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Phase Equilibria of the Systems Containing Silver Iodide and Alkali Iodide. II.[†] AgI-NaI-H_2O System

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Phase diagrams were constructed for the equilibria of the AgI–NaI–H_2O system at temperatures 0—70 °C. A compound AgI·NaI·$3H_2O$ was isolated, and the compound was found by means of X-ray analysis to belong to the orthorhombic system with cell constants $a=8.78$, $b=33.5$, and $c=6.48$ Å.

The formation of a series of compounds, probably of the type $K_n[AgI_{1+n}]$, was recognized for the binary system of AgI and KI.[1–4)] They can be formed by a solid state reaction at high temperatures or by mixing the components with a small amount of water or from a concentrated aqueous solution. This type of compound often crystallizes with a solvent of crystallization. Marsh and Rhymes[5)] described a series of crystalline compounds such as 2AgI·KI·$2C_3H_6O$, where C_3H_6O denotes acetone. The present authors[6)] have studied the phase equilibria of the AgI–KI–H_2O system and reported the formation of a new compound 2AgI·KI·$2H_2O$.

The phase equilibria of the AgI–NaI–H_2O system at 25 °C were studied by Krym.[7)] His phase diagram, however, is obviously incomplete, since he did not notice the existence of the solid phase of NaI·$2H_2O$. The present paper deals with an investigation of this system over a wide temperature range together with an X-ray study of a compound formed in this system.

Experimental

Materials. Silver iodide of extra pure grade was used. It was found by means of X-ray powder method to be γ-AgI (cubic), containing a small amount of β-AgI(hexagonal). Sodium iodide of extra pure grade was dried at 110—120 °C to a constant weight.

Determination of Composition. Desired amounts of AgI, NaI and water were introduced into a stoppered flask and thermostated for various periods of time depending on the experimental temperature (*ca.* 3 hr(70 °C)—24 hr(0 °C)). After the equilibrium had been attained, the solution was pipetted out and weighed, and then dried to a constant weight. The loss in weight was regarded to correspond to the quantity of the water involved. A large amount of water was added to the residue. After complete precipitation of AgI, the supernatant solution was carefully removed. The NaI in the residue was removed completely by repeating the procedure several times. It was confirmed that recovery of AgI was over 99%.

At temperatures below 40 °C, the formation of a crystalline compound, other than the components, was observed in a range of appropriate proportions of the components. As this compound crystallized from very concentrated solutions, supersaturation of the solutions often occurred. In the determination of the number of the water of crystallization, high temperature and humidity were avoided as far as possible, since the crystal is unstable in air and easily decomposes to the components even at room temperature. The crystals were washed with a small amount of acetone and dried quickly on a sheet of filter paper and weighed. The weight percentage of each component of the crystal was determined by the same method as that for solutions.

X-Ray Analysis. For the determination of the cell constants of the crystal, a single crystal was inserted into a thin-walled Pyrex glass capillary with a small amount of the mother liquid and sealed off. X-ray oscillation and Weissenberg photographs were taken using Ni-filtered Cu$K\alpha$ radiation. The density measurement was carried out with a picnometer of *ca.* 5 cm^3 and liquid paraffin.

Results and Discussion

The overall compositions of the AgI–NaI–H_2O system and the compositions of the liquid phases in equilibrium with solid phases are given in Table 1.

TABLE 1. COMPOSITON OF THE AgI–NaI–H_2O SYSTEM

Temp. (°C)	Overall composition (wt%)		Composition of liquid phase in equilibrium with solid phase (wt%)		Solid phase
	AgI	NaI	AgI	NaI	
0	11.4	26.6	6.8	28.0	AgI
	16.1	29.8	11.4	31.4	
	25.9	31.5	18.1	34.7	
	28.8	35.5	24.3	37.6	
	24.2	45.3	18.7	47.7	Complex[b)]
	29.8	40.7	21.7	43.7	
	24.8	46.8	18.9	49.5	
	6.8	60.6	7.5	58.4	NaI·$2H_2O$
	13.6	56.4	13.8	56.1	
			0	61.7[a)]	
			24.9	40.6	AgI+Complex
			23.9	41.6	
			17.2	54.0	NaI·$2H_2O$+Complex
30	0.4	10.2	0.2	10.1	AgI
	0.6	19.9	0.8	19.7	
	5.3	28.6	5.1	29.0	
	15.4	33.8	14.3	34.2	
	26.1	36.9	23.4	38.1	
	37.4	38.1	32.5	40.8	
			35.9	42.3	AgI+Complex
	37.0	43.0	30.2	47.4	Complex
	34.0	45.4	29.1	48.5	

[†] Part 1 of this series: see Ref. 6.

