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PHASE EQUILIBRIUM DIAGRAM FOR THE TIN(II) BROMIDE–COPPER(I) BROMIDE SYSTEM

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The phase diagram of the $SnBr_2$ – CuBr system was determined by the method of thermal analysis. One intermediate compound, $CuSn_5Br_{11}$, melting congruently at 218.7 °C, was found.

Among the phase diagrams for the SnY_2–CuY system (where Y = Cl, Br, I), only that for the $SnCl_2$–CuCl system has been reported [1]. This is of the simple eutectic type. A knowledge of the SnY_2–AgY system was also earlier limited to the chlorides. We recently investigated the $SnBr_2$–AgBr [2] and SnI_2–AgI [3] phase diagrams. An increasing tendency to form compounds was found on passing from Cl^- to Br^- and then to I^-. Therefore, the study of the $SnBr_2$–CuBr system was undertaken with the object of verification this tendency in the series of SnY_2–CuY systems.

Experimental

Anhydrous tin(II) bromide was prepared by dehydration of the residue obtained from evaporation to dryness of a solution of tin in concentrated hydrobromic acid (both of analytical grade). The material was refined by multistage vacuum distillation, yielding a pale-yellow final product.

Copper(I) bromide was obtained according to the processes

$$CuBr_2 + Cu = 2CuBr$$

The reaction probably begins at as low as room temperature. During preliminary tests involving mixing small black crystals of $CuBr_2$ with finely powdered copper, we noticed that the mixture grew more pale; storage for 4 months in a closed pot, the mixture became pale-green, and nearly white.

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CuBr was synthetized in sealed evacuated silica tubes. High-purity $CuBr_2$ (Fluka) in the form of small crystals and Cu (5N, Johnson–Matthey) in the form of foil (0.1 mm in tickness) were used as starting materials. A 20% Cu excess was ensured by introducing a rod of copper (5 mm in diameter). The surface of the metal was additionally cleaned by treatment with solutions of hydrochloric and nitric acids. After filling, the tube was evacuated and heated slowly to 110° to remove water adsorbed by the salt. The ampoule was then cooled under vacuum to room temperature, sealed and put into an electric furnace in the horizontal position, heated carefully during 6 h up to 340°, and maintained at this temperature for more than 48 h. This procedure prevented an excessive rise in the vapour pressure of bromine, which was evolved beginning from 180°. As the temperature increased, the colour of the mixture in the ampoule changed from grey to green and then to canary-yellow. The yellow became more intense as the temperature continuoued to rise from 340° to the melting point. When the salt melted ($\sim 500°$), the ampoule was kept at 600° for another 24 h, and it was then taken out of the furnace and cooled in the vertical position. The salt was bright-yellow. It was separated from the excess of copper by dynamic or static vacuum distillation. Dynamic distillation was performed at 650° during a few hours, and static distillation at 850° during a few days. This latter method prevented the product from being oxidized. The bulk condensate after solidification was bright-yellow and transparent. Part of the product was deposited on the top of the ampoule, near the walls the resublimate was compact, yellow, and opaque; little by little it was transformed into white needles which were stuck together in a parallel way on approaching the axis of the ampoule. The obtained material changed its appearance during a few hours in the air, so it had to be stored under vacuum. It is rather surprising that distilled copper(I) bromide is relatively unstable in the air, whereas distilled copper(I) chloride was not affected during several days as reported by Brewer and Lofgren [4]. It has been observed, however, that very thin white layers of CuBr sometimes deposited during distillation did not change colour even after a month.

The liquid–solid equilibra in the $SnBr_2$–CuBr system were studied by thermal analysis. An apparatus for cryometric measurements at high temperature was applied, which permitted determination of the initial solidification temperature with an accuracy of ±0.1 deg. Cooling curves were taken by means of a thermopile consisting of five Ni–Ni/Cr thermocouples connected in series. The thermal electromotive force of the thermopile was measured by the compensation method. Measurements were carried out under an atmosphere of purified argon. Molten salt mixtures weighing approximately 40 g were cooled very slowly (less than 0.5 deg/min) and vigorously agitated. In most cases, crystallyzation was seeded. More details concerning the measurement technique can be found in our previous papers, e.g. [3].

Results

The phase diagram for the $SnBr_2$–CuBr system is presented in Fig. 1.

