[CONTRIBUTION FROM THE APPLIED SCIENCE LABORATORY, UNIVERSITY OF CINCINNATI]

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

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The univariant equilibria of the binary system sodium chlorite–water and the ternary system sodium chlorite–sodium chloride–water have been examined, and the isotherms at 15, 25 and 35° obtained. The transition temperature of sodium chlorite trihydrate–sodium chlorite is 37.4°. No double salts exist in equilibrium with the solutions within the temperature interval 15–35°. Janecke diagrams of the isotherms, with contours of water content are given. A cooling curve showing the transition temperature for sodium chlorite trihydrate–sodium chlorite is also given.

Previous Work.—The system sodium chlorite–water at various temperatures has been reported on by Taylor, White, Vincent and Cunningham.[2] They gave data on the system within the temperature interval 0–60° and gave the transition temperature of sodium chlorite trihydrate–sodium chlorite trihydrate as the stable phase in equilibrium with aqueous solutions at room temperature.[3,4] No data are reported in the literature regarding the ternary system sodium chlorite–sodium chloride and water. As the early investigation on the binary system is not quite complete, the solubility of sodium chloride in pure water has been re-examined.

Materials.—For starting salt, the commercial, technical grade of sodium chlorite was recrystallized three times from distilled water as the trihydrate. This sodium chlorite trihydrate was stored in a cool place in amber bottles. Sodium chlorite trihydrate and solutions of sodium chlorite are stable in the presence of a trace of alkalinity if light is excluded. (*Anal.* sodium chlorite, 58.50%; sodium chloride, 0.00%; sodium chlorate, 0.00%; alkalinity as Na_2O, 0.06%; water by difference, 41.44%). The technical sodium chlorite used in this investigation was donated by The Mathieson Chemical Corporation.

The sodium chloride used in the experiments was obtained from J. T. Baker ("Baker's Analyzed"). The impurities listed were much too small to affect the results. Distilled water was used in all of the experiments.

Experimental.—The experiments were carried out as is customary in equilibrium investigations. Complexes of known composition were prepared from the solid salts and distilled water in Pyrex solubility tubes. Mixtures of solid and liquid were equilibrated by rotation in a large thermostated water-bath at various temperatures for periods of 120 hours or longer. The temperature of the bath was maintained at ±0.1°. Aliquots of liquor, and wet residue solids for analysis were obtained with proper precautions against contamination, and loss of water vapor. The liquid sample was passed through a glass wool filter, without taking the solubility tube or the filter out of the thermostated water-bath. The saturated solutions were taken by means of a calibrated pipet having small stopcocks at each end.

Establishment of equilibrium was proved by rotating the solubility tube for periods of 120 hours or longer, after which the liquid phase and the wet residue were analyzed. The same solubility tube was rotated again for a period of 120 hours or longer and the liquid phase and the wet residue solid were again analyzed. If there was no substantial change in the composition of the liquid phase or the wet residue solid it was taken as proof that equilibrium had been attained.

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

Analytical.—Procedures for the analysis of chlorite, chloride, chlorate, hypochlorite and alkali have been de-

TABLE I

THE BINARY SYSTEM SODIUM CHLORITE–WATER

Solid phase: A, $NaClO_2 \cdot 3H_2O$; B, $NaClO_2$. Composition of the saturated solution between 5 and 60°

Temp., °C.	$NaClO_2$, moles	H_2O, moles	Sp. gr.	w	Solid phase
5				(9.6)	A
15	0.1002	0.820	1.327	8.18	A
17				(7.8)	A
25	.0864	.562	1.375	6.51	A
30				(5.8)	A
35	.1456	.720	1.460	4.94	A
45				(4.5)	B
45	.1596	.684	1.501	4.28	B
60				(4.1)	B