Table 1. (Continued)

Temp. (°C)	Overall composition (wt%)		Composition of liquid phase in equilibrium with solid phase (wt%)		Solid phase
	AgI	NaI	AgI	NaI	
	30.1	50.0	26.6	51.1	$NaI\cdot 2H_2O$+Complex
	28.1	52.0	27.5	51.0	
	23.1	53.7	23.7	52.7	$NaI\cdot 2H_2O$
	16.6	58.3	17.5	56.2	
	12.2	59.5	12.6	58.6	
	7.4	63.3	7.9	61.2	
	3.5	64.4	3.6	63.8	
			0	65.7[a]	
40	4.4	19.2	0.8	19.9	AgI
	11.3	26.1	4.4	28.0	
	17.1	31.8	12.1	33.7	
	24.5	36.3	21.8	37.2	
	33.9	33.5	24.3	37.9	
	37.4	37.4	32.3	40.4	
	39.3	39.4	35.5	41.7	
	40.8	42.9	38.0	44.5	AgI+Complex
			38.1	44.7	
	42.5	41.6	38.2	44.4	
	41.6	42.8	37.7	44.9	
			36.7	46.4	Complex
			35.5	47.3	
			36.3	46.1	
			33.4	48.8	Complex+$NaI\cdot 2H_2O$
	3.5	67.8	4.2	65.1	$NaI\cdot 2H_2O$
	11.4	61.3	11.3	61.1	
	15.3	61.3	18.3	57.2	
			26.4	53.3	
			0	67.3[a]	
50	4.6	18.8	0.9	19.6	AgI
	11.1	25.9	4.7	28.1	
	17.7	26.2	6.5	30.1	
	29.1	31.9	19.9	36.3	
	35.8	37.2	30.5	40.1	
	41.5	41.0	39.5	42.2	
			0	69.4[a]	$NaI\cdot 2H_2O$
			3.2	67.9	
	5.0	67.3	4.7	66.9	
	10.3	64.9	11.0	63.4	
	14.9	62.3	15.7	60.5	
			21.2	58.0	
			34.9	50.5	NaI
	29.4	54.8	30.6	52.8	
			25.7	55.2	NaI+$NaI\cdot 2H_2O$
			37.7	49.7	AgI+NaI
70	11.4	26.4	4.8	28.6	AgI
	27.5	33.5	22.5	37.1	
	41.1	41.1	38.9	41.7	
			36.8	53.2	AgI+NaI
	4.5	76.3	5.5	71.0	NaI
	11.3	70.8	13.2	65.5	
	17.9	69.5	22.4	61.2	
			0	74.2[a]	

a) Solubility of NaI.[8] b) $AgI\cdot NaI\cdot 3H_2O$.

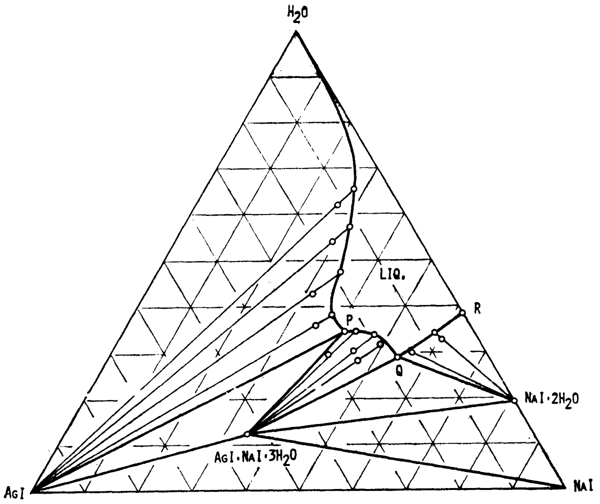

Fig. 1. Phase diagram of the AgI–NaI–H_2O system at 0 °C (wt%).