A somewhat flat, but well-marked maximum in the liquidus curve indicates that an intermediate compound, melting congruently at 218.7°, is formed in the system. The most probable composition of the compound corresponds to the formula $CuSn_5B_{11}$. The eutectic points on both sides of this compound are 10.1 mol% CuBr, 214.9°; and 35.6 mol% CuBr, 203.9°. Thermal halts in the cooling curves, attributed to crystallization of the eutectic mixture at 203.9°, are observed up to almost pure CuBr (e.g. for mixtures containing 1.6 mol% $SnBr_2$). This fact may be taken as proof of the absence of other compounds in the temperature range under investigation in this system.

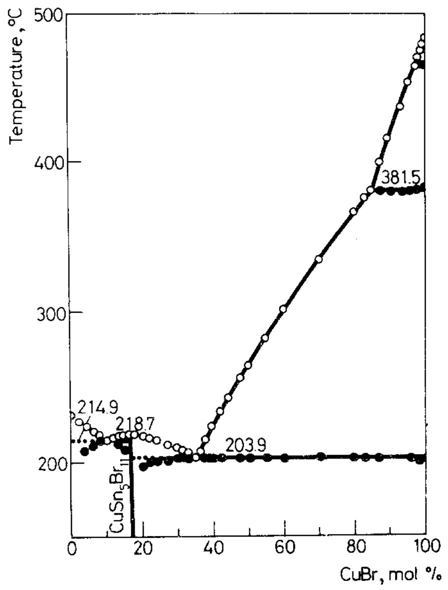

Fig. 1 Phase diagram for the $SnBr_2$–CuBr system

Pure CuBr melts at 485.4°. Higher values of the melting point, e.g. 504° [5], have been reported. It is generally known that a small amount of oxygen causes the melting points of copper(I) halides to rise [6]. In this study, we noticed that when air entered the reaction tube, molten CuBr, which was initially a transparent, ligth-red liquid, was transformed into a black, viscous substance, melting at a temperature elevated by a few degrees.

The melting point and polymorphic transformation temperatures of CuBr determined in this work, together with those determined recently by Ferrante and

Brown [7] by means of a DSC method, are given below:

γ-CuBr ⇄ β-CuBr	⇄ αCuBr	⇄ $CuBr_{liquid}$	Ref.
383.6°	467.9°	485.9°	[7]
383.4°	467.0°	485.4°	this work

Although the accuracy of the method used in this work falls when the liquid disappears, the measured temperatures of the polymorphic transformations of CuBr agree very well with the literature data. The transition β-CuBr ⇄ γ-CuBr is clearly visible in the cooling curves, though it takes place at a temperature about 100 deg lower than the melting point of pure CuBr. The thermal event is more pronounced than that for the transition α-CuBr ⇄ β-CuBr, because the enthalpy of the phase transformation is half as much in the latter case.

α-CuBr exists in only a small range of temperature (about 15 deg); it crystallizes from melts containing more than 97.5 mol% CuBr. Addition of $SnBr_2$ to CuBr does not change the temperature of the polymorphic transformation α-CuBr ⇄ β-CuBr.

A small quantity of $SnBr_2$ decreases the temperature of the transformation β-CuBr ⇄ γ-CuBr only slightly. For a content of $snBr_2$ higher than 2 mol%, this temperature remains constant at 381.5°. This slight depression of the phase transition temperature may be connected with the existence of an inconsiderable limiting solid solution area. β-phase crystallizes from molten mixtures having compositions from 84.7 to 97.5 mol% CuBr. Crystallizaton of the γ-phase occurs in the largest ranges of compositions and temperature.

Discussion

Since an intermediate compound $CuSn_5Br_{11}$ was found in the $SnBr_2$–CuBr system, it may well be that, as in the systems with silver halides, the replacement of Cl^- ion by Br^- ion brings about an increasing tendency to form compounds.

The phase diagrams of binary systems of CuBr with compounds with a common anion are rather rare. They are listed in Table 1.

Table 1 begins with systems forming large areas of solid solutions. Next there are eutectic systems, and finally systems where compounds are formed, first melting incongruently, and finally melting congruently. Such an evolution of the phase diagrams is usually observed when the properties of the pure components, or ions, in the case of salts, become more and more different.

