

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

The Ternary Systems Sodium Iodate–Sodium Chlorate–Water and Potassium Iodate–Potassium Chlorate–Water at 25 and 50°

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Introduction.—The results of studies of ternary systems involving either sodium iodate or sodium chlorate indicated that it would be interesting to investigate the system sodium iodate–sodium chlorate–water. Sodium iodate, for example, is known to exhibit a rather marked tendency to form double compounds with other sodium salts, such as sodium chloride, bromide, iodide, nitrate and sulfate.¹ Sodium chlorate, on the other hand, has been found so far to form only one double salt, namely, $\text{NaClO}_3 \cdot 3\text{Na}_2\text{SO}_4$.² The present solubility measurements on the system sodium iodate–sodium chlorate–water were made for the purpose of extending the information on the two series of salts, alkali iodates and alkali chlorates, and to investigate any possible compound formation or solid solution taking place between the two specific salts at these temperatures. The system potassium iodate–potassium chlorate–water was studied simultaneously, both to extend the measurements to the corresponding potassium salt system and, by taking advantage of the more certain attainment of equilibrium in the latter system, to use it as a check on the analytical method needed for the investigation of the more troublesome sodium salt system. The results of the phase rule study of these systems, at 25 and 50°, indicate no compound formation in either combination, and no solid solution for any of the solid phases, within the limits of experimental accuracy.

Materials and Methods.—The sodium and potassium iodates were recrystallized c. p. material, dried at 100–110°. Analysis by titration with standard sodium thiosulfate (standardized against very pure potassium iodate), showed them both to be 100.0% pure. The chlorates were high grade c. p. material, powdered and dried at 150–200°.

The procedure for the solubility determinations was in general that usually described for similar phase rule investigations. Densities of saturated solutions, reported for the 25° isotherms, were determined by means of pipets calibrated for delivery. Temperatures were controlled to $\pm 0.01^\circ$.

For the analysis of the saturated solutions, the iodate was determined by treatment with excess of potassium iodide and a limited amount of acetic acid, and titration of the

liberated iodine by means of standard thiosulfate solution. Tests showed this method for the determination of iodate in the presence of large amounts of chlorate to be very exact. The procedure was to treat the iodate–chlorate solution, diluted to 50–60 ml., with 5–6 g. of potassium iodide and 2 ml. of glacial acetic acid, and to titrate at once with thiosulfate. In such low acidity the interference due to oxidation of iodide by even large amounts of chlorate, proves to be altogether negligible, while the reaction of the iodate is complete and rapid. Employing this acidity throughout, very small amounts (0.1 to 0.3 g.) of sodium iodate were titrated in the presence of up to 20 g. of sodium chlorate, the determination proving exact in every case (the average error being one part in three thousand).

A similar procedure was described by Barneby,³ who, however, tried it in the presence of much smaller amounts of chlorate only.

The total dissolved solid was determined by evaporation to dryness, and the chlorate salt then calculated by difference.

No difficulty was encountered in the solubility determinations for the potassium salt system. The usual procedure—preparation of complexes of exact composition, analysis of the filtered saturated solution and identification of solid phases by algebraic extrapolation of the tie-lines connecting these two compositions—proved satisfactory and very accurate. To ensure attainment of equilibrium, the mixtures were stirred for periods of five to nine days, and the equilibrium checked by repeated analysis of the solution. The mean error of the extrapolation of tie-lines to the compositions of the pure phases was only 0.09%, verifying the applicability of the titration method employed and the dependability of the experimental procedure in general.

The attainment of solubility equilibrium in the sodium iodate–sodium chlorate system is much slower. Complexes of exact composition can be prepared only from anhydrous sodium iodate, while the stable phase for this salt, for the whole of the 25° and part of the 50° isotherm, is the monohydrate, $\text{NaIO}_3 \cdot \text{H}_2\text{O}$. The hydration of sodium iodate, however, particularly in the presence of high concentrations of other salts, is extremely slow in reaching completion. In every case in which the original sodium iodate was seeded with monohydrate crystals in the presence of dissolved sodium chlorate, even though the solid phase formed was always quite obviously the correct hydrate from its very distinctive appearance, nevertheless the mathematical extrapolation of tie-lines through the points representing saturated solution and total complex was always such as to indicate that the remaining solid contained about 1% either of sodium chlorate (in solid solution) or of unchanged anhydrous sodium iodate. This was observed repeatedly even for mixtures stirred for as long as sixty days (at 25°). Many experiments were

(1) Ricci, *THIS JOURNAL*, **56**, 295 (1934).(2) Ricci and Yanick, *ibid.*, **59**, 491 (1937).(3) Barneby, *ibid.*, **38**, 330 (1916).

made with this procedure, the results of which, however, are not included in the tables here presented, inasmuch as it was proved subsequently that the apparent deviation of the composition of the solid phase from that of pure $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ was due simply to lack of equilibrium or incomplete hydration, and that there is in reality no formation of mixed crystals at all at the temperatures studied.

