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Solubility and Density of Chloric Acid + Sodium Chlorate Solutions

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Solubilities of sodium chlorate were measured in chloric acid solutions ranging in concentration from 5 to 22 mass % $HClO_3$ at temperatures of 25, 35, 45, 55, and 65 °C. Densities of saturated solutions were determined by weighing measured volumes of the solutions. Densities of chloric acid solutions and unsaturated chloric acid + sodium chlorate solutions were determined at 25 °C over a range of solution concentrations using a digital density meter. The solubility data and previously reported data from literature sources were correlated with chloric acid concentration and temperature by multilinear regression. All of the data could be represented graphically by a single line by plotting the ratio of sodium chlorate solubility in chloric acid solution to sodium chlorate solubility in water versus mass percent chloric acid. The specific volume of chloric acid at 25 °C is linear with respect to chloric acid concentration. A parameter determined from the slope of this linear plot and the density of crystalline sodium chlorate were used to correlate densities of chloric acid solutions containing sodium chlorate.

Introduction

Chlorine dioxide is manufactured commercially by reaction of chlorate ions in acidic solution with a reducing agent. Most chlorine dioxide is produced at sites where it is consumed. For these processes, economic, safety, and handling considerations usually favor sodium chlorate and sulfuric acid as the sources of chlorate and hydrogen ions. The choice of feedstocks and reaction stoichiometry fix the relative quantities of byproduct and product. For example, a process that employs sodium chlorate and sulfuric acid, as well as hydrogen peroxide as reducing agent (Burke et al., 1993),

$$2NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2ClO_2 + O_2 + 2H_2O + Na_2SO_4 \quad (1)$$

produces about 1 ton of crystalline sodium sulfate per ton of chlorine dioxide.

Pulp and paper facilities, which are the largest consumers of chlorine dioxide, also consume some, but not necessarily all, of the sodium sulfate produced with the chlorine dioxide. For those plants that consume only a portion of the sodium sulfate, there may be interest in finding ways of reducing the amount of sodium sulfate produced per ton of chlorine dioxide.

Recently, there has been some consideration of chloric acid, $HClO_3$, as a potential substitute for portions of the sodium chlorate and sulfuric acid in chlorine dioxide manufacture. Chlorine dioxide produced from chloric acid,

$$2HClO_3 + H_2O_2 \rightarrow 2ClO_2 + O_2 + 2H_2O \quad (2)$$

is not accompanied by production of sodium sulfate. In theory, the ratio of sodium sulfate and chlorine dioxide produced could be tailored to consumer specifications by adjusting the proportions of sodium chlorate, chloric acid, and sulfuric acid fed to the process. The overall process stoichiometry would be the sum of contributions from eqs 1 and 2.

Various methods have been proposed for producing chloric acid or for producing solutions containing both chloric acid and sodium chlorate (for example, ion exchange as reported by Schlumberger (1974) and Hardee and Sacco (1989), the electrochemical method of Kaczur et al. (1993), bipolar membrane electrodialysis as reported by Paleologou et al. (1992), from hypochlorous acid by chemical reaction by Duncan et al. (1991), and the standard laboratory preparation from barium chlorate in Lamb et al. (1920)).

The literature contains little physical property information on chloric acid solutions and solutions containing both chloric acid and sodium chlorate, especially at temperatures that are of interest in chlorine dioxide manufacture. Safety information (OSHA, 1995) indicates that solutions containing greater than 40 mass % $HClO_3$ are unstable, and that a 40 mass % solution decomposes at its boiling point, 104 °C. Kaczur et al. (1993 and 1994) recently published densities of chloric acid solutions with concentrations from 0.96 to 34.4 mass % $HClO_3$ at 20 °C, and solubilities of sodium chlorate in chloric acid at 0, 15, and 20 °C. They also showed that 38 mass % $HClO_3$ solutions did not measurably decompose when stored for 120 days at 30 and 40 °C in containers having membrane-type vent caps. *The Merck Index* (Stecher, 1968) reports densities of chloric acid solutions at 18 °C. Table 1 lists the data of Kaczur et al. and that from *The Merck Index*. Table 1 also lists sodium chlorate solubilities in water (Kerr-McGee, 1985), which we refer to in a later section.