First of all their sizes should be compared. The third column in Table 1 gives an ionic radius for the cation of the second salt. Ahrens's data set has been used, because it includes a value for the ionic radius of Sn^{2+}, this being absent from the

Table 1 List of phase diagrams of binary systems of CuBr with compounds with a common anion. Characteristic features and absolute magnitude of ionic radius difference between the cations. $|\Delta| = |r_{Cu^+} - r_c| = |0.96 - r_c|$; (i) = compound melting incongruently; (c) = compound melting congruently

System	Characteristic of phase diagram	r_c (Ahrens), Å	$\|\Delta\|$ Å	References
CuBr–AgBr	extended solid solutions	1.26	0.30	8
CuBr–$CdBr_2$	extended solid solutions ($CuCdBr_3$)	0.97	0.01	9
CuBr–NaBr	eutectic	0.97	0.01	10
CuBr–$TbBr_3$	eutectic	0.93	0.03	11
CuBr–$NdBr_3$	eutectic	1.04	0.08	12
CuBr–$PrBr_3$	eutectic	1.06	0.10	12
CuBr–$InBr_3$	eutectic	0.81	0.15	13
CuBr–$PbBr_2$	$CuPb_3Br_7$(i)	1.20	0.24	14
CuBr–KBr	K_2CuBr_4(i)	1.33	0.37	10
CuBr–$SnBr_2$	$CuSn_5Br_{11}$(c)	0.93 (1.17)*	0.03 (0.21)	this work
CuBr–$GaBr_3$	$CuGa_2Br_7$(i) $CuGaBr_4$)c)	0.62	0.34	5

* after Yatsimirskii [15].

classical works of Goldschmidt, Pauling of Zachariasen, and also from more recent elaborations, e.g. those by Waddington or Shannon. The ionic radius of Cu^+ given by Ahrens is 0.96 Å.

The fourth column in Table 1 gives the absolute magnitudes of the differences in cation radius in the systems where CuBr is one of the components. More or less, it may be assumed that as this value rises there is a gradual transition from systems with extended solid solutions through those of eutectic type to the systems where intermediate compounds exist. Exceptions are the CuBr–AgBr, the CuBr–$SnBr_2$ and to a certain degree the CuBr–$CdBr_2$ systems.

The existence of a compound in the CuBr–$CdBr_2$ system is ambiguous and not confirmed. The phase diagram has not been studied since 1911. It is significant that, in systems, where the cation radii are practically the same, solid solutions are formed in a broad range of compositions (50–100 mol% CuBr).

However, there are large areas of solid solutions in the system CuBr–AgBr, in spite of the large difference in cation radius. It seems that the chemical and structural similarities of the two salts could explain this fact.

New compounds are usually formed in systems where the sizes of the cations differ. This is the case, for example, in the CuBr–$GaBr_3$ system, where two compounds exist. In light of this fact, it is surprising that in the system studied here a compound (melting congruently) occurs, though after Ahrens the difference between the ionic radii of Cu^+ and Sn^{2+} is only 0.03 Å.

It is difficult to determine the ionic radius of Sn^{2+}, due to the lack of typically ionic structures among the Sn(II) compounds and to distortion of the corresponding coordination polyhedra [16]. The value of 0.93 Å given by Ahrens is not sure; it seems to be too small. It is hard to believe that the ionic radius of Sn^{2+} is smaller than that of Cd^{2+} (0.97 Å) when the tin(II) ion has two electrons more. It should rather be larger, as in the analogous cases of Pb^{2+} (1.20 Å) and Hg^{2+} (1.10 Å).

Yatsimirskii [15] gives a value of 1.17 Å for the Sn^{2+} ionic radius. He obtained this on the basis of an empirical relation considering ionic radii and ionization potentials. Now, if the difference between the ionic radii of the two cations is equal to $|\Delta| = |r_{Cu^+} - r_{Sn^{2+}}| = |0.96 - 1.17| = 0.21$ Å, the existence of the compound in the $SnBr_2$–CuBr system is more understandable.

A similar high value for the ionic radius of Sn^{2+}, namely 1.22 Å, was given by Shannon and Prewitt [17]. It was obtained for a coordination number 8, based on structural data for $Sn_2M_2O_7$ pyrochlores. Andersson [18], who determined the structure of the crystal lattice of $SnBr_2$, also stated that the coordination number of tin in $SnBr_2$ is 8. Because of the appreciable distortion found in the structures of tin(II) compounds, Shannon rejected the above value, and does not give it in his later work [16] with revised values of the ionic radii.

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Zusammenfassung — Mittels Thermoanalyse wurde das Phasendiagramm des Systemes $SnBr_2$–CuBr ermittelt. Dabei wurde die Verbindung $CuSn_5Br_{11}$ mit dem kongruenten Schmelzpunkt 218.7 °C gefunden.

Резюме — Методом термического анализа определена фазовая диаграмма системы $SnBr_2$–CuBr. Найдено одно промежуточное соединение состава $CuSn_5Br_{11}$, конгруэнтно плавящееся при 218,7°.