159. *Sodium Polyiodides.*

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A phase-rule study of the system $NaI–I_2–H_2O$ at 0° reveals the compounds $NaI_4,2H_2O$ and (possibly) $NaI_2,3H_2O$ stable at that temperature. The latter belongs to a series of polyhalides containing fewer halogen atoms than any hitherto described.

Grace (J., 1931, 594) investigated the system potassium iodide–iodine–water at 25°, and found no evidence for the existence of anhydrous polyiodides of potassium; the compounds KI_3,H_2O and KI_7,H_2O, however, were formed at this temperature, and this conclusion has been confirmed by Briggs, Clack, Ballard, and Sassaman (*J. Physical Chem.*, 1940, **44**, 350), who also examined the system at other temperatures. At the same time Grace made a preliminary examination (unpublished) of the system sodium iodide–iodine–

water and found that, though it was doubtful whether any solid sodium polyiodides were formed at 25°, there was definite evidence for such compounds at lower temperatures. In continuation of this work, we have investigated the system in more detail at 0°, and find that two hydrated polyiodides are formed, one of which is a tetraiodide, $NaI_4,2H_2O$, and the other is probably a di-iodide, $NaI_2,3H_2O$. The composition of the former compound has been satisfactorily established, but further experiments to confirm that of the di-iodide have had to be left unfinished; the results hitherto obtained are therefore reported.

Experimental.

In all cases mixtures of anhydrous A.R. sodium iodide, A.R. iodine, and water were made up by weighing, either into well-stoppered bottles or, in the later experiments, into tubes which could be sealed. The mixtures were warmed to effect complete solution, then cooled with vigorous shaking and placed in a large Dewar vessel containing ice and water and kept in an ice-box. Several months were allowed to elapse for the attainment of equilibrium.

Samples of liquid and of wet solid were removed and analysed by Grace's method (*loc. cit.*); the results are given in the table, and are represented graphically in the diagram, which has

The system $NaI–I_2–H_2O$ *at* 0°.

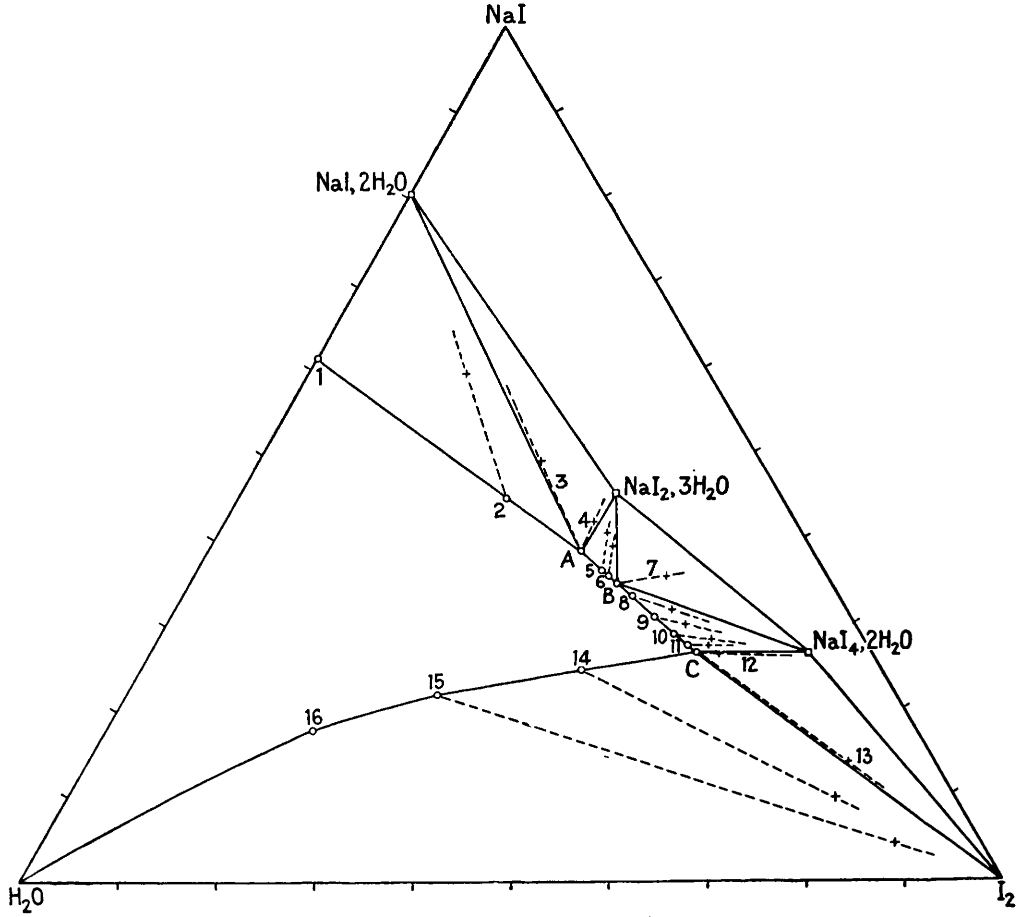
	Composition of liquid phase, %.				Composition of wet solid, %.			Nature of solid phase(s) (as deduced from diagram).
No.	NaI.	I_2.	H_2O.		NaI.	I_2.	H_2O.	
1	61·4	0·00	38·6		—	—	—	$NaI,2H_2O$ (Nos. 1–2)
2	44·9	27·5	27·4		59·3	16·1	24·6	
3	38·4	38·2	23·3	Invariant A (Nos. 3–4)	49·0	29·1	22·0	$NaI,2H_2O$ and $NaI_2,3H_2O$ (Nos. 3–4)
4	38·6	38·1	23·3		42·0	37·9	20·1	
5	36·1	41·6	22·3		40·7	39·9	19·4	$NaI_2,3H_2O$ (Nos. 5–6)
6	35·7	42·3	21·9		39·0	41·2	20·0	
7	34·9	43·9	21·1	Invariant B	35·6	48·3	16·1	$NaI_2,3H_2O$ and $NaI_4,2H_2O$
8	33·2	46·0	20·8		31·6	50·9	17·5	$NaI_4,2H_2O$ (Nos. 8–11)
9	30·8	49·5	19·6		29·9	53·1	17·0	
10	28·7	52·6	18·7		28·0	56·6	15·4	
11	27·5	54·5	18·0		27·5	56·8	15·7	
12	26·7	55·7	17·7	Invariant C (Nos. 12–13)	26·6	58·2	15·3	$NaI_4,2H_2O$ and I_2 (Nos. 12–13)
13	26·7	55·8	17·6		13·9	77·7	8·4	
14	24·7	45·1	30·2		9·6	78·3	12·1	I_2 (Nos. 14–16)
15	21·8	31·9	46·4		4·3	87·0	8·6	
16	17·7	21·2	61·1		—	—	—	

