20 and 80 mol% of silver halide were taken into account. Salts were weighed in the glove box and introduced first into silica ampoules, next sealed under vacuum. Mixtures thus obtained were homogenised by heating in an electric furnace to melting and then cooled slowly to room temperature. Samples for X-ray experiments were then prepared in the glove box and protected by silicon grease and plastic film during exposition. Diffractograms were taken at room temperature.

Results

Both systems: $ZnCl_2$–AgCl and $ZnBr_2$–AgBr (Fig. 1) are of the eutectic type. Only two thermal effects: one – corresponding to the liquidus and the other – corresponding to the eutectic reaction, are shown by DSC thermograms for the whole range of compositions. Thermal effects corresponding to the eutectic reaction are observed on DSC curves even for mixtures with compositions very close to the pure components. This proves that limiting solid solutions are negligible. The melting point of 587 K found for $ZnCl_2$ approaches to higher values given in literature (e.g. 591 K [10]). X-ray diffraction studies showed silver halide and zinc halide to be the only significant phases present at room temperature.

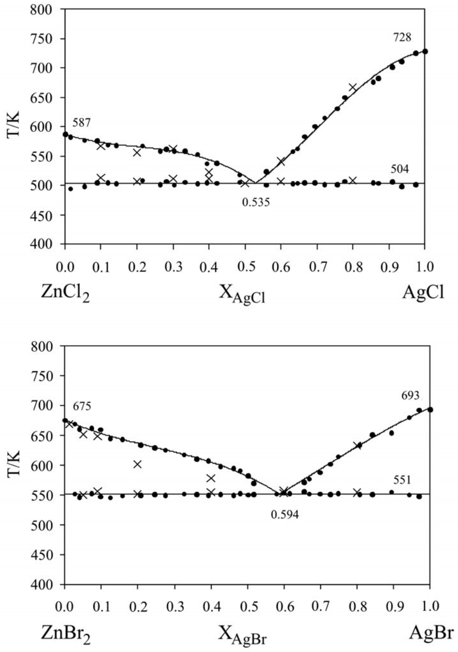

Fig. 1 Phase diagrams for the systems $ZnCl_2$–AgCl and $ZnBr_2$–AgBr; thermal events registered by DSC (•) and by conductivity measurements (x)

Our results show that eutectic points in the systems $ZnCl_2$–AgCl and $ZnBr_2$–AgBr are at 503.5 K, 53.5 mol% AgCl and 551.0 K, 59.4 mol% AgBr, respectively. Eutectic compositions are shifted towards the component with a higher melting point (i.e. silver halide) which is not common for simple binary eutectic systems [18, 19].

Compositions of the eutectic points were determined by the Tamman method [20, 21]. Values of the eutectic thermal effects for a given mixture, determined by means of DSC curves, are plotted *vs.* mole fraction of silver halide in Fig. 2 for the systems $ZnCl_2$–AgCl and $ZnBr_2$–AgBr. The maximum is at the respective eutectic composition.

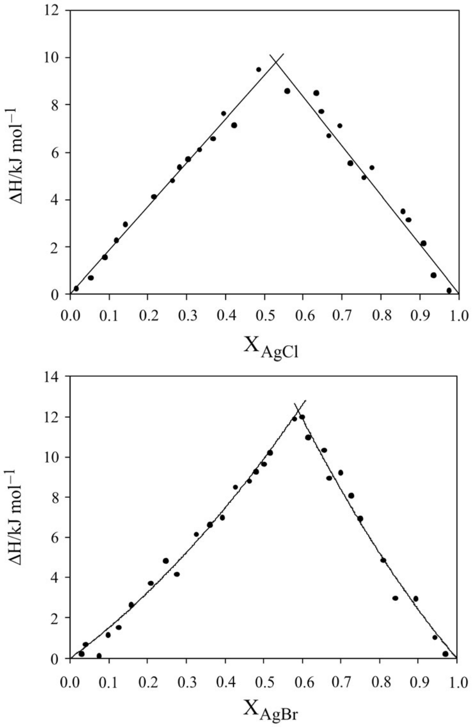

Fig. 2 Thermal effect of the eutectic reaction *vs.* composition in the systems $ZnCl_2$–AgCl and $ZnBr_2$–AgBr

The eutectic thermal effect goes to zero for compositions corresponding to pure components. This confirms that there is no reciprocal miscibility in the solid-state.

