[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Ternary Systems. XVII. Sodium Iodide, Potassium Iodide and Water. XVIII. Sodium Iodide, Sodium Iodate and Water[1]

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The relationships of the iodides and iodates of sodium and potassium have interest with respect to the preparation and separation of the salts from the Chilean caliche. The two ternary systems have been studied at three temperatures, with a view to obtaining solubility data and information as to double salt formation.

XVII. SODIUM IODIDE, POTASSIUM IODIDE AND WATER

The salts were of C. P. grade and were in some cases purified by recrystallization until experience showed that no measurable change was obtained. They were dried in an electric oven at 100° to constant weight, in order that complexes of exactly known composition might be made up. The salts were weighed into stoppered Pyrex tubes with weighed amounts of water and stirred by mechanical inversion in a water thermostat for periods of a few hours, a time which was shown by analysis to be sufficient for attainment of equilibrium. Small samples of the saturated solution were drawn by suction into a pipet with filtration; one such was dried to constant weight in the oven, while a second was analyzed gravimetrically for total iodide content. With these data the composition with respect to the three components was calculated with of course considerable multiplication of errors because of the indirect determination of sodium and potassium. The composition of the solid phases was determined by algebraic extrapolation of the tie lines through the two points representing the saturated solutions and the original complexes taken.[2] The results are given in Table I.

The solubility of the two pure salts at the three temperatures, obtained by the evaporation of the solutions, cannot with advantage be compared with the figures of the average curves given in the "International Critical Tables,"[3] where the inaccuracy given is ±2%, but a comparison with the recent carefully determined figures of Scott and Frazier[4] and Scott and Durham[5] shows agreement with their direct measurements at 25° within one part in 2000 for the potassium iodide and 1 part in 1600 for the sodium iodide; the agreement with their interpolated curves at 8 and 40° appears

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(1) The material of this paper is from the dissertation of Herbert S. Willson, presented in partial fulfilment of the requirements for the degree of Ph.D. at New York University, 1932.

(2) Hill and Ricci, THIS JOURNAL, **53**, 4306 (1931).

(3) "International Critical Tables," 1928, Vol. IV, pp. 235, 239.

(4) Scott and Frazier, *J. Phys. Chem.*, **31**, 459 (1927).

(5) Scott and Durham, *ibid.*, **34**, 1424 (1930).

TABLE I

SYSTEM $KI-NaI-H_2O$

Temp., °C.	Original complex Wt. % KI	Original complex Wt. % NaI	Saturated solution Wt. % KI	Saturated solution Wt. % NaI	Solid phases
8	...	0.00	57.33	0.00	KI
	46.00	17.40	37.54	19.97	KI
	30.22	35.10	19.20	40.55	KI
	16.71	50.58	8.36	55.58	KI
	9.97	59.90	7.44	57.13	KI + $NaI\cdot 2H_2O$
	5.16	60.12	5.82	58.23	$NaI\cdot 2H_2O$
	3.74	60.99	4.13	59.48	$NaI\cdot 2H_2O$
	0.00	...	0.00	62.49	$NaI\cdot 2H_2O$
25	...	0.00	59.78	0.00	KI
	57.62	7.75	50.32	9.29	KI
	52.57	14.40	42.08	17.60	KI
	56.94	18.88	29.79	30.55	KI
	48.33	26.34	21.43	40.11	KI
	45.32	30.63	15.90	46.91	KI
	36.13	39.14	10.60	54.49	KI
	9.24	61.40	7.59	59.35	KI + $NaI\cdot 2H_2O$
	5.78	64.52	7.06	59.71	$NaI\cdot 2H_2O$
	5.97	63.02	6.80	59.97	$NaI\cdot 2H_2O$
	4.20	66.31	5.44	60.74	$NaI\cdot 2H_2O$
	3.60	67.09	4.78	61.35	$NaI\cdot 2H_2O$
	1.38	69.42	2.17	63.15	$NaI\cdot 2H_2O$
	0.00	...	0.00	64.72	$NaI\cdot 2H_2O$
40	...	0.00	61.73	0.00	KI
	61.77	9.79	48.04	13.47	KI
	51.27	19.62	35.55	26.20	KI
	36.78	33.77	21.33	42.04	KI
	30.33	44.62	9.68	57.85	KI
	11.47	62.83	7.23	62.34	KI + $NaI\cdot 2H_2O$
	3.21	70.11	4.81	63.92	$NaI\cdot 2H_2O$
	0.00	...	0.00	67.35	$NaI\cdot 2H_2O$

