The System Sodium Chlorite–Sodium Chlorate–Sodium Chloride–Water at Various Temperatures

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IN PREVIOUS articles, studies of the systems sodium chlorite–sodium chloride–water (*1*), sodium chlorite–sodium chlorate–water (*2*), and sodium chlorate–sodium chloride–water (*3*) were reported. Similar measurements have been made on the system involving all three of the above-mentioned salts. The system is a simple one; no double salts are formed within the temperature interval 25° to 45° C., the solid phases being sodium chlorate, sodium chlorite, sodium chlorite trihydrate, and sodium chloride. No evidence was found for the existence of hydrated sodium chlorate in the equilibrium mixture.

EXPERIMENTAL

As in previous work, the Schreinemaker wet residue method was used. The appratus and procedures were the same. The sodium chlorate and sodium chloride were analytical reagent grade. The water was distilled. The sodium chlorite was prepared from commercial, technical grade sodium chlorite (Olin Mathieson Chemical Corp.) as described previously.

The figures given in the table are in moles of salts and moles of water. The w function is the moles of water divided by the sum of the moles of sodium chlorate, sodium chlorite, and sodium chloride.

Analytical. Procedures for the analysis of chloride, chlorite, chlorate, and alkali, have been described by the work of White (*4*).

The solutions and wet residues were analyzed for chloride ion, chlorite ion, and chlorate ion. The water in the liquid phase and in the wet residue was determined by difference.

RESULTS

In the quaternary system sodium chlorite–sodium chlorate–sodium chloride–water three isotherms have been

Table I. Quaternary System Sodium Chlorite–Sodium Chlorate–Sodium Chloride–Water

Composition of Solution, Moles					Composition of Wet Residue, Moles				Solid Phase[a]
$NaClO_2$	$NaClO_3$	NaCl	w	Sp. Gr.	$NaClO_2$	$NaClO_3$	NaCl	w	
				Data at 25° C.					
0.1763	0.1361	0.6885	7.72	1.273	0.0316	0.0240	0.9285	1.38	*D*
0.2488	0.1418	0.6095	7.29	1.290	0.0612	0.0357	0.9032	1.83	*D*
0.3899	0.1170	0.4984	7.04	1.321	0.0962	0.0335	0.8703	1.72	*D*
0.5340	0.1351	0.4091	6.73	1.356	0.1182	0.0306	0.8512	1.47	*D*
0.2461	0.2124	0.5408	6.84	1.314	0.0456	0.0391	0.9152	1.25	*D*
0.3096	0.2124	0.4788	6.59	1.332	0.0562	0.0389	0.9046	1.18	*D*
0.4210	0.1928	0.3863	6.09	1.361	0.0995	0.0450	0.8555	1.43	*D*
0.5546	0.1806	0.2641	5.43	1.412	0.1577	0.0432	0.7991	1.51	*D*
0.1170	0.1095	0.7737	7.44	1.249	0.0129	0.0113	0.9762	0.92	*D*
0.1252	0.3680	0.5068	6.59	1.338	0.0147	0.0441	0.9410	0.79	*D*
0.1160	0.0997	0.7851	8.07	1.249	0.0119	0.0104	0.9778	0.82	*D*
0.1718	0.2784	0.5498	6.84	1.318	0.0268	0.0435	0.9300	1.03	*D*
0.1752	0.3798	0.4451	6.18	1.358	0.0225	0.0493	0.9283	0.80	*D*
0.1771	0.1096	0.7132	7.77	1.265	0.0227	0.0141	0.9632	0.96	*D*
0.1166	0.6861	0.1972	5.55	1.429	0.0373	0.9004	0.0623	1.74	*C*
0.2304	0.5743	0.1951	5.31	1.443	0.0867	0.8733	0.0578	1.57	*C*
0.3272	0.4863	0.1865	4.96	1.459	0.1084	0.8291	0.0628	1.64	*C*
0.4209	0.4078	0.1706	4.65	1.481	0.1489	0.7907	0.0604	1.60	*C*
0.1270	0.5899	0.2837	5.44	1.424	0.0400	0.8702	0.0900	1.70	*C*
0.1849	0.5483	0.2669	5.31	1.432	0.0600	0.8527	0.0873	1.70	*C*
0.1980	0.6149	0.1872	5.33	1.439	0.0384	0.9254	0.0362	1.04	*C*
0.2979	0.4566	0.2454	4.90	1.452	0.0933	0.8212	0.0856	1.56	*C*
0.1106	0.7947	0.0947	5.67	1.438	0.0178	0.9662	0.0160	0.93	*C*
0.6970	0.1921	0.1109	4.78	1.451	0.8476	0.1021	0.0502	3.96	*A*
0.8023	0.1225	0.0751	5.65	1.420	0.9137	0.0581	0.0282	4.07	*A*
0.7599	0.1832	0.0568	5.33	1.447	0.8754	0.0953	0.0292	4.20	*A*
0.4781	0.3395	0.1831	4.35	1.481	0.1028	0.5294	0.3679	1.13	*C, D*
0.3144	0.4338	0.2519	4.85	1.446	0.0791	0.7714	0.1495	1.47	*C, D*
0.4209	0.3728	0.2058	4.53	1.468	0.1068	0.7230	0.1702	1.36	*C, D*
0.5276	0.3069	0.1655	4.25	1.493	0.1518	0.6765	0.1651	1.49	*C, D*
0.0564	0.5875	0.3560	5.49	1.410	0.0107	0.0244	0.7453	1.07	*C, D*
0.1645	0.5306	0.3050	5.30	1.427	0.0311	0.4167	0.5527	1.01	*C, D*
0.4122	0.3950	0.1934	4.54	1.478	0.0762	0.3779	0.5462	0.85	*C, D*
0.4626	0.3775	0.1696	4.38	1.493	0.1056	0.7497	0.1447	0.99	*C, D*
0.5952	0.3296	0.0754	3.94	1.532	0.3866	0.5892	0.0242	1.84	*A, C*
0.6124	0.3479	0.0396	4.05	1.531	0.4110	0.5748	0.0142	1.98	*A, C*
0.6469	0.1782	0.1749	4.70	1.466	0.7707	0.0893	0.1400	3.54	*A, D*
0.6798	0.1130	0.2071	4.98	1.434	0.6779	0.0565	0.2656	3.20	*A, D*
0.6336	0.3664	0.0000	4.19	1.533	0.3012	0.6988	0.0000	1.53	*A, C*
0.5709	0.3139	0.1153	3.80	1.534	0.5010	0.0878	0.4113	2.09	*A, D, C*