The procedure finally employed to obtain equilibrium results for this system, wherever the solid phase is $\text{NaIO}_3 \cdot \text{H}_2\text{O}$, involved the addition of the component sodium chlorate to mixtures already containing the completely hydrated $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ and water, obtained by stirring sodium iodate and water, seeded with the monohydrate, for several days. As the composition of the total complex could not be known with any accuracy in such a procedure, the wet residue was analyzed in every case, and the solid phase then identified by algebraic extrapolation through saturated solution and wet residue. A check on the attainment of equilibrium was again made and the minimum time allowed (six days at 25°) was found to be sufficient; the analysis of one solution, stirred for six days, gave 1.52% NaIO_3 and 43.00% NaClO_3 ; after nineteen more days, 1.52% NaIO_3 and 42.98% NaClO_3 .

For all other solid phases in both systems, at the temperatures studied, equilibrium was readily attained from the original complexes of exact composition, and the phases were regularly identified by ordinary algebraic extrapolation through solution and total complex. At 50° in the sodium salt system, metastability for either anhydrous or hydrated sodium iodate can be maintained easily, in the first case by starting with anhydrous sodium iodate and not seeding, and in the second case by following the procedure described above, hydrating the sodium iodate completely before addition of sodium chlorate.

TABLE I
SYSTEM $\text{KIO}_3\text{-KClO}_3\text{-H}_2\text{O}$

Saturated solution			Original complex		Solid phase
KIO_3	KClO_3	Density	KIO_3	KClO_3	
---25°---					
8.45	0.00	1.043			KIO_3
7.05	2.31	1.070	20.00	2.00	KIO_3
5.85	5.31	1.082	19.04	4.58	KIO_3
5.43	6.78	1.091	18.00	6.54	$\text{KIO}_3 + \text{KClO}_3$
5.44	6.79	1.092	12.48	12.54	$\text{KIO}_3 + \text{KClO}_3$
5.44	6.81	1.089	6.99	17.92	$\text{KIO}_3 + \text{KClO}_3$
5.42	6.81	1.086	5.01	19.00	$\text{KIO}_3 + \text{KClO}_3$
5.43	6.80	1.090(av.)			$\text{KIO}_3 + \text{KClO}_3$
2.92	7.31	1.068	2.52	20.02	KClO_3
0.00	7.90	1.048			KClO_3
---50°---					
13.21	0.00				KIO_3
10.87	3.71		27.07	3.03	KIO_3
8.76	8.58		25.06	7.00	KIO_3
7.26	13.76		22.04	11.54	$\text{KIO}_3 + \text{KClO}_3$
7.27	13.77		14.03	18.93	$\text{KIO}_3 + \text{KClO}_3$
7.27	13.77		7.98	24.12	$\text{KIO}_3 + \text{KClO}_3$
7.27	13.77(av.)				$\text{KIO}_3 + \text{KClO}_3$
5.27	14.31		4.48	27.04	KClO_3
2.41	15.11		2.03	28.17	KClO_3
0.00	15.78				KClO_3

Results.—The results for the system $\text{KIO}_3\text{-KClO}_3\text{-H}_2\text{O}$ are shown in Table I and Fig. 1;

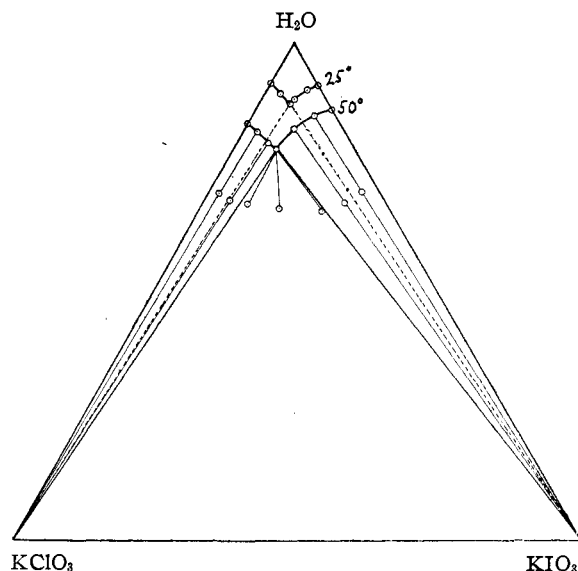


Fig. 1.—System $\text{KIO}_3\text{-KClO}_3\text{-H}_2\text{O}$ at 25 and 50° .

those for the system $\text{NaIO}_3\text{-NaClO}_3\text{-H}_2\text{O}$ in Tables II and III and Figs. 2 and 3.