to be equally good. The solid phases at the three temperatures, as shown in Fig. 1, are limited to the compounds potassium iodide and $NaI\cdot 2H_2O$; no double salt is found, and solid solution was not found to occur, within the degree of accuracy of the work. This degree of accuracy, as tested by the method of algebraic extrapolation of tie lines, is doubtless lessened considerably by the use of an indirect method of analysis and the large multiplication of errors which therefore follows. Extrapolations of the tie lines at three temperatures to the composition of the simple salts assumed gave an average variation of 0.88% from the potassium iodide and of 1.46% from the $NaI\cdot 2H_2O$, with no steady drift to the variation; this leaves no doubt as to the identity of the salts, whether or not it is definitive as to the possible occurrence of solid solution within very narrow limits. It will be noted that at the three temperatures used the isothermally invariant point is well over toward the side of the sodium iodide, leaving only a comparatively short solubility curve for that compound.

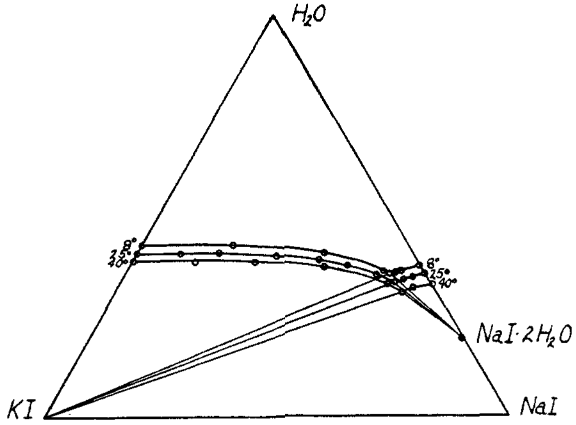

Fig. 1.—The system KI–NaI–H_2O.

XVIII. SODIUM IODIDE, SODIUM IODATE AND WATER

The sodium iodate used in this work was recrystallized from water and dehydrated in an electric oven at 100°. The solubility experiments were conducted as described in the previous section, with the exception that the time given for attainment of equilibrium was from four to seven days. For the analysis, the iodate was determined in a sample by the usual method of iodimetry, thiosulfate being used in the titration. The water was determined in a second sample by evaporation at 100°, the time required for reaching constant weight being about one week. The error brought in during evaporation by oxidation of iodide by iodate was found to be much less than was feared from the color changes which the material showed; it amounted in cases where analysis was made to a loss of only 0.3% of the iodate present, which would affect the figures only in the fourth significant place, and was therefore neglected. During the solubility experiments some slight decomposition, probably photochemical, always took place, as evidenced by the yellow color of the solutions; again, however, analysis showed that the iodine set free amounted to only a few thousandths of one per cent., a wholly negligible amount. The results of the experiments are given in Table II.

Algebraic extrapolation of tie lines through the points showed fairly good concordance; in only four cases is the variation from the true composition more than 1%.

The above figures, when plotted as shown in Figs. 2, 3 and 4, indicate two points of some interest with respect to the system. The first is that the solubility of the iodate is very greatly decreased by the presence of iodide, falling at the saturation point to as low as 0.02% at 8°, and rising

TABLE II

SYSTEM $NaIO_3$–NaI–H_2O

S.S. = solid solution.

	Original complex		Saturated solution			
Temp., °C.	Wt % NaI	Wt. % $NaIO_3$	Wt % NaI	Wt % $NaIO_3$	Density	Solid phases
8	0.00	...	0.00	3.89	1.035	$NaIO_3\cdot 5H_2O$
	5.85	4.39	6.05	1.99	1.069	$NaIO_3\cdot 5H_2O$
	15.08	9.79	17.18	1.44	1.169	$NaIO_3\cdot 5H_2O$
	19.67	10.33	19.47	1.84	1.196	$NaIO_3\cdot 5H_2O$ + S.S.
	27.60	13.42	25.20	0.72	1.249	S.S.
	40.01	5.07	40.70	.08	1.445	S.S.
	55.44	4.53	57.87	.02	...	S.S.
	61.58	5.03	62.44	.02	1.861	S.S. + $NaI\cdot 2H_2O$
	...	0.00	62.49	.00	...	$NaI\cdot 2H_2O$
25	0.00	...	0.00	8.67	1.077	$NaIO_3\cdot H_2O$
	9.93	16.16	11.57	4.23	1.107	$NaIO_3\cdot H_2O$
	20.99	15.94	24.54	2.68	1.253	$NaIO_3\cdot H_2O$
	26.86	8.37	28.70	2.48	1.290	$NaIO_3\cdot H_2O$
	31.25	3.73	31.72	2.41	1.340	$NaIO_3\cdot H_2O$
	30.32	6.07	31.74	2.36	1.340	$NaIO_3\cdot H_2O$
	31.24	7.03	31.99	2.36	1.341	$NaIO_3\cdot H_2O$ + S.S.
	33.03	7.79	33.04	2.04	1.352	S.S.
	36.56	9.09	36.64	1.22	1.377	S.S.
	45.03	5.03	46.08	0.31	...	S.S.
	52.62	9.37	56.83	.17	1.722	S.S.
	67.58	2.34	64.67	.08	...	S.S. + $NaI\cdot 2H_2O$
	...	0.00	64.72	.00	...	$NaI\cdot 2H_2O$
40	...	0.00	0.00	11.70		$NaIO_3\cdot H_2O$
	15.00	7.15	15.33	5.24		$NaIO_3\cdot H_2O$
	16.96	10.54	18.16	4.74		$NaIO_3\cdot H_2O$
	19.23	6.49	19.64	4.47		$NaIO_3\cdot H_2O$
	21.03	8.02	22.06	3.90		$NaIO_3\cdot H_2O$
	26.42	5.09	26.85	3.49		$NaIO_3$
	31.78	8.30	33.65	2.92		$NaIO_3$
	39.84	4.35	40.52	2.78		$NaIO_3$
	39.00	9.97	41.16	2.79		$NaIO_3$ + S.S.
	39.91	9.99	41.30	2.80		S.S.
	40.00	17.14	42.55	2.72		S.S.
	50.31	5.43	51.97	0.58		S.S.
	62.00	4.00	64.40	.47		S.S.
	63.96	4.00	66.15	.32		S.S.
	...	...	67.58	.28		S.S. + $NaI\cdot 2H_2O$
	...	...	67.35	.00		$NaI\cdot 2H_2O$

