the four components and rotated for a short time before analysis. For the curves originating at **b**, **c**, d or e, each with a double salt as one solid phase, the ternary invariant solution was first prepared by seeding and stirring for a period of time known to be sufficient for equilibrium. The fourth component was then added, and the solution was analyzed after further stirring.

The curves e → **3**, b → **2**, and 2 → **3** were easily followed, and the point **3** was reached along each of the three curves **a** → **3**, **e** → **3**, **2** → **3**. Points on curve 2 → **3** were obtained from solution **b** by addition of $Ba(ClO_3)_2 \cdot H_2O$ and seeding with double salt E. Curves **c** → 1 and d → 1 were more difficult to determine because of the narrow 3-dimensional spaces within which the total quaternary composition must fall for the solution to lie on one of these curves.

Curve 1 → 2 was followed by addition of solid $BaBr_2 \cdot 2H_2O$ to solution d and seeding with double salt D. The first point listed in Table IV for this curve was reseeded after the first analysis, and its composition remained constant. The second was made from the last solution on curve **d** → 1 by addition of $BaBr_2 \cdot 2H_2O$. Microscopic examination showed only crystals of the double salts D and E in the solids of the first four solutions listed for curve 1 → **2**; no $Ba(NO_3)_2$ could be observed. The two analyses for point 2 were obtained by addition of $BaBr_2 \cdot 2H_2O$ to the third and fourth solutions, respectively, of curve 1 → 2; the composition, falling on curve b → **2**, therefore fixes the intersection of the two curves as point 2.

Point 1 itself could not be made, either from curve **c** → 1 or from curve d → 1. The complexes intended to give point 1 always gave solutions on the curves intersecting at point 1, because of the difficulty of preparing a total composition in the very limited volume for saturation with the three solids C + D + E. The composition of point 1 was therefore estimated by graphical extrapolation of the three curves d → 1, **c** → 1, and 1 → 2, to their common intersection, the Jänecke diagram of Fig. 3 being used for the salt proportions and the elevation of Fig. 4 for the water content.

The only quaternary invariant congruently saturated with its three solids is point **3**, which is therefore the vapor pressure minimum of the isotherm and the final drying-up point for isothermal evaporation of all solutions in the triangle ABE. With complete solid phase equilibrium, those in CDE dry up at point 1 and those in BDE at point 2. The phase reaction for isothermal evaporation is of the transition type along all three curves meeting at point 1: for d → 1, solution + C → E + H_2O ↗; for **c** → 1, solution + C → D + H_2O ↗; and for 1 → 2, solution + D → E + H_2O↗. The reactions at the incongruently saturated quaternary invariants are: solution + C → D + E + H_2O↗ at point 1, and solution + D → B + E + H_2O↗ at point 2. For practical purposes, therefore, the drying-up point for the whole system is point **3**, where the solution precipitates simultaneously the solids $Ba(ClO_3)_2 \cdot H_2O$, $BaBr_2 \cdot 2H_2O$ and "$Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$" or double salt E. In Fig. 4, the point **3** is seen to be actually the solution of lowest water content for the isotherm. The arrows in Fig. 3 indicate the direction of isothermal evaporation, or, from Fig. 4, the direction of falling water content.

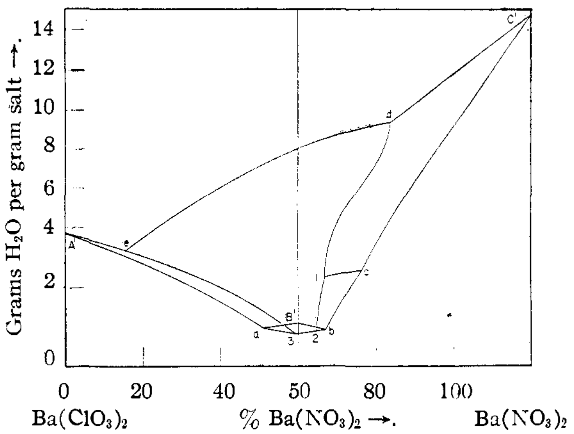

Fig. 4.—System $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O at 10°; elevation (partially schematic showing water content).