TABLE II
SYSTEM $\text{NaIO}_3\text{-NaClO}_3\text{-H}_2\text{O}$ AT 25°

Saturated solution			Wet residue		Solid phase
NaIO_3	NaClO_3	Density	NaIO_3	NaClO_3	
8.57	0.00	1.075			$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
4.51	8.36	1.098	25.12	6.33	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
3.14	16.50	1.146	24.91	12.39	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
2.43	24.67	1.204	27.37	17.78	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
1.97	32.57	1.273	29.77	22.53	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
1.69	38.66	1.332	28.02	27.40	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
1.52	42.99		10.00	38.96	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
(total complex)					
1.46	44.56	1.396	28.04	31.48	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
1.39	46.37	1.404	23.40	35.03	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
1.33	48.13	1.425	28.22	33.83	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
1.30	49.19	1.440	24.57	36.50	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$
Original Complex					
1.29	49.42	1.445	5.99	46.94	$\text{NaIO}_3 \cdot \text{H}_2\text{O} + \text{NaClO}_3$
1.29	49.40		9.98	44.97	$\text{NaIO}_3 \cdot \text{H}_2\text{O} + \text{NaClO}_3$
1.29	49.32	1.441	8.0	47.0	$\text{NaIO}_3 \cdot \text{H}_2\text{O} + \text{NaClO}_3$
1.29	49.44	1.446	4.99	50.49	$\text{NaIO}_3 \cdot \text{H}_2\text{O} + \text{NaClO}_3$
1.29	49.32	1.444	5.0	54.0	$\text{NaIO}_3 \cdot \text{H}_2\text{O} + \text{NaClO}_3$
1.29	49.40		2.05	56.23	$\text{NaIO}_3 \cdot \text{H}_2\text{O} + \text{NaClO}_3$
1.29	49.38	1.444(av.)			$\text{NaIO}_3 \cdot \text{H}_2\text{O} + \text{NaClO}_3$
1.16	49.52	1.444	1.01	55.95	NaClO_3
0.00	50.14				NaClO_3

In the potassium salt system the only solid phases found are the pure anhydrous salts themselves; the algebraic extrapolation of tie-lines indicates, at both temperatures, no solid solution formation on either side of the diagram.

Similarly, in the sodium salt system, no compound formation is found, and the salts again

TABLE III
SYSTEM $\text{NaIO}_3\text{-NaClO}_3\text{-H}_2\text{O}$ AT 50°

Saturated solution Wt. %		Wet residue Wt. %		Solid phase ^b
NaIO_3	NaClO_3	NaIO_3	NaClO_3	
13.49	0.00			$\text{NaIO}_3\cdot\text{H}_2\text{O}$
7.67	10.02	36.02	6.81	$\text{NaIO}_3\cdot\text{H}_2\text{O}$
5.69	16.56	37.87	10.26	$\text{NaIO}_3\cdot\text{H}_2\text{O}$
4.91	20.61	31.69	14.17	$\text{NaIO}_3\cdot\text{H}_2\text{O}$
3.23	33.33	32.49	22.22	$\text{NaIO}_3\cdot\text{H}_2\text{O}$
2.41	43.71	31.24	29.29	$\text{NaIO}_3\cdot\text{H}_2\text{O}$
2.12	48.95	31.48	32.99	$\text{NaIO}_3\cdot\text{H}_2\text{O}$ (m)
1.92	53.20	27.13	38.23	$\text{NaIO}_3\cdot\text{H}_2\text{O}$ (m)
1.87	54.58	32.29	36.23	$\text{NaIO}_3\cdot\text{H}_2\text{O}$ (m) + NaClO_3
Original Complex				
1.87	54.61	12.0	54.0	$\text{NaIO}_3\cdot\text{H}_2\text{O}$ (m) + NaClO_3
1.87	54.59(av.)			$\text{NaIO}_3\cdot\text{H}_2\text{O}$ (m) + NaClO_3
2.50	43.41	17.99	36.52	NaIO_3 (m)
(2.2	45.) ^a			NaIO_3 + $\text{NaIO}_3\cdot\text{H}_2\text{O}$
2.14	47.86	17.01	40.58	NaIO_3
1.75	53.83	16.99	45.48	NaIO_3
1.71	54.69	11.99	53.97	NaIO_3 + NaClO_3
1.68	54.74	2.99	61.01	NaIO_3 + NaClO_3
1.69	54.71(av.)			NaIO_3 + NaClO_3
1.26	54.98	1.01	63.96	NaClO_3
0.00	55.74			NaClO_3

