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

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The phase diagram of the SnI_2–CuI system was determined by the method of thermal analysis. No intermediates were found. It is suggested that limiting solid solutions of SnI_2 in γ-CuI, β-CuI and α-CuI, respectively, are formed. The eutectic point parameters (32.7 mol% CuI, 270.4±0.1 °C) and those of two invariant points (64.0 mol% CuI, 385.3±0.5 °C and 61.5 mol% CuI, 366.6±0.2 °C), corresponding to the equilibria $\alpha + \text{liquid} \rightleftarrows \beta$ and $\beta + \text{liquid} \rightleftarrows \gamma$, respectively, were determined.

Experimental studies on metal iodide systems are rather difficult, primarily because of the thermal stability of iodides compared with that of lower halides. This is probably the reason why only a small number of phase diagrams of copper(I) iodide–metal iodide systems have been published to date. On the other hand, it is found that the copper(I) state becomes more stable as the covalent character of the Cu–X bond increases, e.g. in aqueous halide solutions as halogen is changed from fluorine to iodine [1].

The number of published binary phase diagrams of CuI with other iodides does not exceed a dozen. As concerns the alkali metal iodides, the phase diagrams of the LiI–CuI and NaI–CuI systems are not known. Similarly, the HgI_2–CuI phase diagram has not been described, though Cu_2HgI_4 was reported as far back as in the 19th century [2], and has been studied many times during the last forty years with regard to its physicochemical properties.

The present phase equilibrium studies on the SnI_2–CuI system comprise a continuation of our work on the phase diagrams of the binary systems of $SnBr_2$ with AgBr [3] or with CuBr [4] and of SnI_2 with AgI [5, 6]. It may be presumed that, together with the chloride systems for these pairs of cations, which were investigated earlier [7–11], a knowledge of the phase diagrams for the complete series of these systems would reveal the more general trends that appear on passing from chlorides to iodides and from copper(I) to silver ions.

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Experimental

Tin(II) iodide was prepared by dissolution of tin in hydroiodic acid. On cooling a precipitate appeared in the form of fine red-orange needles. This was dried in a desiccator and then in an electric furnace under a continuous flow of argon. The salt, together with metallic tin, was heated slowly up to ~370°, i.e. about 50 deg higher than the melting point. The product was cooled and distilled several times under vacuum [12].

Copper(I) iodide was obtained from copper(II) sulphate solution, saturated with sulphur dioxide, by precipitation with potassium iodide solution. Sulphur dioxide was bubbled through the solution during the crystallization process. The white precipitate of CuI was washed carefully, and then dried first at 40° for 24 h and then at 230° for 24 h under an argon atmosphere.

All reagents used for the preparation of the salts were of analytical grade.

The liquid–solid equilibria in the SnI_2–CuI system were studied by means of thermal analysis. An apparatus for high-temperature cryometry measurements, resembling that described earlier [5, 13], was adapted for the present purposes. Pieces made of glass and working in a high-temperature end were replaced with silica elements. Temperature was determined by means of Ni/Ni, Cr thermopiles, the thermal emf being measured by the compensating method with an accuracy of ± 1 μV. For mixtures containing more than 70 mol% CuI, a thermopile consisting of three thermocouples was employed while for the others five thermocouples were connected in series. The thermopiles were calibrated via standard freezing points and the results were elaborated in the form of relations of the following power type:

$$t = aE + bE^2 + cE^3$$

where t = temperature, and E = thermal emf of the thermopile. The accuracy of temperature interpolation with these relations was ±0.2 and 0.1 deg for the first and second thermopile, respectively. Measurements were carried out in an atmosphere of purified argon. Molten salt mixtures, weighing about 40 g, were agitated vigorously and cooled very slowly (less than 0.5 deg/min) near an expected beginning of freezing. In most cases, crystallization was seeded to reduce surfusion.

Results

Data arising from cooling curve analysis that were used to establish the SnI_2–CuI phase diagram (Fig. 1) are listed in Table 1.