[a] *A* $NaClO_2 \cdot 3H_2O$, *B* $NaClO_2$, *C* $NaClO_3$, *D* NaCl.

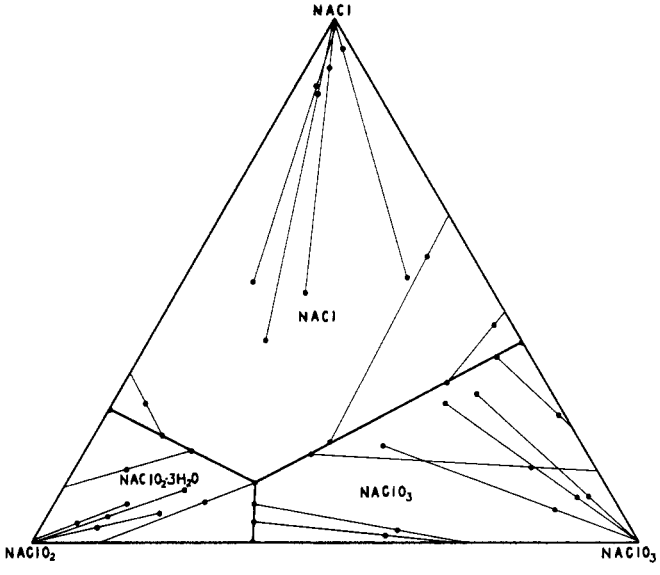

Figure 1. Sodium chlorite–sodium chlorate–sodium chloride–water system at 25° C.

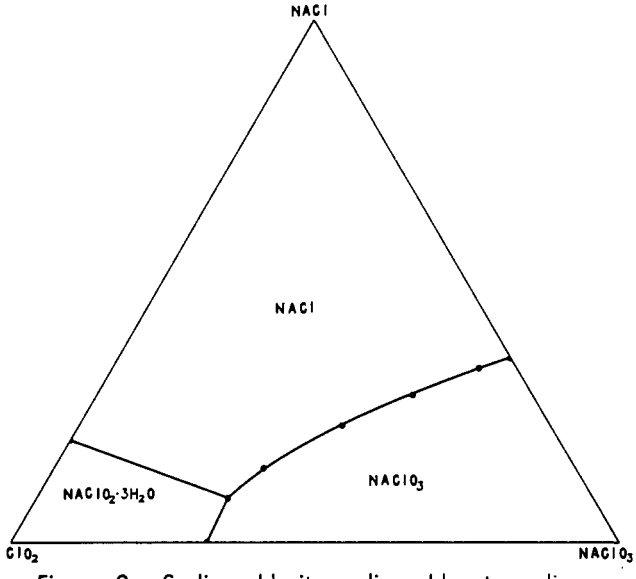

Figure 2. Sodium chlorite–sodium chlorate–sodium chloride–water system at 30° C.

