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

The Ternary Systems Sodium Molybdate–Water–Sodium Chlorate (Bromate, or Iodate) at 25°

BY JOHN E. RICCI AND WILLIAM F. LINKE

The phase diagrams of the three systems sodium molybdate–sodium chlorate–water, sodium molybdate–sodium bromate–water and sodium molybdate–sodium iodate–water, at 25°, were studied as part of the systematic investigation of the solubility relations of the alkali halates, and for purposes of comparison with the corresponding systems involving sodium sulfate.

Experimental

Materials and Solubility Determinations

Sodium molybdate was available as the C. P. dihydrate; from the loss of water when heated to constant weight at 125°, the composition was calculated to be 85.12% Na_2MoO_4, as compared with the theoretical value of 85.11%. Nevertheless, although this was the result for a freshly opened bottle of the material, its composition did not remain constant thereafter, even at room temperature, as found by repeated analysis. It was therefore completely dehydrated to the anhydrous salt at 180°, and stored at 150° for use in the quantitative preparation of the ternary complexes. The purity of this anhydrous salt was found to be 100.0% on the basis of the determination of its molybdate content by means of the Volhard method as previously described for the system Na_2MoO_4–sodium molybdate-sodium nitrate-water.[1]

The C. P. sodium chlorate used was found to be pure within one part per thousand, by reduction to chloride and determination of the chloride by the Volhard method. The reduction was accomplished with sodium nitrite, by a procedure to be described in connection with some work on systems involving barium chlorate. The sodium bromate and sodium iodate, both C. P., were found to be pure within 1 part per thousand, by iodometric titration with standard thiosulfate.

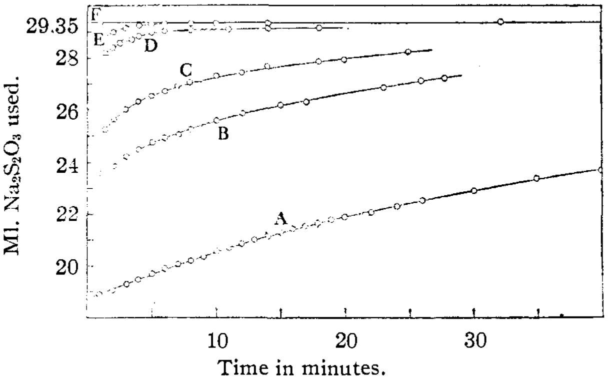

Fig. 1.—Iodometric titration of iodate in presence of molybdate: millimoles; 0.64 KIO_3, 12.4 KI, 6.5 Na_2MoO_4, titrated with 0.1308 *N* $Na_2S_2O_3$. Millimoles of hydrochloric acid present in total volume of 200 ml.: A, 9.70, B, 11.05, C, 11.70, D, 12.35, E, 12.50, F, 12.60.

The ternary solubilities were determined in the usual way, by stirring complexes of known composition, in Pyrex tubes, at 25 ± 0.04°, sampling the solution at equilibrium by means of calibrated pipets supplied with filtering tips, and analyzing the solution for two of the components.

Analytical Method

In each case one of the analytical determinations consisted in evaporating and drying to constant weight at 125°, for the combined percentage of the two salts. In the chlorate system, a second sample was used for the determination of the molybdate by precipitation of silver molybdate, followed by a Volhard titration of the excess of silver in the filtrate, the chlorate offering no interference. This determination of molybdate could not be used for the remaining two systems because of the high insolubility of both silver bromate and silver iodate. It was necessary therefore to determine the iodate or the bromate iodometrically in the presence of molybdate, and the conditions for this analysis had to be examined.

The iodometric determination of either iodate or bromate in presence of molybdate involves possible error from reduction of molybdate by either iodide or thiosulfate, in acid solution. When no care is taken to limit the concentration of the acid used, or to keep the concentration of the molybdate itself low, the end-points with thiosulfate show the color of molybdenum blue, with an accompanying positive error in the determination.