only to 0.3% at 40°. This indicates that sodium iodide can be freed from iodate by recrystallization only with difficulty and only when the initial iodate concentration is lower than the above figures, which may well be the explanation of the very frequent appearance of iodate as impurity in commercial iodide, if the source of the material is such as would contain iodate. It will be shown in a later publication that this condition does not occur in the system containing the two corresponding potassium salts, which may be the reason that the potassium iodide quite regularly has a higher degree of purity than the sodium salt.

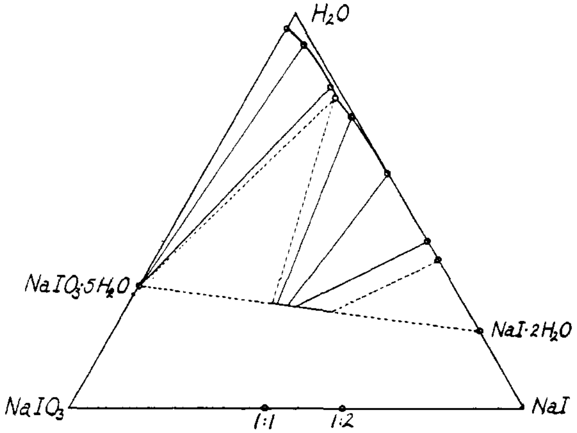

Fig. 2.—8° Isotherm: $NaIO_3$–NaI–H_2O.

The second point of interest is the occurrence of a new complex iodide-iodate, which was found at all three temperatures and which is the saturating phase over a considerable part of the entire range of concentrations. This was found to be not a double salt, but a solid solution of the two hydrated salts $NaIO_3·5H_2O$ and $NaI·2H_2O$. The evidence lies not merely in the failure of the tie lines to intersect with any reasonable constancy at a single point, but also in the isolation and analysis of the solid phase. For this test the ordinary method of filtration and analysis offered difficulty,

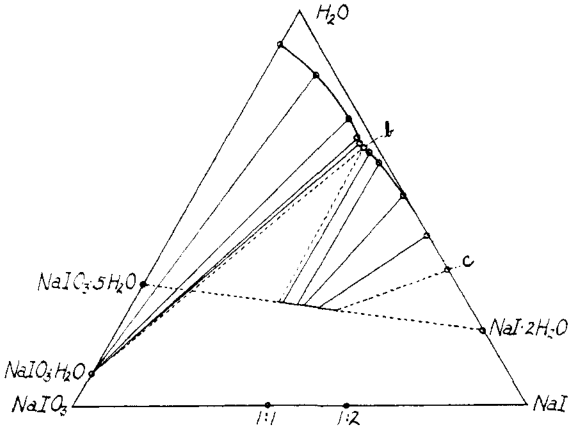

Fig. 3.—25° Isotherm: $NaIO_3$–NaI–H_2O.

for the solid obtained from the solubility experiments was very finely divided and carried a large percentage of highly concentrated solution upon its surface, making a very large correction necessary. To avoid this condition, crystals were slowly grown from a solution made up in the area of undersaturation above the line *b-c* (Fig. 3) by evaporation over sulfuric acid at room temperatures. The crystals thus obtained were well formed and several millimeters in diameter, and could be quickly centrifuged to a condition of superficial dryness so that they ran easily on the glass of a test-tube with no evidence of stickiness; it is quite certain that they could not have contained more than very small amounts of solution. The results of their analysis are given in the first two columns of Table III.