This work determined properties of chloric acid and chloric acid + sodium chlorate solutions at conditions different from those of the previous work. We measured solubilities of sodium chlorate in chloric acid solutions at 25, 35, 45, 55, and 65 °C, and densities of the saturated solutions at these temperatures. We also measured densities of chloric acid solutions and unsaturated chloric acid + sodium chlorate solutions at 25 °C.

Experimental Section

Chemicals. A 1 M chloric acid solution was prepared by combining sulfuric acid solution with barium chlorate solution in stoichiometric proportion. In this process, insoluble barium sulfate precipitates, leaving chloric acid in solution. This solution was filtered and a 3.82 M chloric acid (stock) solution prepared from it. Experimental solutions were prepared by diluting measured volumes of stock solution with water. Barium chlorate monohydrate (99% purity) was purchased from Aldrich Chemical Co. and then purified by recrystallization from saturated solution. Other

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Table 1. Density and Solubility Data from the Literature

t/°C	[$HClO_3$]/ (mass %)	[$NaClO_3$]/ (mass %)	d/ (g·cm^{-3})	source
a. Densities of Chloric Acid Solutions				
20	0.964	0	1.0060	Kaczur et al. (1993, 1994)
20	2.173	0	1.0135	Kaczur et al. (1993, 1994)
20	3.652	0	1.0219	Kaczur et al. (1993, 1994)
20	7.388	0	1.0451	Kaczur et al. (1993, 1994)
20	11.347	0	1.0701	Kaczur et al. (1993, 1994)
20	16.130	0	1.1002	Kaczur et al. (1993, 1994)
20	20.243	0	1.1304	Kaczur et al. (1993, 1994)
20	26.748	0	1.1781	Kaczur et al. (1993, 1994)
20	34.371	0	1.2424	Kaczur et al. (1993, 1994)
18	1	0	1.0044	Stecher (1968)
18	6	0	1.0344	Stecher (1968)
18	10	0	1.0594	Stecher (1968)
18	16	0	1.0991	Stecher (1968)
18	20	0	1.1273	Stecher (1968)
18	24	0	1.1568	Stecher (1968)
18	40	0	1.282	Stecher (1968)
b. Sodium Chlorate Solubilities in Chloric Acid Solutions				
20	18.00	25.50		Kaczur et al. (1993, 1994)
20	21.33	21.36		Kaczur et al. (1993, 1994)
20	25.26	17.17		Kaczur et al. (1993, 1994)
20	29.75	13.57		Kaczur et al. (1993, 1994)
20	35.85	9.32		Kaczur et al. (1993, 1994)
15	20.50	22.30		Kaczur et al. (1993, 1994)
15	32.65	11.33		Kaczur et al. (1993, 1994)
15	35.29	9.99		Kaczur et al. (1993, 1994)
15	42.04	6.35		Kaczur et al. (1993, 1994)
0	42.72	3.95		Kaczur et al. (1993, 1994)
0	51.39	1.42		Kaczur et al. (1993, 1994)
c. Sodium Chlorate Solubilities in Water				
70	0	60.8		Kerr-McGee (1985)
65	0	59.7		Kerr-McGee (1985)
60	0	58.7		Kerr-McGee (1985)
55	0	57.4		Kerr-McGee (1985)
50	0	56.3		Kerr-McGee (1985)
45	0	55.2		Kerr-McGee (1985)
40	0	54.1		Kerr-McGee (1985)
35	0	53.1		Kerr-McGee (1985)
30	0	51.9		Kerr-McGee (1985)
25	0	50.7		Kerr-McGee (1985)
20	0	49.5		Kerr-McGee (1985)
15	0	48.2		Kerr-McGee (1985)
10	0	46.8		Kerr-McGee (1985)
5	0	45.7		Kerr-McGee (1985)
0	0	44.4		Kerr-McGee (1985)

chemicals were purchased from Fisher Scientific, including sulfuric acid (95–98%, certified ACS), hydrochloric acid (12.1 M, reagent ACS), crystalline sodium chlorate (certified ACS), and sodium bicarbonate (certified ACS). Sodium bromide (certified ACS) and potassium iodide (certified ACS) were each dissolved in water to produce 10 wt % solutions. Titrations were performed using (1 ± 0.005) M certified ACS sodium thiosulfate (diluted to 0.10 M) and (2 ± 0.02) M certified ACS sodium hydroxide (diluted to 0.10 M). Starch (certified ACS) and phenolphthalein (certified ACS) indicators were used. Distilled water was used for dilution.