been drawn on a weight-percentage basis. It is clear that there are two polyiodides and that one of these is $NaI_4,2H_2O$. The formula $NaI_2,3H_2O$ for the other polyiodide is based on the fact that the tie lines from its solubility arc (Nos. 5 and 6) both pass very close to the point representing this composition, whilst the direction of the tie line from No. 4, which is on the invariant *A*, precludes the possibility that the compound is a still lower polyiodide, and the suggestion that it might be a tri-iodide is inconsistent with the observations. It is, moreover, found that a mixture of the composition $NaI_2,3H_2O$ solidifies on cooling and contains little or no liquid phase at 0°.

Discussion of Results.

The fact that hydrated polyiodides of sodium exist although, according to Abegg and Hamburger (*Z. anorg. Chem.*, 1906, **50**, 403), no compounds are formed in the anhydrous system, is in conformity with the known facts in the case of potassium, but the formulæ of the compounds formed are remarkable in that the number of iodine atoms combined with each alkali-metal atom is even, whereas in the potassium system it is odd. The latter represents the normal case, for, in the comprehensive series of polyhalides prepared by Cremer and Duncan (J., 1931, 1857; 1933, 181), no compounds containing an even number were encountered and it is commonly assumed that the number of halogen atoms is necessarily odd.

A few even polyhalides have, however, been described. Briggs, Greenwald, and Leonard (*J. Physical Chem.*, 1930, **34**, 1951, 2260) demonstrated the existence of CsI_4 in addition to CsI_3, a result which has been confirmed by Grace (*ibid.*, 1933, **37**, 347), and Harris (J., 1932, 1694) isolated the even polyhalide $2KBr_6,3H_2O$ from solution at 0°. Further, Rae (J., 1931, 1578) has reported the existence of $CsBr_4$ as well as $CsBr_3$, and, although Cremer and Duncan (J., 1931, 1865; 1933, 184) and Harris (J., 1932, 2709) found only $CsBr_3$, this discrepancy may be due to Rae's use of a higher temperature. Recent work by Briggs and his co-workers (*J. Physical Chem.*, 1940, **44**, 325, 350) indicates that an elevation of temperature may sometimes favour the formation of higher polyhalides. No di-iodides or other dihalides of univalent metals, however, appear to have been described before.



The system $NaI-I_2-H_2O$ *at* 0°.
(*Plotted on a weight-percentage basis.*)

It is possible that these even polyhalides have not the simple structures which they appear to have, but are molecular compounds of halides with an odd number of halogen atoms; *e.g.*, $NaI_2,3H_2O$ may be $NaI,NaI_3,6H_2O$, and $NaI_4,2H_2O$ may be $NaI_3,NaI_5,4H_2O$. The second method of formulation would be in better accord with the physicochemical work on solutions of iodine in aqueous alkali-metal monoiodides, which leads to the belief that there is an equilibrium $I' + I_2 \rightleftharpoons I_3'$, I_3' being the preponderating polyiodide ion, with higher polyiodide ions formed in appreciable concentrations when the proportion of iodine is high. An *X*-ray examination of the crystal structure of the solid polyiodides, although presenting certain practical difficulties, would probably settle this point.

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