Solubility Isotherms and Specific Gravities in the Sodium Metaborate–Sodium Chlorate–Water System

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Solubility isotherms at −5°, 0°, 20°, 30°, 40°, 45°, 50°, 60°, and 75° C. were determined in the $NaBO_2$–$NaClO_3$–H_2O system. The solid phases were $NaBO_2 \cdot 4H_2O$, $NaBO_2 \cdot 2H_2O$, and $NaClO_3$. No double salts were formed.

SODIUM metaborate–sodium chlorate solutions are used commercially as herbicides. No previous study of solubility isotherms in the sodium metaborate–sodium chlorate–water system could be found in the literature. In the present investigation, the −5°, 0°, 20°, 30°, 40°, 45°, 50°, 60°, and 75° C. solubility isotherms were determined. Also, specific gravities of solutions containing sodium metaborate and sodium chlorate at 25° C. were determined in the region of practical interest.

EXPERIMENTAL

The starting materials were photographic grade sodium metaborate dihydrate, $NaBO_2 \cdot 2H_2O$, and tetrahydrate, $NaBO_2 \cdot 4H_2O$, United States Borax & Chemical Corp., typical analysis 0.007 and 0.02% SO_4, 0.05 and 0.04% Cl, 0.003 and 0.002% Ca, 1 and 1.5 p.p.m. Fe, respectively, and 10 p.p.m. Al; reagent grade sodium chlorate, J.T. Baker

Table I. Solubility Data in the 1:1:8 = $Na_2O \cdot B_2O_3 \cdot 8H_2O$ or $NaBO_2 \cdot 4H_2O$

Starting Materials				Analysis of Solutions		
Water, grams	1:1:8, grams	1:1:4, grams	$NaClO_3$, grams	$NaBO_2$, wt. %	$NaClO_3$ wt. %	Solid Phases
			−19.3° C.			
630[a]	210	0	477	5.01	34.73	Ice & 1:1:8 & C
			−5° C.			
...	...	...	...	13.2[b]	0.0	1:1:8
151	96.3	0	27.0	9.99	12.08	1:1:8
136.6	82.1	0	56.3	7.57	24.61	1:1:8
117.9	72.3	0	134.8	5.72	37.36	1:1:8 & C
120.0	0	0	160.0	0.0	43.03	C
			0° C.			
				14.5 (6)	0.0	1:1:8
149.9	98.1	0	27.0	10.92	11.74	1:1:8
140.0	78.5	0	56.3	8.37	23.70	1:1:8
119.9	66.0	0	139.1	6.12	37.98	1:1:8 & C
125.2	5.3	0	154.5	1.12	43.12	C
120.0	0	0	160.0	0.0	44.23	C
			10° C.			
120.0	0	0	160.0	0	46.63	C
			20° C.			
				20.0 (6)	0.0	1:1:8
165.1	113.0	0	27.0	16.46	9.18	1:1:8
144.5	104.2	0	56.3	13.02	20.47	1:1:8
117.9	70.0	0	140.0	9.06	39.83	1:1:8 & C
115.0	0	0	160.0	0.0	48.86	C
			30° C.			
				23.6 (6)	0.0	1:1:8
107.1	140.9	0	27.0	18.77	12.26	1:1:8
97.5	121.3	0	56.2	14.78	25.33	1:1:8
56.0	111.0	0	123.0	12.02	38.70	1:1:8 & C
94.8	26.7	0	103.5	5.76	45.22	C
101.0	0	0	174.0	0.0	51.10	C
			40° C.			
				27.9 (6)	0.0	
86.6	161.4	0	27.0	22.97	12.37	1:1:8
78.8	140.0	0	56.2	19.09	25.08	1:1:8
80.0	170.0	0	150.0	16.90	36.34	1:1:8 & C[c]
83.8	34.8	0	156.4	7.64	45.79	C
...	...	...	...	0.0	53.5[b]	C

[a] Ice. [b] Interpolated. [c] Identified by X-ray diffraction. [d] Seed.

Chemical Co., assay 100.0%, analysis 0.01% BrO_3 and 0.003% or less Ca, Mg, and NH_4OH precipitate, Cl, N, SO_4, and Fe; and distilled water. The solubilities were determined by the method previously described (*6*). Solutions of about 200 grams, containing the starting materials shown in Table I, were made up in polypropylene bottles, brought to the operating temperature, usually seeded with about 50 grams of the solid phases desired, and agitated for several hours to several days in a water or brine bath controlled to within 0.1° C. The thermometer was checked against one calibrated by the Bureau of Standards. At least three liquid samples from each mixture were analyzed, and the averages are shown in Table I and Figure 1. In some experiments, indicated in Table I, the solid phases were identified by x-ray diffraction, using ASTM cards 5-0610, 6-0122, and 14-677. Although in some cases a few of the peaks of the 1:1:8 compound were much stronger than in the usual pattern of this compound, there were no unexplained peaks.

Na_2O and B_2O_3 were determined by titration with 0.5*N* HCl using methyl red, followed by addition of mannitol and titration to phenolphthalein with 0.5*N* sodium hydroxide, which had been standardized against recrystallized dry boric acid. The weight per cent of $NaBO_2$ was calculated from the per cent of B_2O_3.