Analytical Methods. Proton and chlorate concentrations in chloric acid and chloric acid + sodium chlorate solutions were determined by titration. Prior to each determination, a 10-mL sample of solution was diluted to 500 mL in a volumetric flask. For proton determination, (25 ± 0.03) mL of the diluted solution was titrated with sodium hydroxide (phenolphthalein indicator). For chlorate determination, the diluted solution was further diluted. In a 500-mL Erlenmeyer flask, 30–35 mL of concentrated (ca. 12 M) hydrochloric acid was added along with approximately 0.5 g of sodium bicarbonate and 10 mL of sodium bromide. After adding 5 mL of the twice-diluted chlorate solution by pipet, the flask was stoppered and the mixture allowed to react for 5–10 min. At the end of this time period, 200 mL of distilled water and roughly 15 mL of potassium iodide were added. The solution was titrated with sodium thiosulfate using starch indicator to determine the total chlorate ion concentration. To examine the reproducibility of results, both titrations were repeated five times on several samples and the results for each sample averaged. For proton analysis, the absolute deviation about the average was 0.5 %. For chlorate analysis, the absolute deviation was 1%.

The stock solution used in preparing samples was analyzed and found to contain (3.82 ± 0.02) M H^+ and (3.81 ± 0.04) M ClO_3^-. No precipitation was observed when a small amount of barium chlorate was added to a sample of the stock solution, nor when a small amount of sulfuric acid was added to a sample of the stock solution. This qualitative test is based on the fact that barium sulfate has a solubility of ca. 10^{-5} M in cold water (Weast, 1978). The stock solution was stored in a Teflon bottle with a screw top in a refrigerator at 0–5 °C.

Saturated Solutions. Sodium chlorate solubility was determined in chloric acid solutions ranging in concentration from about 5 to 22 mass % $HClO_3$ and at temperatures of 25, 35, 45, 55, and 65 °C. The density of each saturated solution was determined at these temperatures by weighing known volumes of the solutions. In a typical experiment, approximately 50 mL of chloric acid solution of known concentration was added to a 100-mL volumetric flask containing a Teflon-coated magnetic stirrer. The flask was placed in a water bath, and the contents were stirred (Corning Model PC-351 stirrer). The bath temperature was controlled (±0.3 °C) by a Fisher Scientific isotemp immersion circulator (model 730). Sodium chlorate was added incrementally to the flask while the solution was stirred and temperature controlled. Each increment was added after the previous increment had dissolved. The additions were continued until solids accumulated at the bottom of the flask. The solution was stirred for an additional period of time (2 h or longer) to assure that it was saturated. In trial experiments ranging in time from 1/2 h to 5 days, it was found that 2 h was sufficient time for the solutions to achieve equilibrium. A (10 ± 0.02) mL sample was removed with a volumetric pipet that was preheated to the same temperature as the solution to prevent formation of crystals on the walls of the pipet. The sample was weighed on an A&D electronic balance (ER-60A) and the density calculated. (In subsequent work we tested for differences in densities determined by this method using a preheated pipet versus a pipet initially at ambient temperature. In experiments using water at elevated temperatures, we found no statistical impact of preheating the pipet on the measured densities.) The sample was analyzed for proton and chlorate concentrations. Density measurements were repeated five times on one of the samples and the results averaged. The absolute deviation about the average was 0.16%, which is equivalent to 0.002 g·cm^{-3}. A few of the chloric acid solutions saturated with sodium chlorate turned a yellow color upon heating to 65 °C, indicating formation of chlorine dioxide. The loss of chloric acid was minimal over the period required to establish equilibrium in solubility experiments. During solubility experiments, these samples were held at the same temperature for an extra hour. We found no measurable differences in the proton and chlorate concentrations when samples taken before and after the extra 1 h period were titrated. The yellow color rapidly disappeared if nitrogen was sparged through the solutions for a few minutes.