The obtained phase diagram is of the eutectic type. In the temperature range under investigation (from the eutectic temperature to the melting point of CuI), no intermediate has been found in this system. The eutectic point is situated at a

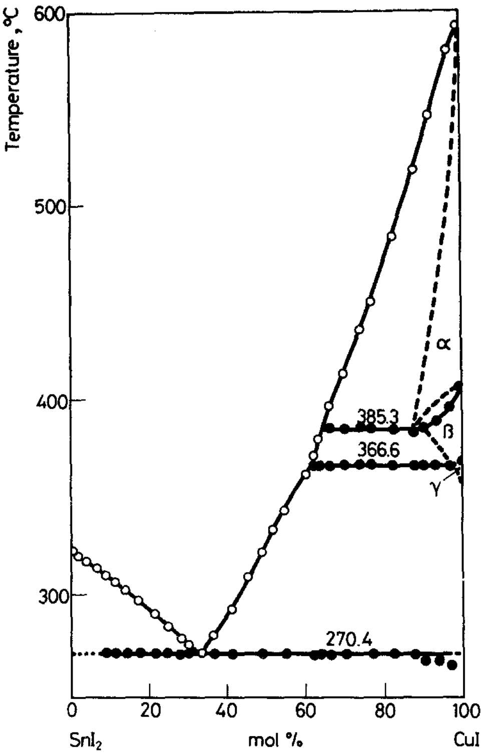

Fig. 1 Phase diagram for the SnI_2–CuI system

composition of 32.7 mol% CuI and a temperature of 270.4±0.1°. Thermal events in the cooling curves corresponding to the eutectic temperature are observed throughout almost the entire range of compositions. However, the cooling curves on the two sides of the eutectic point are not similar. On the right side, immediately beyond the eutectic point, the thermal halts are distinct and clear, keeping still for more than a half an hour. On the left side of the eutectic point, however, for mixtures containing more than 67.3 mol% SnI_2, only a change in slope is observed. Although this becomes more and more well-marked, it does not turn into an arrest. It is very difficult to see this effect for SnI_2-rich mixtures, and the effect disappears above 91.35 mol% SnI_2. On the basis of the cooling curves, it cannot be stated whether the events are lacking due to the solid solubility of CuI in SnI_2 or to the insufficient sensitivity of the measurement technique.

On the other hand, the effects of the polymorphic transformations of CuI are very distinct in the cooling curves and, in spite of lying about 200 deg lower than the melting point, the transition temperatures are measured with a quite good precision. The values obtained in this work (°C) are compared with the available

Table 1 Data for construction of the SnI_2–CuI phase diagram

CuI, mol%	Beginning of an arrest in the cooling curve, °C			
	t_1	t_2	t_3	t_4
0	322.5			
1.72	320.2			
3.83	317.3			
6.30	313.8			
8.65	310.4	270.7		
10.95	307.1	270.8		
13.56	303.1	270.6		
16.94	297.4	270.9		
20.93	290.5	270.6		
24.54	284.3	270.3		
28.00	278.2	270.6		
29.48	275.7	270.3		
32.68	270.4	270.4		
36.22	279.7	270.4		
40.96	292.8	270.2		
45.02	309.2			
48.59	322.0	270.2		
51.71	334.0			
54.45	343.6	270.2		
59.90	361.5			
62.20	371.8	366.5	270.3	
63.34	380.0	366.6	270.4	
66.01	396.4	385.7	366.2	270.0
69.77	413.2	385.0	367.0	270.7
74.09	436.0	385.6	367.2	
76.59	450.1	385.9	366.9	270.6
82.17	483.6	384.8	366.2	270.1
87.76	518.1	384.2	366.7	270.1
89.81		385.6	366.4	267.1
92.02	546.1			
93.42		389.4	366.1	267.0
96.44	579.5	396.2	366.6	264.7
99.37	590.7			
100.00	592.4	406.2	367.9	

literature data [e.g. 14, 15] below:

γ-CuI ⇄ β-CuI	⇄ α-CuI	⇄ CuI_{liquid}	Ref.
367.9	406.4	592.2 ± 0.2	this work
369	407		[14]
370.5	408.5	591 ± 1.5	[15]

