tem is seen to belong to Type II of the Roozeboom classification of such distributions between liquid and solid solutions. Although the experimental points do not actually cross the diagonal as x and y approach 1, as is demanded by Roozeboom's Type II, it may be calculated that with $m = 0.6$ and $K = 100$ in the equation

$$\frac{y}{1-y} = K\left(\frac{x}{1-x}\right)^m \qquad (5)$$

which is derivable from equation (2), the curve of Fig. 5, plotting y against x, will cross the diagonal at $x = 0.99999$, a value beyond experimental handling.

Summary

1. The solubility equilibrium relations in the system $Ba(BrO_3)_2$–$Ba(ClO_3)_2$–H_2O were studied at 25°.

2. The formation of a continuous solid solution of the monohydrates of the two salts at this temperature explains the difficulties in the attempted analytical determination of bromate in the presence of chlorate by precipitation with excess of some barium salt such as barium chloride.

3. The system is found to belong to Type II of Roozeboom's classification of solid solutions, involving positive deviations from ideality.

4. The distribution constant for the two isomorphous salts between their aqueous solutions and the saturating solid solution was determined from a plot of the data. Log K so found = 2.0_0, in fair agreement with the value calculated from the separate aqueous solubilities of the two salts, namely, $\log K = 1.8_1$.

5. The disagreement between calculated and observed distribution constants is attributed chiefly to the uncertainty of the value of the activity coefficient for $Ba(ClO_3)_2 \cdot H_2O$, and it is suggested that the distribution constant derived from this type of equilibrium study may be used for the calculation of such an activity coefficient.

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

The Systems $NaClO_3$–$NaBr$–H_2O, $NaClO_3$–NaI–H_2O and $NaClO_3$–$NaNO_3$–H_2O, at 25°C.

BY J. E. RICCI

The solubility measurements here reported[1] have been made as additions to the systematic study of the equilibrium relations in aqueous systems involving sodium halates, particularly sodium chlorate.[2]

The experimental procedure was that already described for similar investigations. The salts were all C. P. or "reagent" materials, used without further purification. Equilibrium was established in representative instances by constancy of composition upon repeated analysis. Complexes were stirred for at least two days in every case, at a temperature of 25 ± 0.05°.

In the first two systems (I, $NaClO_3$–$NaBr$–H_2O; II, $NaClO_3$–NaI–H_2O) the analysis of the saturated aqueous solution involved argentometric titration of the halide salt, with eosin as adsorption indicator, determination of water in a separate sample by evaporation, and calculation of the sodium chlorate by difference. A few of the halide determinations for the isothermally invariant points were verified by the Volhard method. In the third system (III, $NaClO_3$–$NaNO_3$–H_2O) the chlorate was determined independently by treatment with standard arsenite solution and, after heating with hydrochloric acid, titration of the excess of arsenite by means of standard potassium bromate solution, using indigosulfonic acid as indicator; the sodium nitrate was then calculated by difference, after determination of water by evaporation. The solubilities of the individual salts (with the exception of sodium nitrate) were determined both volumetrically and by evaporation, with very close agreement between the two methods throughout.

The solid phases were in each case the pure separate salts or their respective hydrates stable at 25°, and were easily identified by means of tie-lines, on the ternary diagrams, drawn through the compositions of the original complex and of the corresponding saturated solution. The algebraic extrapolation of these tie-lines shows deviations from the points representing the pure salts or their hydrates, averaging 0.20, 0.21 and 0.34% in the three systems, respectively. This indicates, on the average, a relatively much smaller error in the total experimental procedure involving preparation of complexes, establishment of equilibrium and sampling and analysis of saturated solutions.

The numerical results are listed in Tables I, II and III, in terms of weight per cent. Densities were determined for the whole range of concentration only for the sodium nitrate system. These densities were obtained by using calibrated

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[1] The greater part of the experimental work here reported was performed by A. C. Campbell (system $NaClO_3$–$NaBr$–H_2O), P. Mockridge (system $NaClO_3$–NaI–H_2O) and G. J. Moore (system $NaClO_3$–$NaNO_3$–H_2O), as candidates for the Bachelor's degree at New York University.

[2] Ricci and Yanick, THIS JOURNAL, 59, 491 (1937); Ricci, 60, 2040 (1938); Swenson and Ricci, 61, 1974 (1939); Ricci and Weltman, 64, 2746 (1942).

Table I

System $NaClO_3$–$NaBr$–H_2O at 25°

Original complex, wt. %		Saturated solution, wt. %		Solid phase
$NaClO_3$	NaBr	$NaClO_3$	NaBr	
...	0	50.10	0	$NaClO_3$
58.52	7.99	37.93	11.86	$NaClO_3$
51.96	14.17	29.54	20.72	$NaClO_3$
47.30	20.52	20.87	30.75	$NaClO_3$
43.02	25.08	16.29	36.77	$NaClO_3$
35.05	29.26	15.37	38.10	$NaClO_3$
29.92	34.79	13.87	40.32	$NaClO_3 + NaBr\cdot 2H_2O$
25.00	37.00	13.97	40.18	$NaClO_3 + NaBr\cdot 2H_2O$
15.59	42.68	13.85	40.36	$NaClO_3 + NaBr\cdot 2H_2O$
13.02	46.07	14.03	40.11	$NaClO_3 + NaBr\cdot 2H_2O$
12.14	46.78	13.98	40.18	$NaClO_3 + NaBr\cdot 2H_2O$
Average		13.89	40.28	$NaClO_3 + NaBr\cdot 2H_2O$
8.91	50.42	12.38	41.16	$NaBr\cdot 2H_2O$
6.48	49.96	8.07	43.74	$NaBr\cdot 2H_2O$
6.14	49.24	7.22	44.28	$NaBr\cdot 2H_2O$
0	...	0	48.49	$NaBr\cdot 2H_2O$