On the other hand, the quantity of acid required for the practical determination of iodate in presence of molybdate is greater than that theoretically calculated for the reaction of iodate when present alone

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \qquad (1)$$

The effect is apparently the result of the consumption of hydrogen ion in the formation of poly-molybdates; at a *p*H of 6.5, for example, the principal reaction seems to be[2]

$$3MoO_4^= + 2H^+ \rightleftarrows Mo_3O_{11}^{\equiv} + H_2O \qquad (2)$$

According to this reaction the normal molybdate, sodium molybdate, will act as a buffer, reducing and controlling the concentration of hydrogen ion, upon addition of strong acid required for reaction (1). The effect was studied briefly, with some interesting results.

A number of solutions of identical composition were prepared, each containing an aliquot portion of sodium iodate (0.6400 millimole), sodium molybdate (6.5 millimoles) and potassium iodide (12.4 millimoles), in a volume of 200 ml. The effect of different amounts of strong acid was then tested by adding definite quantities of 1.00 *M* hydrochloric acid to each solution, and titrating the liberated iodine at once with standard thiosulfate. The stoichiometric quantity of acid (3.8 ml.) required according to equation (1) was far from sufficient for the quantitative reduction of the iodate for immediate titration. After the initial end-point had been reached, however, more iodine was gradually released, and the percentage of iodate reduced could be conveniently followed by rapid titration of the additional iodine at small time intervals. The increments in the quantity of iodate reduced at any given time (such as after two minutes) were roughly proportional to the increments in the quantity of acid used in the experiment. Figure 1 plots the volume of thiosulfate used against the time in minutes, time being measured from the moment of adding the acid. The volumes plotted are those of the "end-points" at the times indicated, and the volume needed for complete iodate reduction (the horizontal at 29.35 ml.) was checked by titration of a similar aliquot containing no molybdate. Although all the curves rise toward completion with enough time, it is seen that immediate titration

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[1] Ricci and Doppelt, THIS JOURNAL, **66**, 1985 (1944).

[2] Jander, *Z. anorg. Chem.*, **194**, 383 (1930).

of the iodate gives the full value only in the presence of a certain minimum quantity of acid definitely in excess of that corresponding to equation (1).

A possible explanation of these observations is that while reaction (1) is irreversible under the conditions of the experiment, and ordinarily very rapid, its velocity will be negligible below a certain value of the hydrogen ion concentration, for given concentrations of the other reactants (iodate and iodide ions). But because of reaction (2), which effectively decreases the hydrogen ion concentration below the value expected upon the addition of any definite quantity of strong acid, the result is an incomplete immediate reduction of iodate, leaving a solution in which the hydrogen ion concentration is fixed by equilibrium constants involved in reactions of the type of (2), and by the actual quantities of molybdate and acid used. Since reaction (1) is irreversible, however, it now continues slowly, with a rate fixed, for the series of tests, by the hydrogen ion concentration and hence by the quantity of acid used, the solution remaining buffered throughout by the molybdate. The greater the initial quantity of acid used, the greater is the initial reduction of iodate and the sooner is the true end-point reached.

As seen from Fig. 1, 12.6 millimoles of the strong acid had to be present in order to obtain the correct end-point within one minute after the addition of the acid. Since 3.8 millimoles is needed for reaction (1), we may say that the (maximum) quantity of hydrogen ion taken up by the molybdate was 8.8 millimoles, a ratio of 1.35 hydrogen ion per molybdate ion. Referring to equation (2) this would mean that the polymerization may have produced a still higher poly-anion than the tri-molybdate, especially since an equilibrium must be involved, with incomplete reaction. The experiments were repeated, changing only the quantity of sodium molybdate to 9.7 millimoles per aliquot. A set of curves similar to Fig. 1 was again obtained, but now the quantity of the acid needed for immediate titration was 17.4 millimoles, corresponding again to a "consumption" of 1.40 moles H^+ per $MoO_4^{=}$. Nevertheless these results are not quantitatively very significant, for they were obtained primarily with attention to the problem of defining conditions for the analytical work. But with modifications (as by adding the iodide to the mixture of iodate, molybdate and acid), it is proposed to use this procedure in the course of investigations now being carried on, on the equilibria of molybdic acid in aqueous solutions.