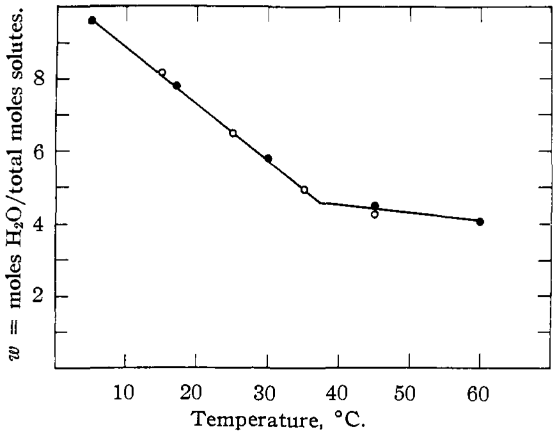

Fig. 1.—The system sodium chlorite–water at various temperatures.

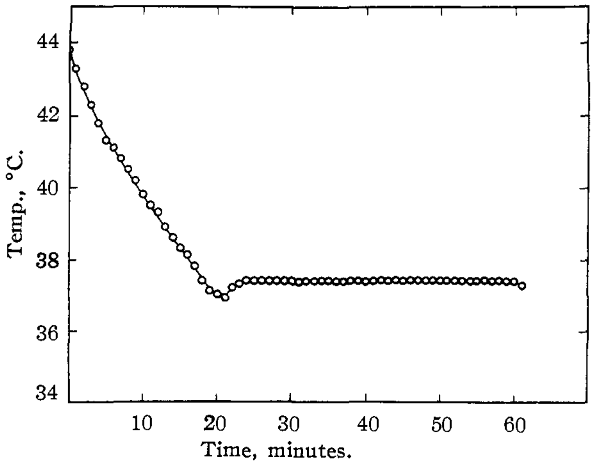

Fig. 2.—Cooling curve for molten sodium chlorite trihydrate.

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[2] M. C. Taylor, J. F. White, G. P. Vincent and G. L. Cunningham, *Ind. Eng. Chem.*, **32**, 899 (1940).

[3] G. R. Levi, *Gazz. chim. ital.*, **52**, 417 (1922); **53**, 532 (1923).

[4] E. Artini, *Atti. accad. Lincei*, [5] **II**, 31, 65 (1922).

scribed by White.[5] The water in the liquid phase and the wet residue solid were determined by difference. The composition of the solid phase was determined by Schreinemaker's residue method.

The Binary System Sodium Chlorite–Water.—In the literature the determinations of Taylor, White, Vincent and Cunningham[2] are usually cited. Our results for this binary system are summarized in Table I, which shows in parentheses the values of Taylor, White, Vincent and Cunningham. Since the determination of the transition temperature of sodium chlorite trihydrate–sodium chlorite depends to a marked degree upon the value taken for the solubility of sodium chlorite at 45°, where there is the greatest divergence in the data, we have determined the transition temperature by running a cooling curve on molten sodium chlorite trihydrate. This cooling curve is shown in Fig. 2. This independent determination of the transition temperature shows that it is 37.4° which is in good agreement with the transition temperature obtained from the break in the curve in Fig. 1, and with the transition temperature of 38° as reported by Taylor, White, Vincent and Cunningham.

TABLE II

THE TERNARY SYSTEM SODIUM CHLORITE–SODIUM CHLORIDE–WATER

Solid phase: A, $NaClO_2 \cdot 3H_2O$; C, NaCl.