Breaks or changes of slopes on the conductivity curves as a function of temperature may often be assigned to phase transitions [22]. A few examples of conductivity runs, when plotting logarithm of the specific conductivity *vs.* reciprocal of the absolute temperature are shown in Fig. 3.

Temperatures of phase transitions determined by conductivity measurements generally agree with those determined by the differential scanning calorimetry method (Fig. 1). A drastic change of conductivity during the eutectic reaction (Fig. 3) allows to obtain a very reliable value of the eutectic temperature. As far as the temperature of liquidus is concerned, we observe that in the systems $ZnCl_2$–AgCl and $ZnBr_2$–AgBr the agreement is better on the silver halide side. Even for compositions quite close to the eutectic point, two transitions (liquidus and eutectic reaction) are observed (Fig. 3e). On the zinc halide side, discrepancies are apparently highest at around 40 mol% of silver halide (extended to 30 mol% in the $ZnCl_2$–AgCl system) which may be connected with glass formation. A special feature in both systems is that at around 10 mol% of silver halide, conductivity of two-phase mixture (solid zinc halide + liquid solution) practically does not change with temperature (Figs 3a and d).

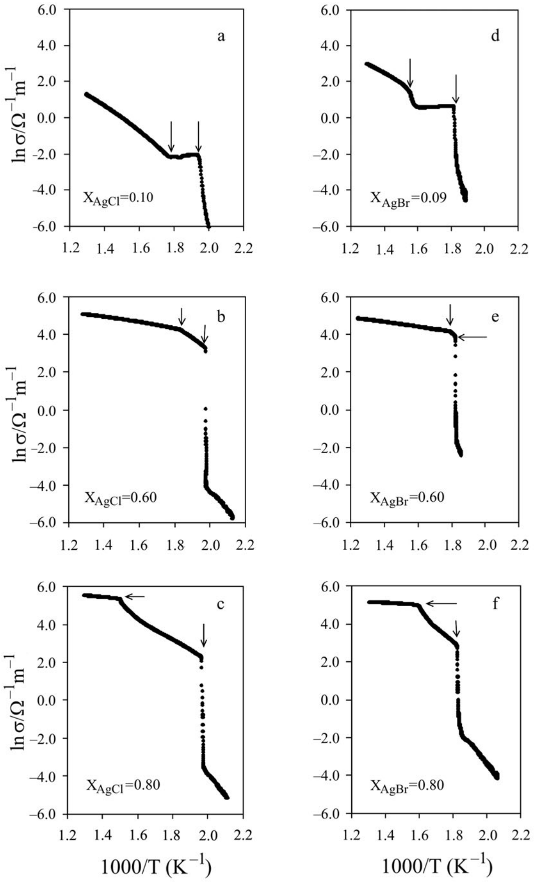

Fig. 3 Examples of phase transitions observed on conductivity curves in the system $ZnCl_2$–AgCl: a, b, c and in the system $ZnBr_2$–AgBr: d, e, f

Conclusions

Equilibrium phase diagrams for the $ZnCl_2$–AgCl and $ZnBr_2$–AgBr systems are of the simple eutectic type. Solid solubility is negligible. No intermediate compound was found. The similarities of the two systems may arise from similarities between respective components: silver halides and zinc halides. In contrast for example, in the ZnI_2–AgI system [23], where structural properties of AgI are very different from those of AgCl and AgBr, the equilibrium phase diagram exhibits formation of solid solution areas and of an intermediate phase as well.

A value of melting point of $ZnCl_2$, measured in this work using differential scanning calorimetry for very pure anhydrous zinc chloride is 587 K. Low values given in literature like 548 K [9] are questionable.

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