For the final analytical work, it was found, after some additional tests with further variation of the quantity of molybdate present, that ~0.15 g. of sodium iodate, in a final volume of 200 ml., could be determined with an accuracy of one part per thousand, using from 5 to 25 ml. of 1 *M* hydrochloric acid in excess of the minimum necessary for immediate titration.

The corresponding reaction for the iodometric determination of bromate requires a higher hydrogen ion concentration to be comparable in speed and completeness with the reduction of iodate. Kolthoff and Sandell[3] recommend the use of at least 5 ml. of 4 *M* hydrochloric acid for every 25 ml. of bromate solution to be analyzed, for immediate titration. Kolthoff even suggests the use of some molybdate as a catalyst.[4] In high concentrations of molybdate, however, this high acidity leads to positive errors from the reduction of molybdate; with 0.7 *M* as the final concentration of hydrogen chloride in a small final volume, the end-points, for the analysis of the ternary solutions in the present study, were colored a deep blue-green, the reaction continuing on standing. The interference was eliminated, while still obtaining rapid reduction of the bromate, by using the same final concentration of hydrogen chloride but in a large volume (~200 ml.), to decrease the molybdate concentration, and by taking care to mix thoroughly during titration, since local excesses of thiosulfate soon attack the molybdate at this acidity. In this way it is possible to determine the bromate in presence of a relatively large quantity of molybdate, with probably no error caused by the molybdate.

Results

The analytical results are presented, in terms of weight per cent., in Tables I–III, and shown graphically in Figs. 2 and 3. The solubilities of the individual salts were averaged from determinations from both undersaturation and supersaturation; they agree substantially well with previously published figures. The solutions in the first system (Na_2MoO_4–$NaClO_3$–H_2O) were sampled after one week of stirring, and the equilibrium was verified by repeating the sampling and analysis of a number of them after an additional three weeks of stirring. In the second system (Na_2MoO_4–$NaBrO_3$–H_2O) all the solutions were sampled and analyzed twice: after two and

TABLE I

Na_2MoO_4–$NaClO_3$–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %			
Na_2MoO_4	$NaClO_3$	Na_2MoO_4	$NaClO_3$	Density	Solid phase[a]
...	0.00	39.38	0.00	1.432	A
46.49	3.35	36.11	4.23	1.441	A
44.92	6.86	32.42	9.04	1.441	A
39.91	11.18	28.53	14.12	1.440	A
39.67	15.93	22.83	21.94	1.442	A
34.10	22.10	17.95	29.14	1.453	A
30.10	26.77	14.59	34.39	1.466	A
26.97	29.90	13.04	37.05	1.472	A
24.28	34.96	11.77	39.21	1.478	A + B
20.00	39.95	11.75	39.25	1.479	A + B
14.95	45.02	11.81	39.17	1.481	A + B
Average		11.77	39.21	1.479	A + B
9.39	51.60	11.74	39.29	1.476	B
7.52	50.73	8.87	41.85	1.465	B
4.68	54.92	5.72	44.70	1.456	B
2.08	58.12	2.60	47.60	1.438	B
0.00	...	0.00	50.02	1.433	B

[a] A = $Na_2MoO_4 \cdot 2H_2O$; B = $NaClO_3$.