The addition of SnI_2 lowers the transition temperatures. The temperature of the $\beta \rightleftarrows \gamma$ transition changes very slightly, falling by about 1 deg, while that of the $\alpha \rightleftarrows \beta$ transition falls by more than 20 deg. These depressions are probably connected with the formation of limiting solid solutions of SnI_2 in α-, β- and γ-CuI. The possible range of the γ-phase does not exceed 3 mol% SnI_2, while that of the β-phase may reach 10 mol% SnI_2 and that of the α-phase must be even more extended. Within the compositions from 90 to 100 mol% CuI, it is difficult to record the α-phase $\rightleftarrows$ β-phase transformation, the temperature of this transition not being constant. For instance, at a composition of 93.42 mol% CuI, the effect was observed only in the heating curves. When the content of SnI_2 is increased, beginning from 10 mol% SnI_2, the temperature becomes fixed within ± 0.5 deg. The average value calculated on the basis of seven experimental points, was 385.3°. The constancy of the temperature should be indicative of three phase equilibria: two solid phases (α and β) in equilibrium with liquid of liquidus composition (64.0 mol% CuI). The range of existence of the α-phase might be shifted to lower temperatures due to the formation of limiting solid solutions of SnI_2 in α-CuI. Similarly, at 366.6° the liquid having a composition of 61.5 mol% CuI is in equilibrium with the β-phase and the γ-phase. The temperature is constant within ± 0.2 deg from about 3 mol% SnI_2. The above temperature is the average of eleven determinations. Boundaries for suggested areas of limiting solid solutions are marked by dashed lines in Fig. 1.

Discussion

The phase diagram determined for the SnI_2–CuI system in this work resembles that of the PbI_2–CuI system [16]. What is more, in the systems AX_2–CuX (where A = Sn, Pb, and X = Cl, Br, I) the mode of transformation on passing from chloride through bromide to iodide is the same for the Sn(II) and Pb(II) salts. The chloride systems are of the eutectic type [7–11]. The bromide systems exhibit compound formation: $CuSn_5Br_{11}$, melting congruently [4], and $CuPb_3Br_7$, melting incongruently [16]. The iodide systems are of the eutectic type, with solid solubility in CuI.

A gradual replacement of the halide ions $Cl^- \rightarrow Br^- \rightarrow I^-$ is usually presumed to imply monotonous changes in properties. For example, the ability to form solid solutions is larger as the size of the common anion grows, and this is evidenced in the above-mentioned systems. However, the tendency to form compounds, which increases on passing from the chlorides to the bromides, is not observed at all in the iodide systems. Similarly, neither the melting points of the tin(II) halides [13] nor those of the lead(II) halides [17] vary monotonously, as is seen from the data

Table 2 Melting points (°C) of the tin(II) ([13] and this work) and lead(II) [17] halides

	Cl	I	Br
Sn	250	322	231
Pb	498	402	370

compiled in Table 2. The bromides have lower melting points than the respective chlorides and iodides. Perhaps the forms of the phase diagram are influenced by the runs of the melting points for the pure salts. To emphasize a dissimilarity in the properties of the tin(II) halides, it should also be remembered that each of them has a different type of crystal structure [18, 19].

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Zusammenfassung — Mittels Thermoanalyse wurde das Phasendiagramm SnI_2–CuI bestimmt. Es konnten keine Intermediäre gefunden werden. Es scheint, daß Grenzmischkristalle von SnI_2 und γ-CuI, β-CuI, α-CuI gebildet werden. Es wurden ein Eutektikum (32,7 mol% CuI, 270,4 ± 0,1 °C) und zwei den Gleichgewichten α + Flüssigkeit $\rightleftarrows \beta$ und β + Flüssigkeit $\rightleftarrows \gamma$ entsprechende invariante Punkte (64,0 mol% CuI, 385,3 ± 0,5 °C und 61,5 mol% CuI, 366,6 ± 0,2 °C) gefunden.

Резюме — Методом термического анализа определена фазовая диаграмма для системы SnI_2–CuI, где не наблюдалось образования промежуточных продуктов. Предложено образование ограниченных твердых растворов иодида олова, соответственно, в γ-CuI, β-CuI и α-CuI. Определены параметры для эвтектической точки (32,7 мольных% CuI, 270,4 ± 0,1°) и для двух инвариантных точек (64,0 мольных% CuI, 385,3 ± 0,5° и 61,5 мольных% CuI, 366,6 ± 0,2°), соответствующих равновесиям α + жидкость $\rightleftarrows \beta$ и β + жидкость $\rightleftarrows \gamma$.