Finally, the composition may be represented, in the units given in Table IV, in a regular tetrahedron with water as one of the corners. Radial projection from the water apex to the salt base gives the Jänecke diagram of Fig. 3. Orthogonal projection on the same base gives the "orthogonal diagram," which, labeled with primed letters, is plotted together with the Jänecke projection in Fig. 3. The data of Table IV may be plotted directly as an orthogonal diagram after addition of one third of the water percentage to each of the salt percentages.

NEW YORK, N. Y. RECEIVED FEBRUARY 15, 1951

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

Some Aqueous Ternary Systems Involving Barium Halates

BY JOHN E. RICCI AND ARTHUR J. FREEDMAN

The system $Ba(BrO_3)_2$–$BaCl_2$–H_2O forms the incongruently soluble double salt $Ba(BrO_3)_2 \cdot BaCl_2 \cdot 2H_2O$ at each of the temperatures studied, 10, 25, 45°; its range of stability increases slightly with rising temperature. The following systems form neither compounds nor solid solutions at 25°: $Ba(ClO_3)_2$–$BaCl_2$–H_2O, $Ba(BrO_3)_2$–$BaBr_2$–H_2O, $Ba(BrO_3)_2$–$Ba(NO_3)_2$–H_2O, $Ba(IO_3)_2$–$BaBr_2$–H_2O, $Ba(IO_3)_2$–$Ba(NO_3)_2$–H_2O and $Ba(IO_3)_2$–$Mg(IO_3)_2$–H_2O. Mixtures made up from barium iodate, iodic acid and water form the incongruently soluble anhydrous compound $Ba(IO_3)_2 \cdot I_2O_5$, so that the measurements are reported as part of the system $Ba(IO_3)_2$–I_2O_5–H_2O. A few points on the 25° isotherm of the system $Mg(IO_3)_2$–HIO_3–H_2O are reported indicating a marked increase in the solublity of magnesium iodate tetrahydrate in high concentrations of iodic acid, with the formation of very dense and viscous solutions.

This is a report on some further aqueous ternary systems involving barium halates, continuing the work on these systems previously published. The material already reported includes the study of the solid solution of barium bromate monohydrate with barium chlorate monohydrate,[1] the solubility of barium iodate in the presence of foreign electrolytes[2] and in dioxane–water solvents,[3] the double salt $Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$ in the system $Ba(IO_3)_2$–$BaCl_2$–H_2O[4] and the double salt $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$ in the quaternary system $Ba(ClO_3)_2$–$BaBr_2$–$Ba(NO_3)_2$–H_2O.[5]

The present work reports the double salt $Ba(BrO_3)_2 \cdot BaCl_2 \cdot 2H_2O$ and the polyiodate $Ba(IO_3)_2 \cdot I_2O_5$ as new compounds.

Most of the materials were the same as those used in similar investigations and the general procedure was also the same. Barium chlorate monohydrate, barium bromate monohydrate, barium chloride

---

(1) J. E. Ricci and S. H. Smiley, THIS JOURNAL, **66**, 1011 (1944).

(2) S. Naidich and J. E. Ricci, *ibid.*, **61**, 3268 (1939).

(3) T. W. Davis, J. E. Ricci and C. G. Sauter, *ibid.*, **61**, 3274 (1939).

(4) J. E. Ricci, *ibid.*, **73**, 1375 (1951).

(5) J. E. Ricci and A. J. Freedman, *ibid.*, **74**, 1765 (1952).

dihydrate and barium nitrate were commercial C.P. products used without further purification after satisfactory analysis to check their purity. The preparation of the barium bromide dihydrate used has already been described.[5] One of the two samples of C.P. barium iodate monohydrate used contained too little water; it was therefore leached with water until its solubility was constant, and it was then rinsed with some acetone and dried in air. The product contained 96.34% $Ba(IO_3)_2$ as compared with the theoretical 96.43%. Magnesium iodate was used as the tetrahydrate, which is stable in air. Prepared as described by Hill and Moskowitz,[6] it contained 83.76% $Mg(IO_3)_2$, the theoretical being 83.86%. One sample of the iodic acid used was a commercial C.P. product containing 99.82% HIO_3 by determination of iodate and of acid. Another sample was made from C.P. I_2O_5 and water. The solution was evaporated under an infrared lamp until the acid began to crystallize, and the process was completed at ~40° in a stream of air. When ground and stored in vacuum over anhydrone, constant composition was reached after about two weeks, at 99.66% HIO_3. The solubility of the two samples was the same.