Unsaturated Solutions: Density Measurements. Chloric acid solutions with concentrations 1.01, 1.50, 1.98, 2.46, 2.97, and 3.43 M were prepared by dilution of the

3.82 M $HClO_3$ stock solution. The chloric acid + sodium chlorate solutions were prepared by adding crystalline sodium chlorate to these chloric acid solutions. All solutions were analyzed for acid and chlorate concentrations.

A Kyoto Electronics Model DA-210 digital density meter was utilized to measure densities of the solutions at 25 °C. To operate this unit, the solution is introduced into a U-shaped sample tube which is rigidly supported at its open ends. The sample tube is electromagnetically excited to vibrate at its natural frequency. From the frequency change caused by the presence of the solution inside the sample tube, the density of the solution is determined. This instrument provides measurements with accuracies to 0.000 01 $g{\cdot}cm^{-3}$. (The densities are reported to only four decimal points in this work, because of the limitation in the accuracy in determining solution component concentrations.) The temperature of the sample cell of the Kyoto Electronics density meter was maintained at (25 ± 0.01) °C by circulating water from a controlled temperature bath (VWR Scientific Model 1157) around the sample cell. The meter was calibrated using air (0.001 18 $g{\cdot}cm^{-3}$ at 25 °C) and HPLC grade water (0.997 07 $g{\cdot}cm^{-3}$ at 25 °C). The air was dried by passing it through a column containing a desiccant (calcium carbonate).

A typical density measurement involved the following steps. The solution was injected slowly into the sample tube using a Hamilton gas tight 5-mL syringe. The sample was allowed to equilibrate thermally for 2 min, and density was recorded. The sample was withdrawn with the syringe. The sample cell was rinsed with deionized water for 20 s. The sample tube was purged with dry air for approximately 3 min or until the density of air approached the density of dry air used in the calibration. This ensured that the cell was completely dry. The above sample injection, rinsing, and purging cycle was repeated for each solution. Periodically the calibration was checked by measuring the density of HPLC grade water.

Results and Discussion

Saturated Solutions. Table 2 lists results of solubility and density measurements for chloric acid solutions saturated with sodium chlorate. At each experimental temperature, there are four or five sets of data. Columns 2 and 3 show, respectively, the concentration of chloric acid determined by proton analysis and the concentration of sodium chlorate determined as the difference between chlorate and proton concentrations. The mass percents of chloric acid and sodium chlorate in columns 4 and 5 were calculated from the molar concentrations and densities. These mass percents are accurate to within about 0.1% for chloric acid and 0.3% for sodium chlorate as determined from the accuracy limitation of the proton and chlorate titration procedures. The mass percent of water was determined by subtracting the mass percent of chloric acid and sodium chlorate from 100.

Table 2. Composition and Density of Chloric Acid Solutions Saturated with Sodium Chlorate

$[HClO_3]$/M	$[NaClO_3]$/M	$[HClO_3]$/(mass %)	$[NaClO_3]$/(mass %)	$[H_2O]$/(mass %)	d/($g{\cdot}cm^{-3}$)
		t = 25 °C			
3.43	2.64	21.6	21.0	57.4	1.339
2.46	3.71	15.3	29.1	55.6	1.356
1.81	4.30	11.1	33.4	55.5	1.372
1.36	4.99	8.3	38.3	53.5	1.388
1.05	5.36	6.3	40.8	52.8	1.398
		t = 35 °C			
3.34	2.83	20.8	22.3	56.9	1.353
2.34	4.03	14.4	31.3	54.3	1.371
1.66	4.87	10.0	37.1	52.9	1.399
1.22	5.38	7.3	40.6	52.1	1.412
0.90	5.77	5.4	43.3	51.4	1.420
		t = 45 °C			
3.27	3.40	20.1	26.3	53.6	1.375
2.36	4.44	14.3	33.8	51.9	1.397
1.70	5.17	10.1	38.9	51.0	1.415
1.27	5.73	7.5	42.7	49.8	1.428
		t = 55 °C			
3.14	3.81	19.0	29.0	52.1	1.399
2.25	4.78	13.4	35.8	50.8	1.420
1.66	5.51	9.7	40.8	49.5	1.439
1.25	6.00	7.3	44.1	48.6	1.449
0.99	6.38	5.7	46.6	47.7	1.459
		t = 65 °C			
3.03	4.38	18.0	32.9	49.1	1.419
2.20	5.41	12.9	39.9	47.3	1.445
1.63	6.00	9.4	43.8	46.8	1.460
1.25	6.45	7.2	46.6	46.2	1.473
0.97	6.94	5.5	50.0	44.5	1.479