Table I. (Continued)

Composition of Solution, Moles					Composition of Wet Residue, Moles				Solid
$NaClO_2$	$NaClO_3$	NaCl	w	Sp. Gr.	$NaClO_2$	$NaClO_3$	NaCl	w	Phase[a]
				Data at 30° C.					
0.7512	0.0000	0.2488	5.46	1.4150	...	...	...	...	*D*
0.5520	0.0000	0.4480	6.74	1.3245	...	...	...	...	*D*
0.3160	0.0000	0.6840	7.84	1.2642	...	...	...	...	*D*
0.0850	0.0000	0.9150	8.70	1.2152	...	...	...	...	*D*
0.0000	0.0000	1.0000	9.01	1.1955	...	...	...	...	*D*
0.5380	0.4620	0.0000	4.30	1.5142	...	...	...	...	*C*
0.1804	0.8196	0.0000	5.11	1.4621	...	...	...	...	*C*
0.0000	1.0000	0.0000	5.49	1.4560	...	...	...	...	*C*
1.0000	1.0000	0.0000	5.79	1.4120	...	...	...	...	*A*
0.8743	0.0000	0.1257	5.41	1.4310	...	...	...	...	*A*
0.9190	0.0910	0.0000	5.20	1.4444	...	...	...	...	*A*
0.7890	0.2110	0.0000	4.35	1.5075	...	...	...	...	*A*
0.0000	0.6459	0.3541	5.41	1.4091	...	...	...	...	*C, D*
0.0611	0.6050	0.3339	5.30	1.4235	...	...	...	...	*C, D*
0.1972	0.5201	0.2827	5.01	1.4415	...	...	...	...	*C, D*
0.3407	0.4352	0.2241	4.63	1.4695	...	...	...	...	*C, D*
0.5111	0.3470	0.1419	3.99	1.5111	...	...	...	...	*C, D*
0.8025	0.0000	0.1975	4.95	1.4395	...	...	...	...	*A, D*
0.6790	0.3210	0.0000	3.49	1.5645	...	...	...	...	*A, C*
0.5994	0.3140	0.0866	3.51	1.5360	...	...	...	...	*A, C, D*
				Data at 45° C.					
0.1367	0.1379	0.7254	7.70	1.269	0.0196	0.0201	0.9603	1.09	*D*
0.2425	0.2658	0.4917	6.46	1.338	0.0349	0.0386	0.9265	0.95	*D*
0.3124	0.3665	0.3211	5.39	1.409	...	...	...	...	*D*
0.7818	0.0000	0.2182	5.51	1.444	0.1538	0.0000	0.8462	1.08	*D*
0.6712	0.0000	0.3288	5.98	1.378	0.1136	0.0000	0.8863	1.00	*D*
0.5338	0.0000	0.4662	6.75	1.329	0.0798	0.0000	0.9202	1.01	*D*
0.2769	0.0000	0.7231	7.89	1.262	0.0312	0.0000	0.9688	0.88	*D*
0.1476	0.0000	0.8524	8.38	1.234	0.0169	0.0000	0.9831	0.96	*D*
0.0000	0.0000	1.0000	9.01	1.200	...	...	...	...	*D*
0.1605	0.6682	0.1713	4.69	1.487	0.0523	0.8912	0.0565	1.52	*C*
0.3187	0.6055	0.0758	4.21	1.526	0.1116	0.8614	0.0270	1.50	*C*
0.7340	0.1842	0.0818	3.58	1.561	0.7881	0.1465	0.0654	2.84	*B*
0.8012	0.1303	0.0685	3.83	1.543	0.8953	0.0684	0.0363	1.97	*B*
1.0000	0.0000	0.0000	4.46	1.508	...	...	...	...	*B*
0.9244	0.0000	0.0756	4.34	1.504	0.9522	0.0000	0.0478	2.70	*B*
0.8710	0.0000	0.1290	4.35	1.501	0.6737	0.0000	0.3257	1.80	*B, D*
0.1382	0.6375	0.2243	4.42	1.487	0.0396	0.6945	0.2659	1.26	*C, D*
0.2845	0.5418	0.1737	4.09	1.515	0.0762	0.5243	0.3995	1.07	*C, D*
0.4932	0.4013	0.1055	3.50	1.574	0.1613	0.5021	0.3366	1.13	*C, D*
0.0000	0.7228	0.2772	4.75	1.458	...	...	...	...	
0.6979	0.2069	0.0952	3.50	1.569	0.5973	0.1375	0.2652	2.30	*B, D*
0.7567	0.1359	0.1074	3.72	1.543	0.5645	0.0782	0.3573	2.17	*B, D*
0.8710	0.0000	0.1290	4.39	1.561	...	...	...	...	*B, D*
0.6107	0.3412	0.0483	3.07	1.621	0.5485	0.4205	0.0310	1.92	*B, C*
0.6312	0.3688	0.0000	3.07	1.646	0.5613	0.4387	0.0000	1.58	*B, C*
0.5953	0.3305	0.0740	3.05	1.620	0.5080	0.2922	0.1998	1.67	*B, C, D*