System $Ba(BrO_3)_2$–$BaCl_2$–H_2O.—The results for this system, studied at 10, 25 and 45°, are listed in Table I, and the relations at 25° are plotted in Fig. 1. The table gives only the compositions of invariant points and the data required for the determination of the formula of the double salt. For the solubility curve of $Ba(BrO_3)_2 \cdot H_2O$ at 10°, the solubility was found to be depressed to 0.232, 0.201, 0.190 and 0.187% $Ba(BrO_3)_2$ (A) in presence of 6.57, 12.98, 18.99 and 22.34% $BaCl_2$ (B), respectively; at 25° the values are 0.446, 0.373, 0.338 and 0.323% A for 5.91, 14.21, 20.16 and 23.64% B; and at 45°, 0.825 and 0.658% A in presence of 11.94 and 22.40% B, respectively.

TABLE I

SYSTEM $Ba(BrO_3)_2$ (A)–$BaCl_2$ (B)–H_2O (W)

Original complex Wt. % A	Original complex Wt. % B	Saturated solution Wt. % A	Saturated solution Wt. % B	Density	Solid phase
Temperature: 10°					
...	0.00	0.456	0.00	1.001	A·W
Average		.185	22.52	1.237	A·W + A·B·2W
14.26	25.81	.161	23.78	1.253	A·B·2W
14.78	25.99	.159	23.92	1.264	A·B·2W
Average		.144	24.91	1.267	A·B·2W + B·2W
0.00	...	0.00	24.93	1.265	B·2W
Temperature: 25°					
...	0.00	0.788	0.00	1.003	A·W
Average (*a*)		.321	23.93	1.254	A·W + A·B·2W
13.52	26.36	.296	24.64	1.265	A·B·2W
12.97	26.99	.266	25.52	1.274	A·B·2W
12.49	27.46	.249	26.18	1.283	A·B·2W
Average (*b*)		.226	27.02	1.294	A·B·2W + B·2W
0.00	...	0.00	27.06	1.292	B·2W
Temperature: 45°					
...	0.00	1.529	0.00		A·W
Average		0.623	25.53	1.274	A·W + A·B·2W
14.98	27.61	.560	26.04	1.275	A·B·2W
15.00	28.50	.493	27.20	1.290	A·B·2W
14.60	28.67	.473	27.46	1.291	A·B·2W
Average		.392	29.60	1.318	A·B·2W + B·2W
0.00	...	0.00	29.78	1.321	B·2W

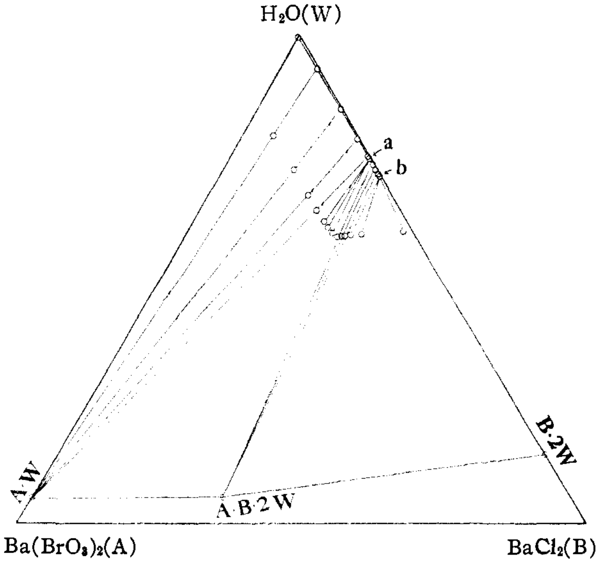

Fig. 1.—System $Ba(BrO_3)_2$–$BaCl_2$–H_2O at 25°.