Table 3. Mulilinear Regression and Statistical Analysis

a. Equation No. 3: $C_4 = 45.9 + 0.192C_1 - 1.71C_2 + 0.0167C_3$

C_4 = $[NaClO_3]$/(mass %), C_1 = t/°C, C_2 = $[HClO_3]$/(mass %), C_3 = $[HClO_3]$/(mass %))^2

predictor	coeff	std dev	t-ratio	p	VIF
constant	45.875	0.363	126.56	0.000	
C_1	0.1923	0.00727	26.44	0.000	1.5
C_2	−1.7117	0.0267	−64.12	0.000	8.8
C_3	0.0167	0.000625	26.76	0.000	9.7

$s = 0.7579$, $R^2 = 99.8\%$, $R^2(\text{adj}) = 99.8\%$

Analysis of Variance

source	DF	SS	MS	F	p
regression	3	9906	3302.0	5781.9	0.000
error	39	22.3	0.6		
total	42	9928.3			

b. Equation No. 4: $C_3 = 0.997 - 0.0314C_1 + 0.000247C_2$

C_3 = [$[NaClO_3]$/(mass %) (in $HClO_3$(aq) at t/°C)]/[$[NaClO_3]$/(mass %) (in H_2O at t/°C)], C_1 = $[HClO_3]$/(mass %), C_2 = ($[HClO_3]$/(mass %))^2

predictor	coeff	std dev	t-ratio	p
constant	0.9967	0.00412	241.66	0.000
C_1	−0.03139	0.000483	−65	0.000
C_2	0.000247	0.000011	22.91	0.000

$s = 0.013\ 78$, $R^2 = 99.8\%$, $R^2(\text{adj}) = 99.8\%$

Analysis of Variance

source	DF	SS	MS	F	p
regression	2	3.21	1.606	8458.46	0.000
error	40	0.0076	0.0002		
total	42	3.2196			

These data were correlated, along with previously published solubilities at 0, 15, and 20 °C listed in part b of Table 1 (Kaczur et al., 1993, 1994), and selected solubilities of sodium chlorate in water, reported for the temperature range 0−65 °C, listed in part c of Table 1 (Kerr-McGee, 1985). The resulting expression,

$$[NaClO_3]/(\text{mass }\%) = 45.9 + 0.192t/°C - 1.71[HClO_3]/(\text{mass }\%) + 0.0167([HClO_3]/(\text{mass }\%))^2 \quad (3)$$

was determined by multilinear regression using the software package MINITAB (1990). Table 3, part a, shows the least squares estimators and the analysis of variance table for this regression. For all coefficients in eq 3, the t-ratios are large, indicating that each estimated parameter is significant. The adjusted coefficient of multiple determination, R_a^2, for the fit indicates that 99.8% of the scatter in the data is explained by the model. The large F value in the analysis of variance table indicates that the regression is significant. The model assumes that the random error components are normally and independently distributed with constant variance. A complete check of these assumptions was made by residual analysis, which indicated no reason to doubt the validity of the model (Neter et al., 1990).