x	Compn. of soln., w	Sp. gr.	Compn. of wet residue x	Compn. of wet residue w	Solid phase
		Temp. 15°			
0.1046	7.59	1.331	0.0260	3.83	A
.2591[a]	7.05	1.339	.0825	4.12	A
.3509	6.48	1.345	.1170	3.91	A
.3790	6.30	1.349	.2273	3.51	A, C
.4958	6.93	1.310	.9259	0.99	C
.6471	7.62	1.272	.9406	1.23	C
.7821	8.18	1.243	.9705	1.12	C
.8891	8.58	1.217	.9876	1.02	C
1.0000	9.08	...	....	..	C
		Temp. 25°			
0.0779	6.17	1.391	0.0255	3.72	A
.1579	6.07	1.391	.0490	3.89	A
.1858	5.95	1.395	.0645	4.02	A
.2571	5.57	1.400	.2368	3.74	A, C
.3717	6.31	1.349	.8750	1.26	C
.5438	7.13	1.296	.9084	1.49	C
.6156	7.49	1.278	.9385	1.21	C
.6971	7.96	1.260	.9574	1.18	C
.8426	8.38	1.229	0.9769	1.21	C
1.0000	9.01	...	....	..	C
		Temp. 35°			
0.0423	4.66	1.465	0.0192	3.67	A
.0848	4.46	1.470	.0313	3.44	A
.0921[a]	4.44	1.472	.0519	3.87	A
.1339	4.26	1.483	.2899	2.92	A, C
.3328	5.96	1.363	.8639	1.24	C
.5214	6.97	1.301	.9156	1.27	C
.6301	7.49	1.273	.9308	1.40	C
.7672	8.13	1.244	.9574	1.46	C
.8829	8.58	1.222	.9858	1.21	C
1.0000	8.96	...	....	..	C

[a] Tube put in bath for 5 and 10 days.

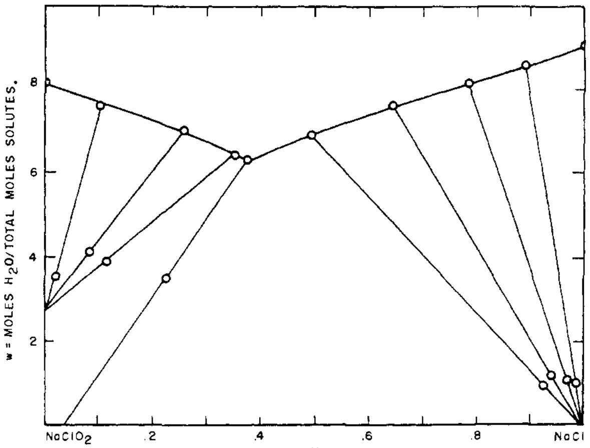

Fig. 3.—The system sodium chlorite–sodium chloride–water at 15°.

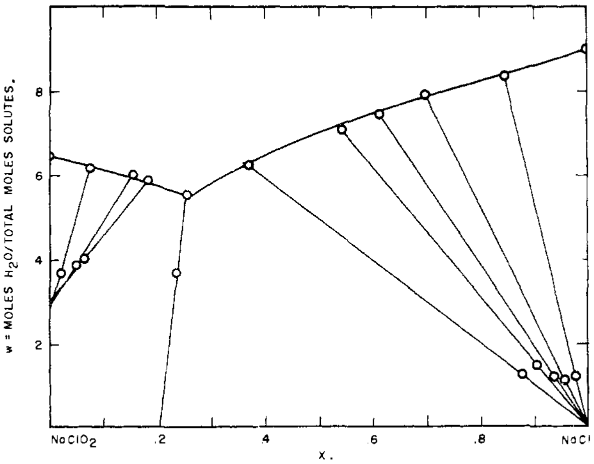

Fig. 4.—The system sodium chlorite–sodium chloride–water at 25°.

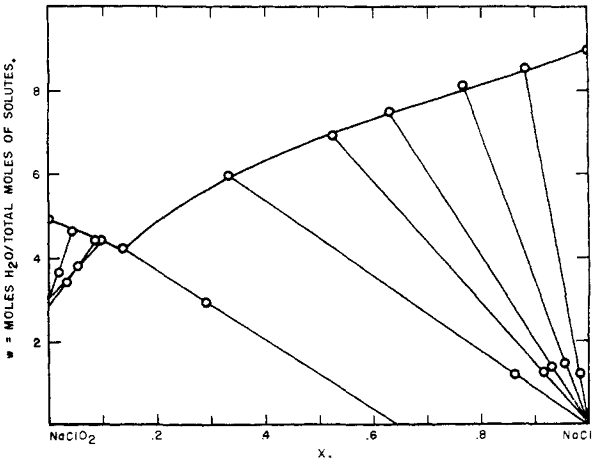

Fig. 5.—The system sodium chlorite–sodium chloride–water at 35°.