The saturated solutions were analyzed for bromate by iodometry with standard sodium thiosulfate, and for total solid by evaporation with final heating to constant weight at 300°. Equilibrium was checked by reanalysis, the minimum time of stirring being 8 days. Because of the possible resemblance with the system $Ba(IO_3)_2$–$BaCl_2$–H_2O,[4] all the complexes were first seeded with the double salt $Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$. As expected, a double salt of similar formula and with similar solubility relations easily formed, and each isotherm involves the three solid phases $Ba(BrO_3)_2 \cdot H_2O$, $Ba(BrO_3)_2 \cdot BaCl_2 \cdot 2H_2O$, and $BaCl_2 \cdot 2H_2O$. As might be expected from the lower hydration of the double salt compared to its component salts, its range of stability, measured as the percentage range between the limiting solutions saturated with two salts, increases slightly with temperature. Under the microscope, the double salt crystals appeared to be well formed, transparent needles, probably monoclinic in type. Although similar to the monoclinic crystals of barium bromate monohydrate, they seemed to be somewhat shorter and thicker. They were distinct from the larger crystals of $BaCl_2 \cdot 2H_2O$.

The formula of the incongruently soluble double salt was determined by algebraic extrapolation of the eight tie-lines for the three temperatures. The 1:1 salt ratio is clear from Fig. 1, and the intersections of the tie-lines with the 1:1 salt ratio line give an average of 2.03 moles of water per mole of the 1:1 double salt, with an average deviation for the eight intersections of 0.05.

Some Simple Systems at 25°.—Measurements were made on the following systems, all found to be simple at 25°: I, $Ba(ClO_3)_2$–$BaCl_2$–H_2O[7]; II, $Ba(BrO_3)_2$–$BaBr_2$–H_2O; III, $Ba(BrO_3)_2$–Ba-

---

(6) A. E. Hill and S. Moskowitz, THIS JOURNAL, 53, 941 (1931).

(7) For the 20° isotherm of this system, see C. di Capua and A. Bertoni, *Gazz. chim. ital.*, 58, 249 (1928).

$(NO_3)_2$–H_2O; IV, $Ba(IO_3)_2$–$BaBr_2$–H_2O; V, $Ba(IO_3)_2$–$Ba(NO_3)_2$–H_2O; VI, $Ba(IO_3)_2$–$Mg(IO_3)_2$–H_2O. The analysis for system I involved the determination of total solid and the Volhard method for chloride; for II–V, total solid and iodometric titration of bromate or iodate. In VI, the concentration of barium iodate in the saturated solution was found to be negligible, since sulfuric acid gave no observable precipitate; the iodometric titration of iodate was therefore taken as measurement of magnesium iodate in the solution. The concentration of $Mg(IO_3)_2$ in the solution saturated with both salts was thus the same as the pure solubility of $Mg(IO_3)_2 \cdot 4H_2O$ (see Table IV).

TABLE II

SYSTEM $Ba(ClO_3)$ (A)–$BaCl_2$ (B)–H_2O (W) AT 25°

Original complex Wt. % A	Original complex Wt. % B	Saturated solution Wt. % A	Saturated solution Wt. % B	Density	Solid phase
...	0.00	27.42	0.00	1.263	A·W
37.62	5.03	23.06	6.35	1.294	A·W
33.60	10.57	18.94	13.16	1.338	A·W
30.01	14.94	15.74	18.29	1.373	A·W
Average		14.73	21.06	1.398	A·W + B·2W
9.03	34.97	11.22	22.48	1.373	B·2W
9.01	34.89	11.21	22.45	1.371	B·2W
4.11	37.98	5.22	24.90	1.327	B·2W

The data for the first system are listed in Table II. Because of the possible formation of similar double salts, the complexes of systems I–V were seeded both with $Ba(BrO_3)_2 \cdot BaCl_2 \cdot 2H_2O$, the double salt just reported, and with $Ba(ClO_3)_2 \cdot 6Ba(NO_3)_2 \cdot 12H_2O$, previously reported.[5] Nevertheless, no new solid phase appeared, the only solids present being the simple salts or their hydrates: $Ba(ClO_3)_2 \cdot H_2O$, $BaCl_2 \cdot 2H_2O$, $Ba(BrO_3)_2 \cdot H_2O$, $BaBr_2 \cdot 2H_2O$, $Ba(NO_3)_2$, $Ba(IO_3)_2 \cdot H_2O$, $Mg(IO_3)_2 \cdot 4H_2O$. The solubility of barium bromate was found to be depressed to 0.395, 0.320, 0.257, 0.229 and 0.220% $Ba(BrO_3)_2$ in presence of 12.71, 24.15, 36.19, 44.21, and 49.92% (saturation) of $BaBr_2$. With $Ba(NO_3)_2$ the observed values were 0.593, 0.570, 0.568, 0.571, 0.573% $Ba(BrO_3)_2$ for 2.44, 4.74, 7.07, 8.60 and 9.23% $Ba(NO_3)_2$, the last being the solution saturated with both salts. In systems IV and V the solubility of barium iodate was found first to fall and then to rise, because of the ionic strength effect, with increasing concentration of the second barium salt: from 0.042% in pure water to 0.013, 0.017, 0.026, 0.045, 0.068 and 0.075% in 11.19, 22.34, 33.46, 44.61, 49.02 and 50.07% (saturation) of $BaBr_2$, and to 0.019, 0.023, 0.027, 0.031, 0.033% in 2.50, 4.75, 7.14, 8.69 and 9.22% (saturation) of $Ba(NO_3)_2$.