Table II

System $NaClO_3$–NaI–H_2O at 25°

Original complex, wt. %		Saturated solution, wt. %		Solid phase
$NaClO_3$	NaI	$NaClO_3$	NaI	
...	0	50.10	0	$NaClO_3$
55.03	9.11	38.72	12.40	$NaClO_3$
42.93	19.86	27.62	25.23	$NaClO_3$
40.31	26.79	18.67	36.53	$NaClO_3$
28.30	38.98	10.28	48.78	$NaClO_3$
30.14	41.13	7.11	54.63	$NaClO_3$
34.01	41.07	5.44	58.56	$NaClO_3$
16.93	54.77	4.50	61.52	$NaClO_3 + NaI\cdot 2H_2O$
25.92	52.02	4.28	61.74	$NaClO_3 + NaI\cdot 2H_2O$
15.31	60.91	4.08	61.79	$NaClO_3 + NaI\cdot 2H_2O$
8.33	63.92	4.20	61.73	$NaClO_3 + NaI\cdot 2H_2O$
4.93	64.13	4.51	61.61	$NaClO_3 + NaI\cdot 2H_2O$
Average		4.32	61.68	$NaClO_3 + NaI\cdot 2H_2O$
2.12	67.63	2.83	62.65	$NaI\cdot 2H_2O$
1.29	65.92	1.43	63.67	$NaI\cdot 2H_2O$
0.95	67.43	1.22	64.00	$NaI\cdot 2H_2O$
0	...	0	64.80	$NaI\cdot 2H_2O$

Table III

System $NaClO_3$–$NaNO_3$–H_2O at 25°

Original complex, wt. %		Saturated solution, wt. %			
$NaClO_3$	$NaNO_3$	$NaClO_3$	$NaNO_3$	Density	Solid phase
...	0	50.10	...	1.432	$NaClO_3$
56.99	7.06	43.98	9.26	1.481	$NaClO_3$
49.82	14.31	38.82	17.47	1.517	$NaClO_3$
48.96	18.09	35.72	22.65	1.528	$NaClO_3$
43.93	22.98	34.28	25.96	1.549	$NaClO_3 + NaNO_3$
38.95	30.03	34.29	25.95	1.557	$NaClO_3 + NaNO_3$
34.10	33.77	34.28	25.90	1.552	$NaClO_3 + NaNO_3$
30.23	40.44	34.28	25.91	...	$NaClO_3 + NaNO_3$
27.93	40.05	34.28	25.96	1.554	$NaClO_3 + NaNO_3$
Average		34.28	25.94	1.553	$NaClO_3 + NaNO_3$
27.59	37.32	32.15	27.08	1.548	$NaNO_3$
22.11	43.02	27.34	29.72	1.505	$NaNO_3$
9.65	68.90	20.96	33.94	1.468	$NaNO_3$
10.04	54.94	13.85	38.66	1.440	$NaNO_3$
4.99	59.98	6.93	43.27	...	$NaNO_3$
0	...	0	47.87	1.389	$NaNO_3$

pipets in the sampling of the saturated liquids for analysis; they are relatively less precise and dependable than the analytical results themselves.

The data are not shown graphically since the relations involve no unusual features. The values, however, all lie on smooth curves; and the systems are seen to be of the simplest type, each with two branches for the solubility curve, one for each of the separate component salts, and with no indication of the formation of either solid solutions or double salts. The isothermally invariant solutions saturated with two salts have the compositions

	% $NaClO_3$	% 2nd salt	Density
I	13.89	40.28 (NaBr)	1.583
II	4.32	61.68 (NaI)	1.911
III	34.28	25.94 ($NaNO_3$)	1.553

A few determinations were also made on the equilibrium relations of the first system, $NaClO_3$–$NaBr$–H_2O, at 50°, enough to show that the principal isothermally invariant point, at this temperature, containing 43.0% sodium chlorate and 16.2% sodium bromide, involves as solid phases sodium chlorate and anhydrous sodium bromide, instead of the dihydrate of the latter salt, which in the binary aqueous system is stable up to $\sim$ 51.0°.

The absence of complexity in the sodium nitrate system is in some contrast with the relations in the system $KClO_3$–KNO_3–H_2O at the same temperature. These salts form a limited series of solid solutions consisting of potassium chlorate containing (at 25°) up to 14.37 *M* % of potassium nitrate, while no potassium chlorate is found to dissolve in the potassium nitrate phase.[3] This behavior seems to be related to the dimorphism of potassium nitrate. While the stable rhombic form of potassium nitrate changes to a monoclinic variety only at 129°, the solid solution seems to involve the unstable monoclinic form since potassium chlorate is itself monoclinic at room temperature. On the other hand, the stable rhombic potassium nitrate, which is the actual potassium nitrate phase of the ternary aqueous system, does not take up any of the monoclinic chlorate. For the sodium salts, however, the nitrate is simply rhombohedral, and while the chlorate appears to be at least dimorphous, its usual form is cubic, and no solid solution at all is observed in the system as studied at 25°.

Summary

Solubility measurements are given for the systems I, $NaClO_3$–$NaBr$–H_2O, II, $NaClO_3$–NaI–H_2O and III, $NaClO_3$–$NaNO_3$–H_2O, at 25°. These salt pairs form neither double salts nor solid solutions at this temperature.

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[3] At 25°: Toda, *J. Chem. Soc.* (Japan), **43**, 320 (1922), in "International Critical Tables," Vol. 4, p. 314 (1926). At 16°: Herbette, *Compt. rend.*, **143**, 128 (1906).