In eq 3, the influences of temperature and [$HClO_3$] (mass %) on sodium chlorate solubility appear in separate terms, indicating that the influences of these two variables are not significantly coupled. This conclusion is supported by the small variance inflation factor (VIF) for t/°C, where VIF is a measure of multicollinearity. Because the two influences act independently, the temperature dependence of sodium chlorate solubility in chloric acid solution at any given chloric acid concentration has the same functional form as the temperature dependence of sodium chlorate in water. The following expression takes these features into account:

$$F(t/°\mathrm{C}) = 0.997 - 0.0314[\mathrm{HClO_3}]/(\text{mass }\%) + 0.000247([\mathrm{HClO_3}]/(\text{mass }\%))^2 \quad (4)$$

where $F(t/°\mathrm{C})$ is the ratio of solubility of $NaClO_3$ in $HClO_3$ solution to the solubility of $NaClO_3$ in water, both measured at the same temperature, t/°C. $F(t/°\mathrm{C})$ values were determined by dividing [$NaClO_3$] (mass %) in chloric acid + sodium chlorate + water solutions by the [$NaClO_3$] (mass %) in water from part c in Table 1. (An equation that correlates the data in part c of Table 1, [$NaClO_3$]/(mass %) (in water) = 206.4 exp[−419.3/(t/°C + 273.15)], can be used instead of the tabulated values. The coefficient of multiple determination, R^2, is 0.9998.)

The parameters in eq 4 were determined by multilinear regression using MINITAB. Part b of Table 3 lists the regression coefficients and the analysis of variance table. The t-ratio for each coefficient is very high, indicating that each is significant in the model. The large F value in the analysis of variance table indicates that the regression is also significant. The adjusted coefficient of multiple determination, 0.998, implies that 99.8% of the variability in the data can be explained by the model. Residual analysis showed that the model assumptions hold for the fitted line.

In theory, the constant in eq 4 should equal 1.00. If the constant is fixed at this value, the optimal values of the two coefficients in eq 4 change only slightly, but still within the 95% confidence intervals for the original parameters, leading to the expression

$$F(t/°\mathrm{C}) = 1.00 - 0.0319[\mathrm{HClO_3}]/(\text{mass }\%) + 0.000255([\mathrm{HClO_3}]/(\text{mass }\%))^2 \quad (5)$$

The adjusted coefficient of multiple determination, R_a^2, for the curve fit using eq 5 is 99.8%.

Figure 1 shows the correspondence between predictions of eq 5 and the solubility data determined in this study as well as those from the literature. Plotting the data in this manner allows data that were measured at all temperatures, from 0 to 65 °C, to be represented by a single line.

Unsaturated Solutions: Density Measurements. Table 4 contains concentration−density data measured at 25 °C. For chloric acid + water solutions and for unsaturated chloric acid + sodium chlorate + water solutions, densities were determined using a Kyoto Electronics density meter. As in Table 2, chloric acid concentration was determined by proton analysis, and the concentration of sodium chlorate determined as the difference between chlorate and proton concentrations. Mass percents were calculated from molar concentrations and densities.

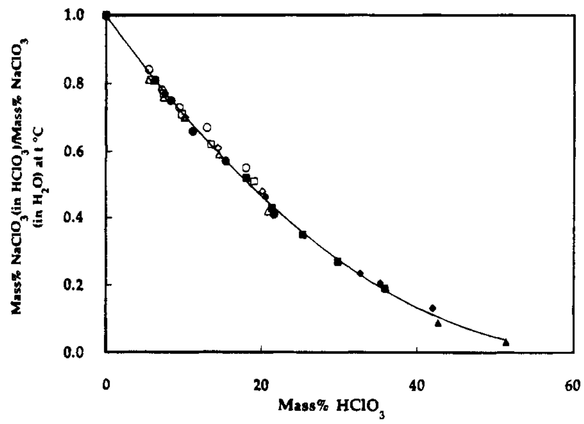

Figure 1. Correlation of sodium chlorate solubility in chloric acid solutions (data at 0, 15, and 20 °C and for $NaClO_3$ in H_2O are literature values; see Table 1, parts b and c): (○) 65 °C, (□) 55 °C, (◇) 45 °C, (△) 35 °C, (●) 25 °C, (■) 20 °C, (◆) 15 °C, (▲) 0 °C.