System $Ba(IO_3)_2$–I_2O_5–H_2O at 25°.—The complexes for this system were prepared from $Ba(IO_3)_2 \cdot H_2O$, HIO_3 and water. Because of the separation of the solid compound $Ba(IO_3)_2 \cdot I_2O_5$, however, it is necessary to consider the results as part of the system $Ba(IO_3)_2$–I_2O_5–H_2O, a situation similar to that already reported in connection with the compound $AgIO_3 \cdot I_2O_5$.[8]

Solutions containing less than 45% iodic acid were sampled with delivery pipets fitted with filter paper tips. The more viscous solutions of higher concentration were sampled by means of specific gravity pipets fitted with ground glass caps. Filter paper, however, could not be used for filtration of solutions above 60% in concentration. For these highest concentrations, the liquid–solid mixture was allowed to settle after centrifuging at high speed for a few moments; the clear liquid was then sampled without filtration. The densities fall on a smooth curve and are essentially densities of pure solutions of I_2O_5.

For the analysis, no barium could be detected in any of the ternary solutions by treatment with dilute sulfuric acid. Titration with sodium hydroxide, with phenolphthalein as indicator, was used as determination of iodic acid. That the concentration of barium iodate was negligible was confirmed by the fact that analyses of representative solutions for iodic acid both alkalimetrically and iodometrically gave identical results.

In terms of $Ba(IO_3)_2$, I_2O_5 and water, the pertinent data are listed in Table III and plotted in Fig. 2. An incongruently soluble compound is formed, with the composition $Ba(IO_3)_2 \cdot I_2O_5$. It is flanked by the solid phases $Ba(IO_3)_2 \cdot H_2O$ and HIO_3 (or $I_2O_5 \cdot H_2O$). Figure 2 may also be taken as representing part of the system BaO–I_2O_5–H_2O, with respect to the solid phases $BaO \cdot I_2O_5 \cdot H_2O$, $BaO \cdot 2I_2O_5$, and $I_2O_5 \cdot H_2O$, but it is convenient to consider the data in terms of the components chosen in Table III and Fig. 2.

TABLE III

SYSTEM $Ba(IO_3)_2$(A)–I_2O_5(B)–H_2O(W) AT 25°

Original complex Wt. % A	Original complex Wt. % B	Saturated solution Wt. % B	Density	Solid phase
..	0.00	(0.042% A)		A·W
5.06	50.28	53.09	1.80$_5$	A·W
Average (a)		53.29	1.80$_4$	A·W + A·B
9.98	55.82	58.92	1.97$_0$	A·B
9.99	57.25	60.73	2.01$_9$	A·B
5.05	64.50	66.76	2.27	A·B
5.06	65.36	67.70	2.31	A·B
4.93	66.23	68.56	2.35	A·B
5.00	68.38	71.00	2.47	A·B
Average (b)		71.47	2.49	A·B + B·W
0.00	...	71.47	2.49	B·W