Chlorate was determined either by boiling with SO_2, with determination of the resulting chloride by the Volhard method, or by addition of excess $FeSO_4$ with H_2SO_4, boiling, and back-titration with $Na_2Cr_2O_7$, using barium diphenylamine sulfonate indicator. The $FeSO_4$ solution was standardized with $K_2Cr_2O_7$ in the presence of H_3PO_4.

To determine the invariant point saturated with $NaBO_2 \cdot 4H_2O$, $NaBO_2 \cdot 2H_2O$, and $NaClO_3$, a solution of the estimated composition at this point was made up using 371 grams of H_2O, 532 grams of $NaBO_2 \cdot 4H_2O$, and 497 grams of $NaClO_3$, heated to 40° C., and placed in a Dewar flask provided with a cover, thermometer, and stirrer. With stirring, 240 grams of $NaBO_2 \cdot 4H_2O$, 380 grams of $NaBO_2 \cdot 2H_2O$, and 140 grams of $NaClO_3$, preheated to 40° C., were added. The slurry was stirred for two hours. After the temperature became constant at 41.6° C., samples of the solution were taken.

To determine the invariant point in equilibrium with ice, $NaBO_2 \cdot 4H_2O$, and $NaClO_3$, 630 grams of crushed ice (made from distilled water) was mixed with 210 grams of $NaBO_2 \cdot 4H_2O$ and 477 grams of $NaClO_3$ in a covered,

$NaBO_2$–$NaClO_3$–H_2O System

1:1:4 = $Na_2O \cdot B_2O_3 \cdot 4H_2O$ or $NaBO_2 \cdot 2H_2O$ C = $NaClO_3$

Starting Materials				Analysis of Solutions		
Water, grams	1:1:8, grams	1:1:4, grams	$NaClO_3$, grams	$NaBO_2$, wt. %	$NaClO_3$, wt. %	Solid Phases
			41.6° C.			
371	532	380	497	18.43	34.82	1:1:8 & 1:1:4 & C
			45° C.			
				30.8[a]	0.0	1:1:8
75.1	177.4	0	22.5	26.62	10.24	1:1:8
69.1	167.8	0	38.3	24.12	17.76	1:1:8
59.5	132.5	40[d]	63.0	21.81	27.89	1:1:8 & 1:1:4[c]
61.3	96.2	50[d]	67.5	21.04	29.57	1:1:4
58.4	84.7	50[d]	131.9	18.44	35.97	1:1:4
81.4	40.1	0	153.5	8.56	45.97	C
101.0	0	0	174.0	0.0	54.5	C
			50° C.			
				34.1 (6)	0.0	1:1:8
64.3	183.7	0	27.0	30.04	11.06	1:1:8[c]
56.3	170.8	50[d]	27.9	29.65	12.97	1:1:8 & 1:1:4[c]
58.5	135.4	50[d]	31.5	29.18	13.79	1:1:4[c]
60.2	158.6	0	56.2	25.22	21.76	1:1:4[c]
60.2	108.6	50[d]	56.2	23.99	24.45	1:1:4
53.5	87.3	50[d]	134.2	18.67	36.97	1:1:4 & C
66.2	40.1	0	168.7	9.78	45.87	C
...	...	...	...	0.0	55.6[b]	C
			60° C.			
				38.3 (6)	0.0	
49.5	137.2	50[d]	38.2	29.58	16.65	1:1:4
42.7	216.9	0	141.3	19.74	38.28	1:1:4 & C
64.8	49.9	0	160.3	11.07	46.74	C
101.0	0	0	174.0	0.0	57.82	C
			75° C.			
				42.2 (6)	0.0	1:1:4
61.0	0	161.0	28.0	33.90	14.93	1:1:4
54.0	0	141.0	56.0	26.56	29.86	1:1:4
26.2	96.6	50.0	127.2	22.99	38.66	1:1:4 & C
61.7	46.3	0	167.0	10.03	51.61	C
70	0	0	180.0	0.0	61.15	C
			98° C.			
77.6	0	0	182.0	0.0	66.28	C