TABLE II

Na_2MoO_4–$NaBrO_3$–H_2O AT 25°

Original complex wt. %		Saturated solution wt. %			
Na_2MoO_4	$NaBrO_3$	Na_2MoO_4	$NaBrO_3$	Density	Solid phase[a]
...	0.00	39.38	0.00	1.432	A
45.98	1.50	38.30	1.80	1.442	A
45.02	3.20	37.09	3.86	1.453	A
40.01	7.00	35.57	6.33	1.466	A + B
38.93	11.03	35.58	6.29	1.468	A + B
35.48	10.49	35.60	6.28	1.470	A + B
Average		35.58	6.30	1.468	A + B
30.00	14.98	32.64	7.49	1.440	B
25.04	18.02	27.53	9.86	1.398	B
20.03	21.96	22.44	12.56	1.363	B
14.54	24.98	16.18	16.35	1.326	B
10.00	29.97	11.47	19.40	1.304	B
4.41	32.48	4.85	24.42	1.278	B
0.00	...	0.00	28.29	1.264	B

[a] A = $Na_2MoO_4 \cdot 2H_2O$; B = $NaBrO_3$.

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[3] Kolthoff and Sandell, "Textbook of Quantitative Analysis," The Macmillan Company, New York, N. Y., 1943, p. 624.

[4] Kolthoff, *Z. anal. Chem.* **60**, 348 (1921).

TABLE III

Na_2MoO_4–$NaIO_3$–H_2O AT 25°

Original complex wt. % Na$_2$MoO$_4$	Original complex wt. % NaIO$_3$	Saturated solution wt. % Na$_2$MoO$_4$	Saturated solution wt. % NaIO$_3$	Density	Solid phase[a]
...	0.00	39.38	0.00	1.432	A
45.92	0.50	39.16	0.58	1.437	A
45.97	1.50	38.63	1.79	1.450	A
45.48	4.51	38.46	2.20	1.453	A + B
43.41	6.54	38.51	2.18	1.452	A + B
43.34	6.55	38.43	2.21	1.451	A + B
38.63	9.97	38.43	2.21	1.454	A + B
38.01	9.98	38.47	2.18	1.455	A + B
Average		38.46	2.20	1.453	A + B
33.99	10.00	37.23	2.24	1.436	B
28.85	9.97	31.49	2.54	1.368	B
22.34	10.04	24.24	3.08	1.277	B
16.52	10.06	17.89	3.42	1.204	B
10.50	10.98	11.41	4.16	1.143	B
5.06	12.95	5.57	5.67	1.099	B
0.00	...	0.00	8.49	1.074	B

[a] A = $Na_2MoO_4 \cdot 2H_2O$; B = $NaIO_3 \cdot H_2O$.

again after three more weeks of stirring. The agreement in both of these systems was within the very small experimental error. In the sodium iodate system, the numerical results were not reproducible with the same precision as in the preceding cases, the percentage of sodium iodate showing variations of 0.03 out of 1 to 4% in analyses following the first week of stirring. These variations may be caused by decomposition of the iodate brought about by the grease used in closing the solubility tubes or by possible impurities when unrecrystallized sodium molybdate was used, or they may reflect the slowness frequently noted in the attainment of equilibrium for saturation with sodium iodate.[5] At any rate the final uncertainty of the results is of no significance in fixing the phase diagram. The densities are estimated to be correct to ±0.003, and are plotted as function of the total percentage of dissolved salts, in Fig. 4.

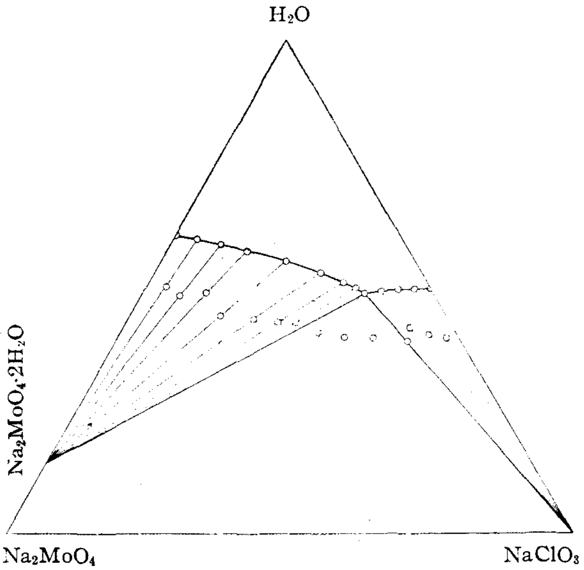

Fig. 2.—System Na_2MoO_4–$NaClO_3$–H_2O at 25°.