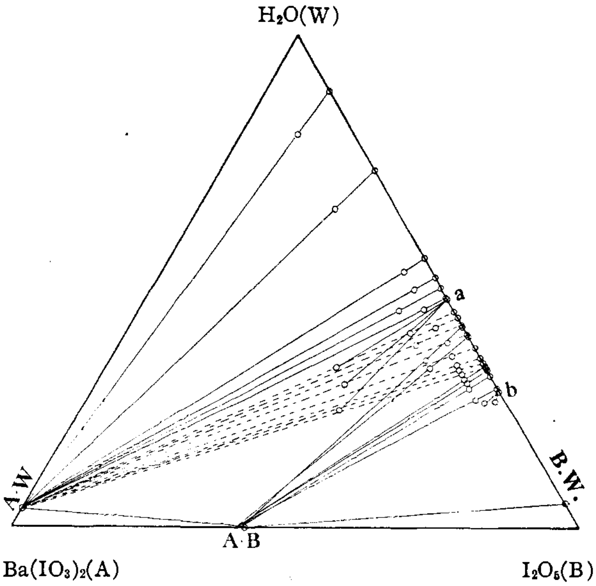

Fig. 2.—System $Ba(IO_3)_2$–I_2O_5–H_2O at 25°.

The determination of the solubility curve of the compound was difficult because the new solid did

---

(8) J. E. Ricci and I. Amron, THIS JOURNAL, **73**, 3613 (1951).

not form easily near the incongruently saturated isothermally invariant point **a**. (Similar difference in attainment of equilibrium between points **a** and **b** was noted for the double salts in the systems $Ba(ClO_3)_2$–$Ba(NO_3)_2$–H_2O and $BaBr_2$–$Ba(NO_3)_2$–H_2O[5].) All complexes made up from the substances $Ba(IO_3)_2 \cdot H_2O$, HIO_3, and water with compositions falling in the triangle A·W – **a** – A·B and therefore intended to give solution **a** when seeded with the compound, gave instead points on the metastable solubility curve of $Ba(IO_3)_2 \cdot H_2O$, with compositions changing extremely slowly toward point **a**. (Many of the solutions first giving this hydrate as solid phase were thus shown to be metastable by marked decrease in I_2O_5 content upon further stirring.) It was evident that to obtain the solution **a** it would be necessary to start with the compound already present as a solid phase. Some complexes were therefore brought to equilibrium with solid compound near the line A·B – **b**; with addition of $Ba(IO_3)_2 \cdot H_2O$ and water, their total compositions were then brought into the triangle A·W – **a** – A·B, this area being estimated from rough estimates of point **a**. The solutions were then analyzed after 35 days of stirring. In this way the three complexes shown in Fig. 2 as giving solution **a** were obtained.

The formula of the compound has been taken from the intersection of the six tie-lines for the complexes with the compound as sole solid phase. When the tie-lines were extrapolated to the base of the triangle constructed with $Ba(IO_3)_2$, HIO_3 and water as components, they intersected the base fairly sharply close to the 1:1 formula $Ba(IO_3)_2 \cdot 2HIO_3$, but with a positive error in respect to HIO_3 greater than might be expected from the known dependability of the operations involved. The compositions were then recalculated in terms of $Ba(IO_3)_2$, I_2O_5, and water, when a similar situation in the system $AgIO_3$–"HIO_3"–H_2O had been satisfactorily explained as involving the formation of the anhydrous polyiodate $AgIO_3 \cdot I_2O_5$.[8]

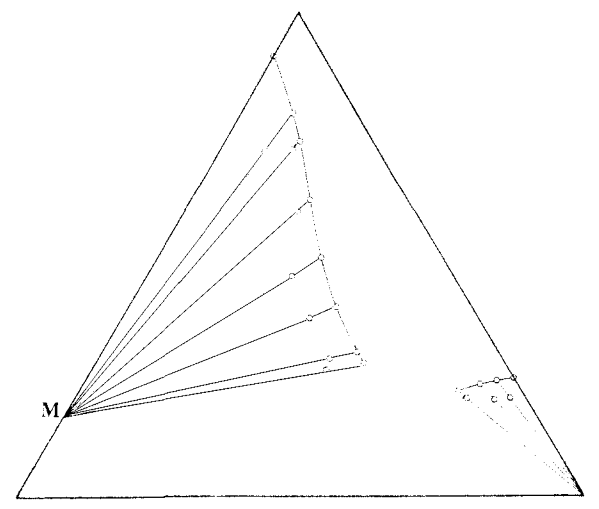

Fig. 3.—Part of the system $Mg(IO_3)_2$–HIO_3–H_2O at 25°: M, $Mg(IO_3)_2 \cdot 4\ H_2O$.