The Ternary System Sodium Chlorite–Sodium Chloride–Water.—In this system three isotherms have been worked out: 15, 25 and 35°. The data

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(5) J. F. White, *Am. Dyestuff Reportr.*, **31**, 484 (1942).

are summarized in Table II and shown in Figs. 3, 4 and 5. They show only the trihydrate of sodium chlorite already known and pure sodium chloride.

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Anion Exchange Studies. XIII. The Alkaline Earths in Citrate Solutions[1,2]

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The anion-exchange behavior of the alkaline earths was studied in citrate solutions with a strong base anion-exchange resin. The elements were found to adsorb, and there were sufficient differences in their adsorbabilities to permit their separation from each other. In addition, separation of the alkaline earths from alkali metals, rare earths and a few other elements was demonstrated. The implications of the anion-exchange results on the strength and composition of citrate complexes of the alkaline earths are discussed.

Recent investigations by a number of techniques, including cation exchange, have shown that the alkaline earths form relatively strong citrate complexes in citrate solutions. For most of these elements the formation of a monocitrate complex has been proposed according to the equation

$$M^{++} + Cit^{-3} \rightleftharpoons MCit^{-} \qquad (1)$$

where M^{++} = alkaline earth ion and Cit^{-3} = citrate ion. Stability quotients

$$k^{m}{}_{01} = m_{MCit}/m_{Cit}m_{M} \qquad (2)$$

were estimated to be *ca.* 1700 for Mg[3a,b]; *ca.* 1600 to 1700 for Ca[3a,c,g]; *ca.* 500 to 800 for Sr[3a,c,d,g,h]; *ca.* 200 for Ba[3e]; and *ca.* 100 for Ra.[3f] Strong citrate complexing also has been reported for Be.[4] Although the charge and formula of this complex (or complexes) has not been determined, there is little doubt that it is negatively charged. On the basis of this information on the stability constants of the alkaline earths, one could assume that they exist principally as negatively charged species at moderate citrate concentrations, and hence that they could be adsorbed by anion exchange resins. A systematic study of the anion exchange behavior of the alkaline earths in citrate solutions was carried out over the concentration range *ca.* 5×10^{-3} to *ca.* 1 M $(NH_4)_3Cit$. The elements were found to be adsorbable, as expected, and a number of separations based on differences in adsorbability were achieved. Confirmation of the existence of the complexes $MCit^{-}$ was obtained, as well as evidence for the existence of complexes $M(Cit)_2^{-4}$.

Experimental

Adsorbabilities were measured with the same relatively highly cross-linked "strong base" anion-exchange resin (polystyrene-divinylbenzene quaternary amine resin, Dowex-1, 200–230 mesh) which was used in the earlier work. The resin, initially in the chloride form, was converted to the citrate form[2] by treating a column of the resin with 0.5 M $(NH_4)_3Cit$ solution of *p*H *ca.* 8 until the effluent gave negligible chloride test with $AgNO_3$. The column was then washed with water to remove excess $(NH_4)_3Cit$. The top section, which contained visible adsorbed impurities (principally Fe(III)) was discarded and the remaining resin air-dried. Portions of the resin were analyzed for moisture by drying over Anhydrone at 60° and all-resin weights refer to the Anhydrone-dried material. The citrate content of the resin was determined by eluting[5] the citrate from a weighed amount of resin with a known volume of standardized HCl solution and by washing the resin with water to recover the excess HCl. The combined effluents were analyzed for chloride by titration with standard $AgNO_3$ and for total acid with standard base. From the differences in the chloride analyses of the original HCl solutions and of the effluents, the amount of chloride retained by the resin was calculated to be 1.49 moles per liter of bed (chloride form), in good agreement with previous values for the capacity of the resin.[6] The citrate content of the effluent was determined from the acid titrations and the chloride titrations and was found to be 0.50 mole of H_3Cit per l. of bed (chloride form). Thus 0.33 mole of $Cit^{\equiv}$ was eluted per mole of Cl^{-} adsorbed, substantiating that the resin originally was essentially in the citrate form and contained only negligible amounts of acid citrates.