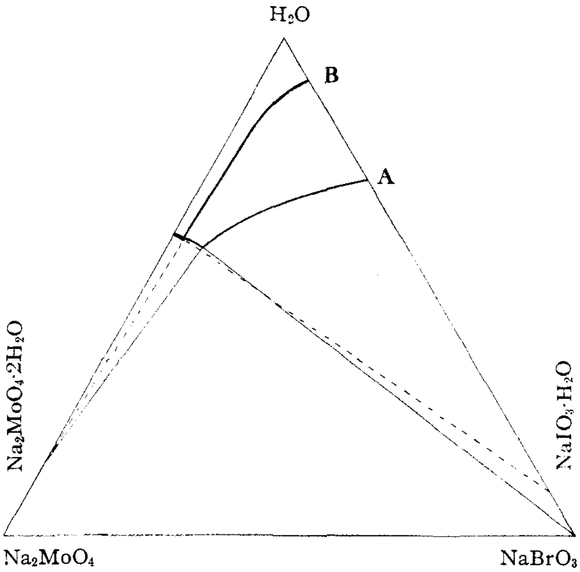

Fig. 3.—Systems (A) Na_2MoO_4–$NaBrO_3$–H_2O and (B) Na_2MoO_4–$NaIO_3$–H_2O, at 25°.

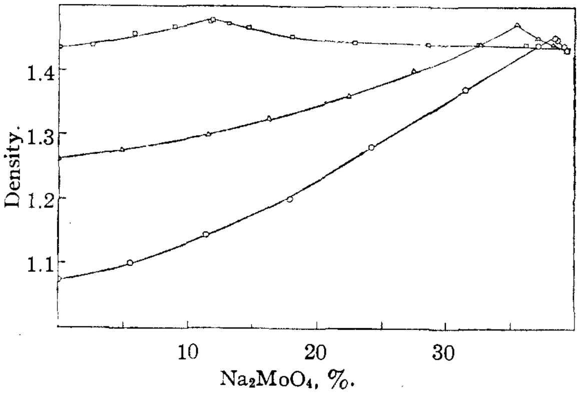

Fig. 4.—Densities of saturated solutions at 25°: □, Na_2MoO_4–$NaClO_3$–H_2O; △, Na_2MoO_4–$NaBrO_3$–H_2O; ○, Na_2MoO_4–$NaIO_3$–H_2O.

The systems are all three of the simplest type, as seen in Figs. 2 and 3, involving neither solid solution nor double salts. The solid phases are clearly the pure single salts (hydrated in the case of the molybdate and the iodate). The average absolute error of the extrapolation of the tie-lines to the compositions of these salts is 0.16% for the chlorate system, 0.19% for the bromate system and 0.19% for the iodate system.

It was expected that these systems would have a certain degree of similarity with the corresponding systems involving sodium sulfate in place of sodium molybdate, in view of the isomorphism of these salts as decahydrates; but the expected

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(5) Hill and Ricci, THIS JOURNAL, 53, 4305 (1931).

resemblance was not found, at least at the temperature studied. Sodium sulfate forms a double salt with the chlorate, $3Na_2SO_4 \cdot NaClO_3$,[6] a solid solution with the bromate,[7] and two double salts with the iodate, $NaIO_3 \cdot 3Na_2SO_4$ and $NaIO_3 \cdot 4Na_2SO_4$.[8] It is not impossible, of course, that the results here reported are partially metastable, and that more complex, stable phases have simply failed to crystallize.

Summary

1. The ternary systems Na_2MoO_4–$NaClO_3$–H_2O, Na_2MoO_4–$NaBrO_3$–H_2O and Na_2MoO_4–$NaIO_3$–H_2O have been studied at 25°. Unlike the corresponding sodium sulfate systems, these are of the simple type, involving neither double salts nor solid solutions at this temperature.