Table 4. Densities of Chloric Acid + Sodium Chlorate Solutions at 25 °C

[$HClO_3$]/ M	[$NaClO_3$]/ M	[$HClO_3$]/ (mass %)	[$NaClO_3$]/ (mass %)	[H_2O]/ (mass %)	d/ (g·cm^{-3})	d(est)/ (g·cm^{-3})
		Unsaturated Solutions				
3.82	0	27.2	0	72.8	1.1854	1.185
3.59	0.85	24.8	7.4	67.8	1.2222	1.230
3.43	0	24.8	0	75.2	1.1647	1.166
3.15	0.97	22.0	8.5	69.5	1.2123	1.215
3.06	2.00	20.4	16.8	62.8	1.2672	1.278
2.97	0	21.9	0	78.1	1.1429	1.143
2.70	1.13	18.9	10.0	71.1	1.2051	1.202
2.47	2.30	16.5	19.4	64.1	1.2634	1.266
2.42	3.38	15.4	27.1	57.5	1.3267	1.334
2.46	0	18.6	0	81.4	1.1176	1.118
2.30	1.13	16.5	10.2	73.3	1.1774	1.183
2.18	2.23	14.9	19.2	65.8	1.2340	1.250
2.08	3.32	13.4	27.0	59.6	1.3099	1.312
1.98	0	15.2	0	84.8	1.0946	1.094
1.85	1.24	13.5	11.4	75.1	1.1580	1.169
1.66	2.55	11.5	22.3	66.2	1.2188	1.247
1.52	3.52	10.0	29.3	60.7	1.2811	1.301
1.50	0	11.8	0	88.2	1.0706	1.071
1.34	1.48	9.7	13.5	76.7	1.1646	1.156
1.24	2.89	8.5	24.8	66.7	1.2397	1.243
1.14	4.25	7.3	34.3	58.4	1.3204	1.326
1.01	0	8.1	0	91.9	1.0462	1.047
0.89	1.48	6.6	13.8	79.6	1.1411	1.135
0.73	4.07	4.8	33.4	61.8	1.2962	1.292
		Saturated Solutions				
3.43	2.64	21.6	21.0	57.4	1.339	1.333
2.46	3.71	15.3	29.1	55.6	1.356	1.354
1.81	4.3	11.1	33.4	55.5	1.372	1.356
1.36	4.99	8.3	38.3	53.4	1.388	1.381
1.05	5.36	6.3	40.8	52.9	1.398	1.387

Figure 2 shows density data for chloric acid solutions from Table 4 (nos. 25, 27, 30, 34, 38, 42, and 46), measured at 25 °C. The densities are plotted as a function of chloric acid concentration. Also plotted are densities listed in part a of Table 1, reported by Kaczur et al. (1993, 1994) at 20 °C and in Stecher (1968) at 18 °C. In spite of temperature differences, data from the three studies fall approximately on the same line in Figure 2.

Figure 3 is a plot of the reciprocal of chloric acid solution density (or specific volume) versus the mass percent concentration of chloric acid. The data were fit very accurately by a straight line (R^2 = 0.99997) with slope −0.005 84. The linearity of the plot indicates that the specific volume of the solution is the sum of specific volumes of solution ingredients in their pure form. However, this model cannot be proven for chloric acid solutions because chloric acid is unstable; i.e., it does not exist in a pure state, but rather exists stably only in aqueous solutions of concentrations equal and below about 40 mass % $HClO_3$. Therefore, in the following equation, the pa-

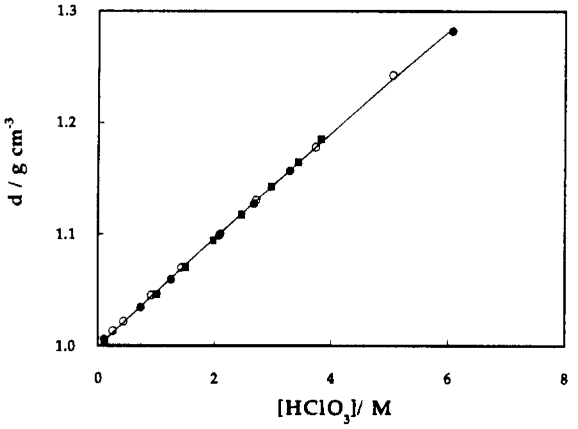

Figure 2. Density of chloric acid solutions at various temperatures: (■) this work, 25 °C, (○) Kaczur et al. (1993, 1994), 20 °C, (●) Stecher (1968), 18 °C.