The adsorbabilities of Be(II) and Mg(II) were rather high and were most conveniently determined by the equilibrium method,[7] although a few check experiments were also carried out by the column method.[7] The adsorbabilities of the other alkaline earths were relatively low and hence were determined by the column method.

In the equilibrium method, samples of resin and solution were shaken for at least several hours. The Be(II) solutions were analyzed radiometrically (54d Be^7) by counting liquid samples in a re-entrant hole sodium iodide scintillation counter.[8] The Mg(II) analyses were carried out either radiometrically (21b Mg^{28}), spectrographically, or by flame spectrophotometry.[9]

As in earlier work, amounts of resin and solution were chosen so that approximately half of the metal was removed from the solution at equilibrium. Distribution coefficients D (amount per kg. of Anhydrone dry resin/amount per liter

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper: F. Nelson and K. A. Kraus, THIS JOURNAL, **76**, 329 (1954).

[3] (a) A. B. Hastings, F. S. McLean, L. Eichelberger, S. L. Hall and E. DaCosta, *J. Biol. Chem.*, **107**, 351 (1934); (b) R. Nordbo, *Skand. Arch. Physiol.* **80**, 341 (1933); See *C. A.* **33**, 454^4 (1939); (c) J. Muus and H. Lebel, *Kgl. Danske Vedenskab. Selskab. Math-fys. Medd.* **13**, No. 19 (1936); see *C. A.* **31**, 1722^1 (1937); (d) N. R. Joseph, *J. Biol. Chem.* **164**, 529 (1946); (e) J. Schubert and J. W. Richter, THIS JOURNAL, **70**, 4259 (1948); (f) J. Schubert, E. R. Russell and L. S. Myers, *J. Biol. Chem.*, **185**, 387 (1950); (g) J. Schubert and L. Lindenbaum, THIS JOURNAL, **74**, 3529 (1952); (h) J. Schubert, *J. Phys. Chem.*, **56**, 113 (1952).

[4] See *e.g.* (a) I. Feldman, W. F. Neuman, R. A. Dannley and J. R. Havill, THIS JOURNAL, **73**, 4775 (1951); (b) A. W. Thomas and H. S. Miller, *ibid.*, **58**, 2526 (1936).

[5] F. Nelson and K. A. Kraus, *ibid.*, **76**, 329 (1954).

[6] K. A. Kraus and G. E. Moore, *ibid.*, **75**, 1457 (1953).

[7] K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

[8] C. J. Borkowski, Report ORNL-1153 (1951).

[9] We are indebted to Mr. M. Murray and Mr. W. R. Laing of the ORNL Analytical Division for the spectrographic and flame spectrophotometric analyses.

The Mg^{28} tracer was prepared by a spallation reaction (chlorine) in the 184 inch Berkeley cyclotron (see Lindner, *Phys. Rev.*, **91**, 642 (1953)). The tracer was purified by carrying on $Fe(OH)_3$, removing Fe(III) by anion exchange in chloride solutions (G. E. Moore and K. A. Kraus, THIS JOURNAL, **72**, 5792 (1950)), followed by cation exchange using 0.5 M HCl as eluent. We are indebted to Dr. R. K. Sheline for γ-ray spectrum analysis of the purified Mg^{28} tracer (purity > 99%).