In terms of Fig. 2, then, the six tie-lines reach the base at 39.90% I_2O_5, with an average deviation from the mean of 0.34, while the theoretical percentage of I_2O_5 in $Ba(IO_3)_2 \cdot I_2O_5$ is 40.66%. On the other hand, the tie-lines intersect the line joining $Ba(IO_3)_2$ and $I_2O_5 \cdot H_2O$, on which would lie the compound "$Ba(IO_3)_2 \cdot 2HIO_3$," at 41.56 ± 0.32% I_2O_5, as compared to the theoretical 39.79%. While the choice between the two formulas is not clear cut, the agreement in the first case is better. Since the extrapolation multiplies the errors by nine (on the average) for the six tie-lines involved, the difference between 39.90 and 40.66% I_2O_5 may be accounted for on the basis of an average cumulative operational error of 1 to 1.5 parts per thousand in the combined determination of the compositions of saturated solution and total complex for each tie-line.

The other solid phases of the isotherm are $Ba(IO_3)_2 \cdot H_2O$ and "HIO_3" or $I_2O_5 \cdot H_2O$. The solubility curve of the latter is too short for detection in the present system. The solid phase is known to be HIO_3 at 25° from Groschuff's work,[9] from the ternary system $LiIO_3$–HIO_3–H_2O[8] and from some tie-lines in the following partial study of the 25° isotherm of the system $Mg(IO_3)_2$–HIO_3–H_2O.

System $Mg(IO_3)_2$–HIO_3–H_2O at 25°.—A few points have been determined for the solubility relations in this system at 25°. Although very incomplete, the results are interesting, and since the work is not at present being continued, it is reported here in connection with the corresponding barium iodate system. For the analysis of the solutions, the HIO_3 was determined by titration with sodium hydroxide to the methyl red end-point. Total iodate was then determined on the neutralized sample. In half of the analyses this was done iodometrically with sodium thiosulfate after tedious aliquoting of the solution. Later this procedure was replaced by the more convenient one of titrating the whole neutralized sample with standard sulfuric acid after addition of excess potassium iodide and excess sodium thiosulfate, the methyl red again serving as indicator.

The results are listed in Table IV and plotted in Fig. 3, in terms of $Mg(IO_3)_2$, HIO_3 and water as the

TABLE IV

PART OF THE SYSTEM $Mg(IO_3)_2$–HIO_3–H_2O AT 25°

A = $Mg(IO_3)_2$; B = HIO_3; W = H_2O

Original complex Wt. %		Saturated solution Wt. %			
A	B	A	B	Density	Solid phase
...	0.00	8.55	0.00	1.079	A·4W
20.09	8.79	11.04	10.04	1.217	A·4W
15.05	13.52	12.68	13.99	1.301	A·4W
20.37	20.23	16.93	21.38	1.456	A·4W
28.45	26.07	21.01	29.61	1.695	A·4W
29.94	33.15	24.28	36.63	1.978	A·4W
30.11	41.00	24.92	45.17		A·4W
32.13	41.61	24.81	47.71		A·4W
10.38	69.24	11.21	66.85		B
5.54	74.56	6.69	70.37	2.57	B
3.02	77.10	3.22	72.71	2.55	B
0.00	...	0.00	75.32	2.49	B

---

(9) E. Groschuff, *Z. anorg. Chem.*, **47**, 331 (1905).

components. The unusual S-shaped solubility curve of $Mg(IO_3)_2{\cdot}4H_2O$ in presence of iodic acid is to be noted. The marked increase of the solubility of the salt in high concentrations of iodic acid suggests possible complex polyiodate ions of magnesium in the solution. According to the configuration of the incomplete curves, it is also possible that some solid compound may form in the intermediate region. All the complexes studied were seeded with the compound $Ba(IO_3)_2{\cdot}I_2O_5$ reported above, and they were then stirred for long periods of time, 5–7 months, but no new solid phases appeared. The solutions containing more than 40% iodic acid were very viscous and difficult to sample. It was necessary to allow the mixture to settle for many days before the liquid could be filtered. According to the densities already noted some very dense solutions may be expected in the intervening region.