^a By interpolation. ^b (m) = Metastable.

exist in the pure state, without the formation of mixed crystals, within the limits of the accuracy of the algebraic extrapolation of tie-lines. For the case of the phases anhydrous sodium chlorate

the algebraic mean being less than 0.004%. For the monohydrate of sodium iodate as solid phase, the extrapolation was by means of the saturated solution and the composition of the wet residue. At 25° , at which temperature the wet residue can be analyzed quite accurately, the mean absolute deviation of the extrapolated tie-lines from the point representing $\text{NaIO}_3\cdot\text{H}_2\text{O}$ was 0.14%, the mean algebraic error being only -0.03% . At 50° , however, a wet residue cannot be analyzed so accurately, due to evaporation during sampling; as a consequence the absolute average error of extrapolation at this temperature was 0.38%, the algebraic average, however, being only -0.08% .

It can be said, therefore, that for all phases and at both temperatures the salts exist in the pure state, without formation of mixed crystals.

Anhydrous sodium iodate exists as a stable solid phase for the system $\text{NaIO}_3\text{-NaClO}_3\text{-H}_2\text{O}$ at 50° , at high concentrations of sodium chlorate, even though the transition temperature between anhydrous and monohydrated sodium iodate in the binary system with water is 23.4° above this temperature. At the same time the solubility curve of the monohydrate can be followed con-

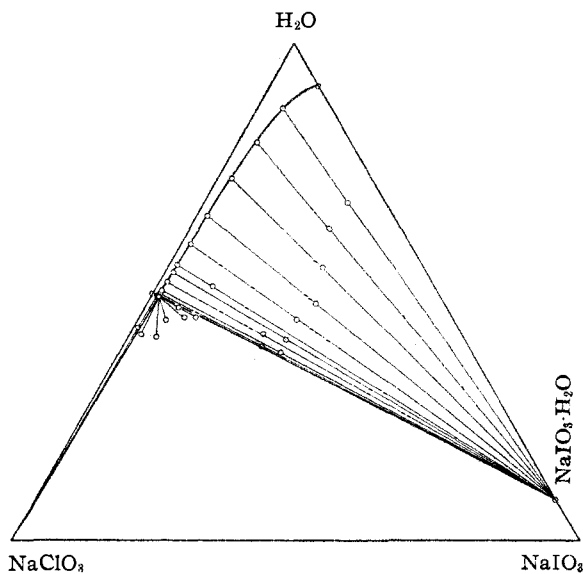


Fig. 2.—System $\text{NaIO}_3\text{-NaClO}_3\text{-H}_2\text{O}$ at 25° .

and anhydrous sodium iodate, this accuracy is quite high, since the extrapolation is performed through the accurately analyzed solution and the composition of a total complex of exact preparation. The mean absolute deviation from purity for these solid phases, as indicated by the extrapolations for both temperatures, was 0.026%,

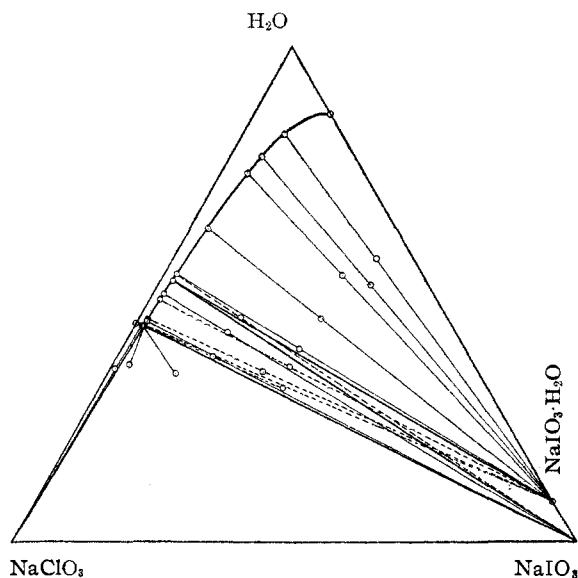


Fig. 3.—System $\text{NaIO}_3\text{-NaClO}_3\text{-H}_2\text{O}$ at 50° .