2. Some observations are reported on the interference of molybdate in the iodometric titration of iodate and bromate.

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[6] Ricci and Yanick, THIS JOURNAL, **59**, 491 (1931).

[7] Ricci, *ibid.*, **57**, 805 (1935).

[8] Foote and Vance, *Am. J. Sci.*, **19**, 203 (1930).

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

The Spectra of the Doubly Charged Positive Ions of Some *p,p'*-Diaminotriphenylmethane Dyes

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In two recent investigations by the authors[1] the spectra of some N-phenylated *p,p'*-diaminotriphenylmethyl ions were measured and compared with the spectrum of malachite green. In this article we shall report measurements of the spectra of the second ions of the same dyes, and compare the effects of phenylations with those on the spectra of the first ions.

The formulas of the second ions used are shown The ions II, III, IV and V are tautomeric, thus the tautomer of III is $C_6H_5N^+H_2C_6H_4C(C_6H_5){=}C_6H_4{=}N^+(CH_3)_2$. These tautomers lack the resonance arising from the conjugation of the terminal phenyl groups and the rest of the molecule. For this reason we believe that they exist at much lower concentrations then the ions II, III, IV and V.

Experimental Procedure

The spectra of the second ions were measured with a Beckman quartz spectrophotometer, using 1-cm. cells. A slit width of 0.02 mm. was used in the visible, but this was progressively increased more than tenfold as the measurements were carried to shorter wave lengths. The molarities of the dyes were of the order of magnitude of 10^{-5}. In two cases (VI and VIII) the concentrations were varied but no changes of molecular extinction coefficients were observed for a twofold change of concentration. The spectra were measured from 800 to 240 mμ. The dyes were dissolved as their color bases (carbinols or methyl ethers). These color bases were the same materials that had been used to measure the spectra of the first ions. Descriptions of them can be found in the references already given.

The solvent was glacial acetic acid. This solvent was chosen because the spectra of the first ions had been measured in it, because in acetic acid, the equilibria between the quinoidal second ions and their benzenoidal solvates are rapidly achieved and favor the quinoidal ions, and because acetic acid is a solvent in which very weak bases can be readily neutralized. This last property of the solvent is important, for the first ions of many of these dyes are exceedingly weak bases.

The acid to convert the first to the second ions was concentrated sulfuric acid whose density was 1.84 g./cc. The amounts of sulfuric acid were determined by volume. We shall give the concentrations of sulfuric acid as volume percentages, so that henceforth a per cent. of sulfuric acid connotes that volume of sulfuric acid of density 1.84 g./cc. made up to 100 volumes with glacial acetic acid. No significant solvent effect of change in the proportions of acetic acid and sulfuric acid on the spectra of the dyes was observed, so we have assumed that differences in the wave lengths of bands are due to differences in structure alone, even though the measurements may have been made in very different proportions of acetic acid and sulfuric acid.

A mixture of our acetic acid (boiling range 0.1°) and sulfuric acid after standing showed absorption when compared with a freshly prepared, but otherwise similar mixture. This absorption extended over the range measured, but was greatest from 260–280 mμ. The extinction of a two per cent. sulfuric acid that had stood for seven days was 0.3 at 260 mμ. This absorption was probably due to the action of the sulfuric acid on traces of impurities in the acetic acid. Errors due to this cause were eliminated by filling the comparison cell of the spectrophotometer with a mixture of acetic acid and sulfuric acid that had not only the same composition, but was also the same age as the mixture used to dissolve the dye.

To obtain the spectrum of a second ion, it is better to eliminate the first ion than to correct for the absorption due to the first ion. To make

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[1] Tolbert, Branch and Berlenbach, THIS JOURNAL, **67**, 887 (1945); Branch, Tolbert and Lowe, *ibid.*, **67**, 1693 (1945).