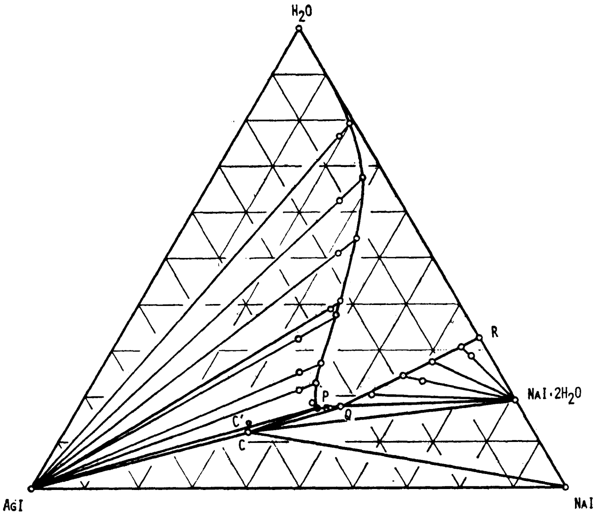

Fig. 2. Phase diagram of the AgI–NaI–H_2O system at 40 °C (wt%).

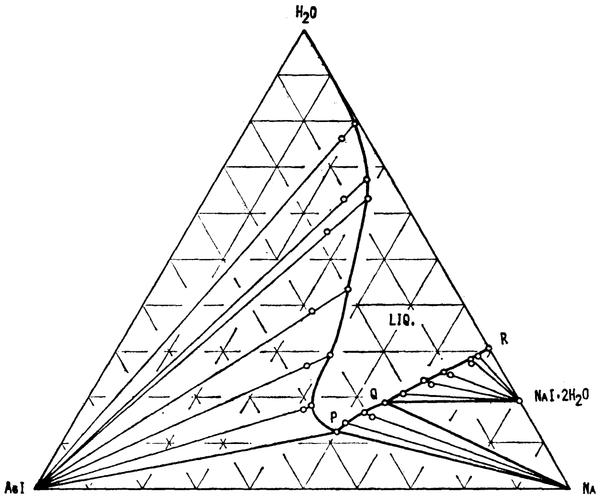

Fig. 3. Phase diagram of the AgI–NaI–H_2O system at 50 °C (wt%).

The weight percentages of the components were plotted on an equilateral triangle. Examples are shown in Figs. 1—3. Each corner of the triangle represents pure components. Points P and Q in these figures are invariant points, and R denotes the solubility of NaI in pure water.

A compound containing all the three components crystallizes under appropriate conditions. It should be identical with the one Krym[7] found in his study of the AgI–NaI–H_2O system at 25 °C, and to which he gave the formula $AgI \cdot NaI \cdot 3.5H_2O$. The compound was analyzed and the results are given in Table 2.

Table 2. Chemical composition (wt%)

	AgI	NaI	H_2O
	50.7	36.2	13.1
	52.3	34.9	12.8
	51.4	35.7	12.9
	52.5	34.7	12.8
Mean	51.7	35.4	12.9
Calcd as $AgI \cdot NaI \cdot 3H_2O$			
	53.5	34.2	12.3
Calcd as $AgI \cdot NaI \cdot 3.5H_2O$			
	52.4	33.5	14.1

It is evident that the mole ratio of AgI to NaI is 1: 1, but the number of water of crystallization is not clear. It seems to be a $3H_2O$ rather than a $3.5H_2O$ compound.

An alternative way to presume the chemical formula is the Schreinemaker plot. In the region in which the compound coexists with solution, total composition–solution composition tie lines should converge on the point which represents the true composition of the compound. However, from the data at 0 °C as well as at other temperatures, no decisive conclusion has been drawn, since the experimental points have uncertainties due to errors in the chemical analysis. Nevertheless, a $3H_2O$ compound is considered more plausible on the following grounds. The invariant point P (filled circle) in Fig. 2 represents the average composition of the solution in equilibrium with both the solid AgI and the compound (see Table 1). The position of C′ ($3.5H_2O$ compound) is incompatible with the positions of P and AgI, making it impossible to construct the phase diagram at 40 °C. On the other hand, if the $3H_2O$ compound is assumed, no inconsistency is found in constructing the phase diagrams at 40 °C and other temperatures.