NEW YORK, N. Y. RECEIVED FEBRUARY 15, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Activity Coefficient of Benzene in Aqueous Salt Solutions

BY W. F. MCDEVIT AND F. A. LONG

The effects of electrolytes on the solubility of benzene in aqueous solutions have been determined at 25°. The salting-out effect varies greatly among the various electrolytes and salting-in is observed for perchloric acid. A limiting law for the influence of electrolytes on the activity of non-polar solutes has been developed which relates the magnitude of the salt effect to the volume changes which occur when salt and water are mixed. This law can also be expressed in terms of Gibson's *Pe*, the "effective pressure" exerted by a salt in solution. Qualitatively the data for benzene agree well with the predicted salt effects.

Knowledge of the influence of electrolytes on the activity coefficient of benzene in aqueous solutions can be helpful from two standpoints in reaching a better understanding of the interactions between ions and neutral molecules. Since benzene is a compact non-polar molecule, this system can provide a basic example of the general phenomenon and the interpretation of the results should be less complex than for polar non-electrolytes. Furthermore, data on benzene are of value for comparison with the rather extensive data which already exist for various benzene derivatives.

This paper gives solubilities of benzene at 25° in water and in a number of electrolyte solutions. The resulting activity coefficients are discussed in terms of various theories of salt effects and more particularly in terms of other properties of the aqueous electrolyte solutions themselves. Comparison of the data for benzene with those for benzene derivatives will be considered in a later paper.

After these experiments were started, the authors learned of a similar investigation made at 30° for several electrolytes by Saylor, Whitten, Claiborne and Gross[1] using a different analytical procedure. It will be seen later that the data agree well for most of the electrolytes studied by both groups. Determinations of the solubility of benzene in a few electrolyte solutions have been also made by Schramm, Klapproth and Westheimer[2] and are in reasonable agreement with the present results.

Experimental

The benzene solubilities were determined by a variation of the Euler method in which a measured excess volume of benzene is added to the aqueous solution, and after equilibration, the volume of undissolved benzene is determined by measuring its length in a precision bore tube which leads from the top of the apparatus. The chief difference from the usual procedure is that the benzene phase is not dispersed into the aqueous, *i.e.*, equilibration is done across an unbroken phase boundary. Magnetic stirring of the aqueous phase makes it possible to attain equilibrium solubility in about 24 hours. The flask volume is approximately 500 ml.

All experiments were made at 25.00 ± 0.02°. The aqueous solutions were made up by weight from redistilled water and reagent grade electrolytes. The benzene was redistilled from reagent grade, thiophene-free material. On the basis of duplicate runs both with water and salt solutions we estimate that the solubilities are accurate to within 0.5%.

Results

The average value obtained for solubility of benzene in pure water is 1.77_5 moles per liter which agrees quite well with the values reported in the literature.[3]

Table I gives the results of the measurements in salt solutions. The listed values of f, the molar activity coefficient of benzene in the salt solution, are calculated from the relation

$$f = S_0/S$$

where S_0 and S are the molar solubilities of benzene in water and salt solution, respectively. (This definition assumes that f_0, the activity coefficient of benzene in saturated water solution, is unity which is entirely reasonable in view of the low solubility.) For completeness, data of Saylor, Whitten, Claiborne and Gross at 30° (re-calculated to molar concentration units) for salts which we have not studied are also included in Table I.[4] The last column of the table gives k_s, the limiting slope of $\log f$ *versus* salt molarity. Actually for all concentrations of the salt solutions studied by us, the data are well represented by the Setschenow equation

$$\log f = k_s C_S$$

---

(1) J. H. Saylor, A. I. Whitten, Imogen Claiborne and P. M. Gross, THIS JOURNAL, **74**, 1778 (1952).

(2) R. M. Schramm, W. Klapproth and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).

(3) (a) A. Seidell, "Solubilities of Organic Compounds," Third Edition, Vol. II, D. Van Nostrand Co., Inc., New York, N. Y.; (b) R. L. Bohon and W. F. Claussen, THIS JOURNAL, **73**, 1571 (1951).

(4) Saylor, *et al.*, also give data for sodium,, lithium, potassium and cesium chlorides and potassium bromide. The agreement with the results of the present study is good, in spite of the 5° temperature difference, except for the case of cesium chloride, where they observe a much lower value of ks.