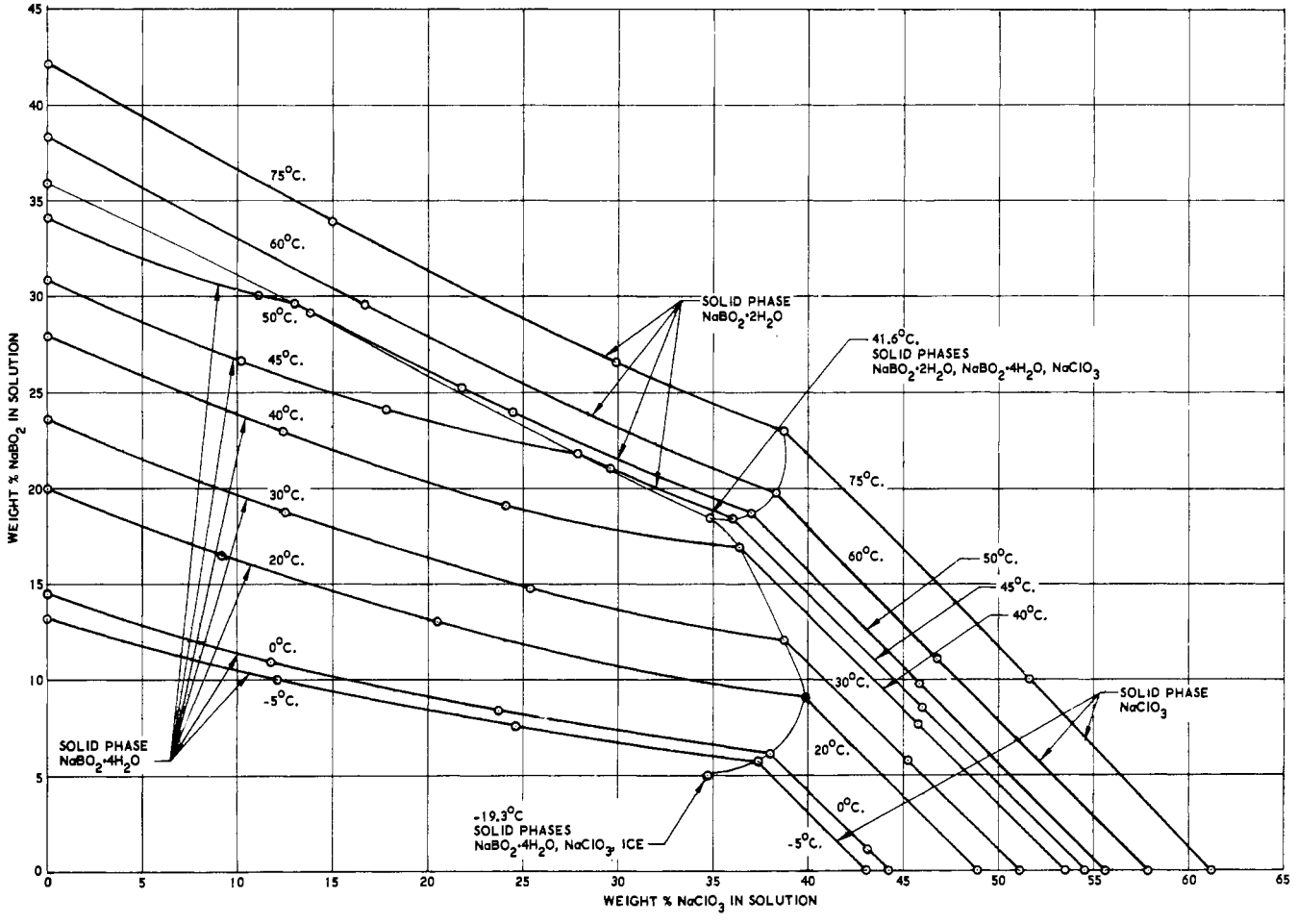

Figure 1. Solubility isotherms in the $NaBO_2$–$NaClO_3$–H_2O System at –5° to 75° C.

Table II. Pycnometric Data on Specific Gravity of Sodium Chlorate–Sodium Metaborate Solutions at 25° C.

$NaClO_3$, %	$NaBO_2$, %	Sp. Gr. 25°/25°
5	5	1.0950
5	10	1.1585
5	15	1.2245
5	19	1.2788
12	5	1.1486
12	10	1.2158
12	15	1.2851
12	17	1.3141
18	5	1.1980
18	10	1.2682
18	15	1.3418
25	5	1.2602
25	10	1.3348
25	13	1.3805

stirred Dewar flask. The ice and the salts were added alternately over a period of 1½ hours. The temperature became constant at –19.3° C., and samples of the liquid were then taken.

For the specific gravity determinations, a pycnometer having a capacity of 25 ml. was filled with the solutions at 25° C. The solutions were made up by weight, using sodium metaborate containing 47.92% $NaBO_2$. The results are given in Table II.

DISCUSSION

Table I and Figure 1 give the experimental solubility results and include values for sodium metaborate from previous work (*6*). The present data for the solubility of sodium chlorate in water are in satisfactory agreement with most literature values (*1, 5, 7, 8*). They do not agree with the results of one early author, who did not describe his experimental method (*2*).

The transition temperature of $NaBO_2 \cdot 4H_2O$–$NaBO_2 \cdot 2H_2O$ at 53.6° C., in contact with the saturated solution in the absence of other salts (*6*), decreases, as the sodium chlorate concentration is increased, to 41.6° C. at the invariant point.

No double salts were found in the $NaBO_2$–$NaClO_3$–H_2O system, although sodium metaborate forms the double salts $NaBO_2 \cdot NaCl \cdot 2H_2O$(*3*), $NaBO_2 \cdot Na_3PO_4 \cdot 18H_2O$(*4*), and $NaBO_2 \cdot NaBO_3 \cdot 4H_2O$(*9*), and sodium chlorate forms the double salt $NaClO_3 \cdot 3Na_2SO_4$(*8*).

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