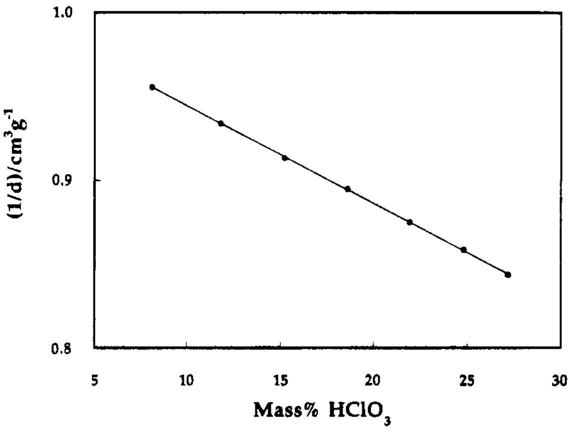

Figure 3. Specific volume of chloric acid solutions at 25 °C: slope = −0.005 846, intercept = 1.003, R^2 = 0.999 94.

rameter Y is substituted for the density of "pure" chloric acid:

$$1/d_{\text{solution}} = [[\text{HClO}_3]/(\text{mass }\%)]/(100Y) + [[\text{H}_2\text{O}]/(\text{mass }\%)]/(100\, d_{\text{H}_2\text{O}}) \quad (6)$$

The slope of the line shown in Figure 3 represents the quantity $1/(100Y) - 1/(100d_{\text{H}_2\text{O}})$. Using the above value of the slope and the density of water (0.997 07 g·cm^{-3}), the predicted value of the parameter Y is 2.39 g·cm^{-3}.

Extension of this model was used to predict densities of chloric acid + sodium chlorate + water solutions.

$$1/d_{\text{solution}} = [[\text{HClO}_3]/(\text{mass }\%)]/(100Y) + [[\text{NaClO}_3]/(\text{mass }\%)]/(100d_{\text{NaClO}_3}) + [[\text{H}_2\text{O}]/(\text{mass }\%)]/(100d_{\text{H}_2\text{O}}) \quad (7)$$

In this equation, the value Y was set at 2.39 g·cm^{-3}, and the density of sodium chlorate was assumed that of the crystalline form, or 2.49 g·cm^{-3} (Weast, 1978−9). Predicted densities of chloric acid solutions and of chloric acid + sodium chlorate + water solutions at 25 °C are compared with experimentally determined values in Table 4, columns 7 and 8. Equation 7 predicts densities to within an average of 0.5%, which in density units is 0.006 g·cm^{-3}. This level of accuracy may be sufficient for design purposes.

In eq 7, the optimal value of the parameter Y that best correlates the density data of the chloric acid + sodium chlorate + water solutions is 2.35 g·cm^{-3}; however, there is only marginal improvement in the accuracy of the correlation using this value instead of 2.39 g·cm^{-3}.

Conclusions

Solubilities of sodium chlorate in chloric acid solutions ranging in concentration from about 5 to 22 mass % $HClO_3$ at temperatures of 25, 35, 45, 55, and 65 °C were correlated with chloric acid concentration (mass %) and temperature. Also included in the correlation were previously reported data measured at 0, 15, and 20 °C, as well as sodium chlorate solubilities in water reported in the temperature range 0−65 °C. All of the data can be accurately represented graphically by a single line if plotted as the ratio of sodium chlorate solubility in chloric acid to that in water versus the mass percent concentration chloric acid.

The reciprocal of chloric acid solution density at 25 °C is linear with respect to chloric acid concentration. A parameter determined from the slope of this linear plot and the density of crystalline sodium chlorate were used to correlate densities of chloric acid solutions containing sodium chlorate, with an accuracy of ±0.006 g·cm^{-3}.

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