tinuously to a metastable isothermally invariant point, at which the solid phases are NaClO_3 and $\text{NaIO}_3\cdot\text{H}_2\text{O}$. The two solubility curves, however—that for anhydrous and that for hydrated sodium iodate—are so nearly parallel and close together that it would be very difficult to determine their point of crossing directly. It can be

estimated, nevertheless, from the concentration of sodium iodate along the two curves, that the isothermally invariant point representing equilibrium between the two forms of the iodate must have the approximate composition 2.2% NaIO₃ and 45% NaClO₃. At higher concentrations of sodium chlorate the anhydrous sodium iodate has the lower solubility and is therefore the stable phase. These relationships are indicated in the table of results for this isotherm, but cannot be shown with any clearness in the figure.

Summary

Solubility measurements are given for the two ternary systems KIO₃-KClO₃-H₂O and NaIO₃-NaClO₃-H₂O at 25 and 50°. Neither compound formation nor solid solution is observed for either system at these temperatures. In the 50° isotherm of the system NaIO₃-NaClO₃-H₂O, anhydrous sodium iodate is found to exist as a stable phase over a limited range of the solubility curve at high concentrations of sodium chlorate. NEW YORK, N. Y. RECEIVED JUNE 17, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Solubility of Halides in Anhydrous Acetic Acid

BY ARTHUR W. DAVIDSON AND WILBERT CHAPPELL

It was reported by Benrath,¹ as early as 1905, that a large number of chlorides are appreciably soluble in glacial acetic acid and may be crystallized unchanged from such solutions. Quantitative data on the solubility of halides in this solvent are limited, however, to the still earlier work of Étard² on mercuric chloride, the studies of Menschutkin on systems of acetic acid with calcium chloride, magnesium bromide and iodide,³ and antimony chloride and bromide,⁴ and the recent determination by Scholl, Hutchison and Chandlee⁵ of the solubility of barium chloride in pure acetic acid and in the presence of various concentrations of sodium bromide.

The present paper includes solubility data, over a wide range of temperature, for sodium, potassium, ammonium, barium, strontium, cupric and mercuric chlorides, as well as for mercuric bromide and iodide. Of these salts, strontium chloride proved to be by far the most soluble at room temperature, and mercuric chloride to have the greatest solubility at the boiling point of the solvent. Experiments with cadmium chloride showed the solubility of this salt to be too small to be measured.

Method

Preparation of Materials.—Pure anhydrous acetic acid was prepared as described in previous papers of this series.

- (1) Benrath, *J. prakt. Chem.*, [2] **72**, 228 (1905); see also Davidson, *THIS JOURNAL*, **50**, 1890 (1928).
- (2) Étard, *Ann. chim. phys.*, [7] **2**, 555 (1894).
- (3) Menschutkin, *Z. anorg. Chem.*, **54**, 89 (1907).
- (4) Menschutkin, *J. Russ. Phys.-Chem. Soc.*, **43**, 1785 (1911).
- (5) Scholl, Hutchison and Chandlee, *THIS JOURNAL*, **55**, 3081 (1933).

All the salts used, except mercuric bromide and iodide, were purified by recrystallization and dried to constant weight under suitable conditions. Mercuric bromide and iodide were prepared by precipitation, and were dried for several days at 110 to 115°.

Determination of Solubility.—In every case except for the chlorides of barium and strontium, the synthetic method, as described in previous papers, was used. Duplicate determinations, with the usual precautions, were made of the equilibrium temperatures. The values given are believed to be correct to within 1° in the case of ammonium chloride and the mercuric halides, and to within 3° elsewhere, even in the case of cupric chloride, which gives a very steep temperature-concentration curve.

For barium and strontium chlorides the analytical method was used for determining solubilities. About 100 cc. of the solvent was placed in contact with an excess of the solid solute in a tightly stoppered bottle, which was then maintained at the desired temperature in a suitably adjusted thermostat. After equilibrium had been reached, filtered samples were withdrawn by means of a pipet with a bit of cotton fitted over its tip, and the chlorine content of each sample was determined by the usual gravimetric method.

Analysis of Solid Phases.—The solids to be analyzed were separated from their saturated solutions by filtration with gentle suction, rapidly pressed between dried pieces of porous tile, and allowed to remain over pellets of sodium hydroxide in a desiccator, for a few minutes only. Samples were then weighed as quickly as possible, and their chlorine content was determined in the usual way.

Results

Cupric, Sodium, Potassium and Ammonium Chlorides.—In the tables given below, *S* denotes the mole percentage of solute, and *T* the corresponding equilibrium temperature. These data are presented graphically in Fig. 1.