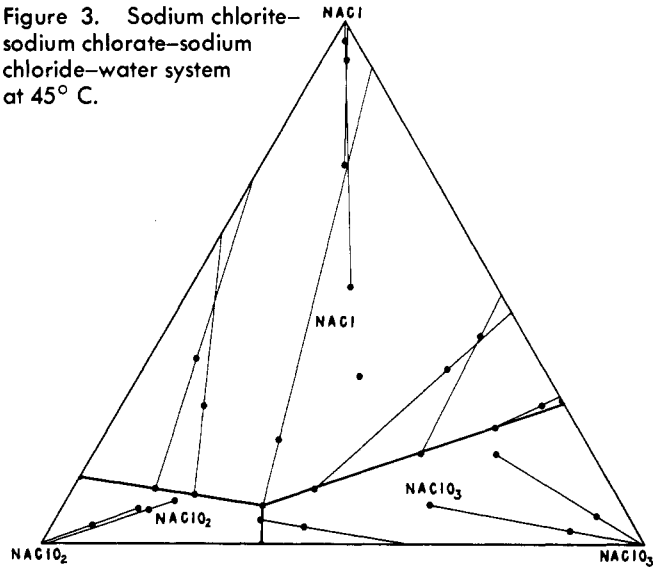

Figure 3. Sodium chlorite–sodium chlorate–sodium chloride–water system at 45° C.

worked out at 25°, 30°, and 45° C. The data are summarized in Table I and shown in Figures 1, 2, and 3. They show only the trihydrate of sodium chlorite already known, sodium chlorite, sodium chlorate, and sodium chloride.

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LITERATURE CITED

(1) Cunningham, G. L., Oey, T. S., *J. Am. Chem. Soc.* **77**, 799 (1955).
(2) *Ibid.*, p. 4498.
(3) Oey, T. S., Koopman, D. E., *J. Phys. Chem.* **62**, 755 (1958).
(4) White, J.F., *Am. Dyestuff Reptr.* **31**, 484 (1942).

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Solubilities of Potassium Chloride and Sodium Iodide in Dimethylsulfoxide-Water Mixtures

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THE SOLUBILITY of potassium chloride in dimethylsulfoxide (DMSO) and water mixtures over the range 0 to 90% water and the solubility of sodium iodide in the same mixtures over the range 0 to 20% water has been measured. The results are reported in Table I. The solubilities in pure dimethylsulfoxide are 0.209 and 15.6 grams per 100 ml. of solution for potassium chloride and sodium iodides, respectively, at 25° C. Hence the solubilities of these two salts in this solvent (dielectric constant = 45) are much less than in water at the same temperature. The solubilities of the salts in the solvent mixtures increase with increasing water content.

Table I. Solubility of Halides at 25° C.

Potassium Chloride DMSO-Water Mixtures

DMSO, Vol., %	Grams/100Ml. Solution	DMSO, Vol., %	Grams/100 Ml. Solution
100	0.209	70	2.567
98	0.348	60	4.582
96	0.397	50	7.497
94	0.446	40	11.40
92	0.518	30	15.92
90	0.623	20	20.97
80	1.262	10	26.16

Sodium iodide in DMSO-Water Mixtures

		Method
100	15.55	Titration
96	18.75	Spectrophotometric
80	35.25	Spectrophotometric

EXPERIMENTAL

The solvent (Stepan Chemical Co., Chicago, Ill.) was distilled at approximately 70° C. under reduced pressure before use. The first half of the distillate was discarded and about two thirds of the remaining solvent was collected. This fraction contained less than 0.005 mole per liter of water.

The solvent was saturated with salt by shaking with an excess of solid salt, in a mechanical shaker, for 1 week. Further shaking did not increase the solubility of the salt as shown by the analyses performed.

The solubility of potassium chloride was determined by withdrawing a 10.00-ml. aliquot of the filtered saturated solution, weighing, evaporating at 110° C., and reweighing. The error by this method was approximately 4%.

The solubility of sodium iodide was determined by withdrawing an aliquot of the filtered, saturated solution, oxidizing with excess potassium dichromate in aqueous hydrochloric acid solution, extracting iodine with carbon tetrachloride, and either titrating with standard thiosulfate solution or determining the iodine concentration spectrophotometrically, using the iodine peak at 520 μ. A plot of standard iodine concentration *vs.* absorbance obeyed Beer's law over the concentration range $0 \leq [I_2] \leq 8 \times 10^{-3} M$.

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