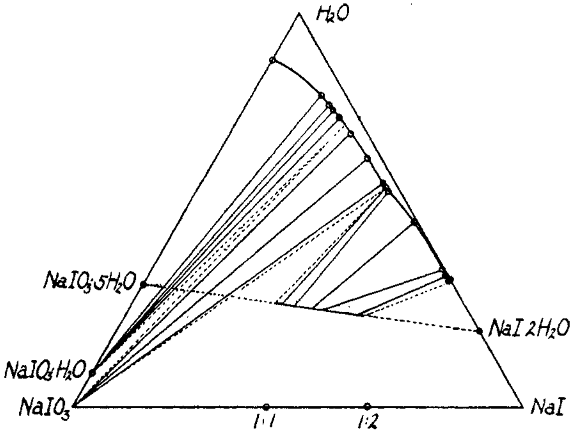

Fig. 4.—40° Isotherm: $NaIO_3$–NaI–H_2O.

TABLE III

ANALYSIS OF SOLID SOLUTIONS

	I	II	III
Wt. % $NaIO_3$	33.24	30.31	35.6
Wt. % NaI	38.09	44.41	40.2

These first two points will be found to represent quite different compositions, and to fall fairly close to the line drawn as representing the series of solid solutions. The third analysis represents a sample taken directly from a solubility experiment and filtered rapidly; it was put to dry in a desiccator containing a partially dehydrated mixture of $NaIO_3{\cdot}H_2O$ and $NaI{\cdot}2H_2O$. In two months time it lost 14.64% of water and reached a constant weight which remained unchanged for seven months. The analysis of the solution from which it was formed being known, the necessary correction[6] was made in the analysis of the solid; the corrected analysis, shown in the third column, also falls close to the expected line.

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(6) Hill, THIS JOURNAL, **52**, 3823 (1930).

The wide variation in the composition of the three samples is convincing evidence of solid solution. The position of the three points is sufficiently close to the line joining the composition of $NaI{\cdot}2H_2O$ and $NaIO_3{\cdot}5H_2O$ to indicate that these are the solids entering into the solid solution. That this should be the case at the lower temperature is in no wise striking; but that it should also be so at 40°, some 20° above the transition temperature of $NaIO_3{\cdot}5H_2O$[7] involves the conclusion that the vapor tension of $NaIO_3{\cdot}5H_2O$ in the solid solution is considerably reduced by the presence of the $NaI{\cdot}2H_2O$ in the same molecule.

It will be noted that the area of solid solutions begins quite close to the ratio of 1:1 for the two salts, corresponding to the formula of a comparatively simple double salt, $NaIO_3{\cdot}NaI{\cdot}7H_2O$, and extends with increase in the amount of iodide to a point near to or at the 1:2 ratio, $NaIO_3{\cdot}2NaI{\cdot}9H_2O$. This approximation of solid solution to the composition of stoichiometrical ratios, well known in the case of glaserite, has been noted in a number of interesting cases.[8] In commenting upon these, Timmermans[9] remarks that they may possibly be regarded as examples of Berthollidean compounds of variable composition as opposed to Daltonian compounds of fixed composition. Without committing one's self to any fundamental theory in the matter, one is obliged to note the frequency with which such solid solutions approximate the stoichiometrical ratios, and to suspect that doubtless certain substances have been reported as compounds on this basis whereas they are truly solid solutions.

Summary

1. The system $NaI-KI-H_2O$ has been studied at 8, 25 and 40°; no compound formation occurs.

2. The system $NaIO_3-NaI-H_2O$ has been studied at the same three temperatures; at all of these there exists, over a wide range of liquid concentration, a series of solid solutions of the composition $(NaIO_3{\cdot}5H_2O)_n{\cdot}(NaI{\cdot}2H_2O)_m$, beginning at the 1:1 ratio and extending to approximately the 1:2 ratio.

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[7] Foote and Vance, *Am. J. Sci.*, **16**, 68 (1928); **18**, 375 (1929); Hill and Donovan, THIS JOURNAL, **53**, 934 (1931).

[8] Kurnakow, *Z. anorg. Chem.*, **88**, 109 (1914); Foote and Saxton, THIS JOURNAL, **36**, 1695 (1914); Clendennin and Rivett, *J. Chem. Soc.*, **119**, 1329 (1921).

[9] Timmermans, "La Notion d'Espèce en Chimie," Paris, 1928, p. 16.