King *et al.*[9] studied the dependence of the solubility of AgI in water on the common ion concentration and indicated the existence of anionic and cationic complex ions in solution. Greenslade and Symons[10] measured the UV spectra of the solutions containing AgI and KI in various solvents. They assigned the band at 43800 cm^{-1} to AgI_2^-. The existence of this band was also confirmed by us. Thus the compound is considered to be a complex with the formula $Na[AgI_2] \cdot 3H_2O$.

The complex is a colorless, needle-like crystal. It loses the water of crystallization on exposure to dry air, deliquescing and at the same time decomposing in contact with water vapor. The crystal data of this compound are given in Table 3.

Table 3. Crystal data

Formula	$AgI \cdot NaI \cdot 3H_2O$
Molecular weight	438.7
Melting point	42—43 °C; decompose
Crystal system	Orthorhombic
a	8.78 Å
b	33.5 Å
c	6.48 Å
V	1908 Å^3
d_m	3.11 g cm^{-3}
d_c	3.05 g cm^{-3}
Z	8
Absent spectra	0*kl* when *k* is odd and *h*0*l* when *l* is odd
Possible space group	Pbcm or $Pbc2_1$

It is interesting to note that the solubility curves of AgI are s-shaped and almost independent of temperature. On the other hand, the solubility of NaI is temperature dependent and the extrapolated point to zero concentration of AgI agrees with the solubility of NaI in pure water at each temperature.[8]

According to the phase rule, no more than three phases can coexist in this system. In a region where all three phases are solid, AgI and $NaI \cdot 2H_2O$ can never coexist. Other sets of solids were observed to coexist depending on conditions. Identification of these solids was made by visual observation and the X-ray diffraction method: silver iodide was of yellow powder or thin yellow flakes; NaI white powder or brilliant flakes; $NaI \cdot 2H_2O$ large transparent plates, and the complex transparent needle-like crystals or white spherulites.

Figure 4 was constructed on the basis of the phase diagrams at each temperature. We see that the liquid phase is surrounded with four kinds of surfaces (S_1—S_4), the edges of which are shown with heavy solid lines. Surfaces S_1, S_2, S_3, and S_4 consist of the points repre-

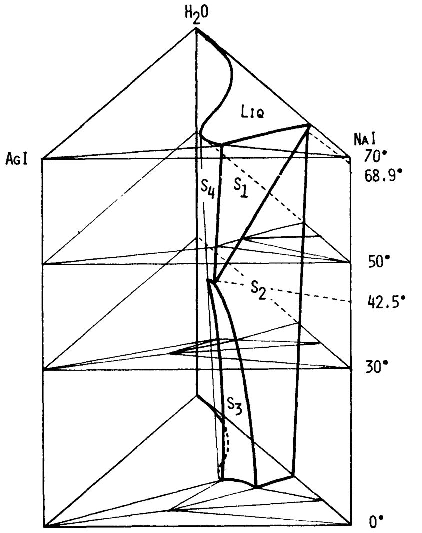

Fig. 4. Three-dimensional representation of the AgI–NaI–H_2O system (wt%).

senting the compositions of the liquid phase in equilibrium with the solids NaI, $NaI \cdot 2H_2O$, $Na[AgI_2] \cdot 3H_2O$, and AgI, respectively. The edges of the surfaces consist of the invariant points. Surfaces S_1 and S_2 are almost flat; S_3 is curved and S_4 is waved. Surface S_3 disappears above the melting point of the complex, and surface S_2 above 68.9 °C8) (or 68.1 °C11)), the decomposition point of $NaI \cdot 2H_2O$. It is not certain whether S_1 is in contact with S_3 or not, since it is difficult to make a study of the phase equilibria in the vicinity of the melting point of the complex. No ambiguity other than this seems to remain in Fig. 4 from the viewpoint of the phase rule.

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