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Vapor Pressure Measurements of Chloric Acid and Chloric Acid + Sodium Chlorate Aqueous Solutions

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Chloric acid + sodium chlorate mixtures have been proposed as a substitute for some of the sodium chlorate and sulfuric acid in the generation of chlorine dioxide. This paper continues our work on physical property characterization of chloric acid + sodium chlorate solutions. A dual ebulliometric setup was employed to evaluate the vapor pressure−temperature relationship of chloric acid and chloric acid + sodium chlorate solutions. The natural log of vapor pressures for chloric acid solutions (1.01−3.82) mol L^{-1} over the temperature range (35−79) °C was a linear function of chloric acid concentration and the reciprocal of the temperature. Vapor pressures were determined for sodium chlorate + chloric acid solutions for (0.85−4.25) mol L^{-1} sodium chlorate, (0.73−3.59) mol L^{-1} chloric acid, and (35−83) °C. All of the data were well correlated by an equation relating the natural log of vapor pressure to sodium chlorate concentration, chloric acid concentration, and the reciprocal of the temperature. Some solutions with high chlorate ion concentrations at high temperatures developed a yellow or pink color. Vapor phase measurements showed that the vapor pressures determined in these experiments are due to water with a trace contribution from another component.

Introduction

Chlorine dioxide, used in bleaching of wood pulp, is generated at pulp and paper mills by reacting acidic sodium chlorate solution with a reducing agent, such as hydrogen peroxide (Burke et al., 1993):

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

This reaction produces approximately 1 ton of sodium sulfate per ton of chlorine dioxide, and mills typically produce 10−30 tons per day of chlorine dioxide (Sokol and Conkle, 1993).

Recent improvements in sulfur recovery have reduced the need for this sulfate byproduct in mills. Excess sulfate is sent to waste (Burke et al., 1993). A means of reducing the amount of sodium sulfate generated is to substitute chloric acid, $HClO_3$, for portions of the sodium chlorate and sulfuric acid. Chloric acid reacts as follows:

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

In theory, the production of sodium sulfate can be tailored to consumer specifications by adjusting the proportions of chloric acid and sodium chlorate in the feed. When chloric acid, sodium chlorate, and sulfuric acid are used, the overall stoichiometry is the sum of contributions from reactions 1 and 2.

Physical property information for chloric acid and chloric acid + sodium chlorate solutions is scarce in the literature, particularly at concentrations representative of chlorine dioxide manufacture. Vapor−liquid equilibrium data and water activities for these solutions have not been reported. Safety information (OSHA, 1995) indicates that a 40 mass % chloric acid solution is unstable. We recently reported solubilities and densities of chloric acid and chloric acid + sodium chlorate solutions (Crump et al., 1995). This paper continues our examination of the physical property data of these solutions. A dual ebulliometric system was employed in which the vapor pressure of a solution containing chloric acid or chloric acid + sodium chlorate was ascertained by comparison with a reference system. We measured the boiling points of chloric acid solutions ranging in concentration from (1−3.8) mol L^{-1}, and these same chloric acid solutions with varying degrees of sodium chlorate added, in the temperature range (35−83) °C. A simple distillation system was used to elucidate the components of the vapor phase above the solution.

Experimental Section

Chemicals. A 1 mol L^{-1} chloric acid solution was prepared from sulfuric acid and barium chlorate as per Lamb et al. (1920). This solution was further concentrated to 3.82 mol L^{-1} [(3.82 ± 0.02) mol L^{-1} H^+ and (3.81 ± 0.04) mol L^{-1} ClO_3^-] and stored in a Teflon bottle with a screw top at (0−5) °C. Experimental chloric acid solutions were prepared by accurately diluting the 3.82 mol L^{-1} stock solution with water. Barium chlorate monohydrate (99% purity) was purchased from Aldrich Chemical Co. and purified by recrystallization prior to use. Sulfuric acid (18 mol L^{-1}, Fisher Scientific, certified ACS) was carefully diluted prior to mixing with the barium chlorate. Crystalline sodium chlorate (certified ACS) was purchased from Fisher Scientific.

We employed a modified version of the Aieta et al. (1984) method for the determination of chlorate ion. This method requires several chemicals. Hydrochloric acid (12.1 mol L^{-1}, reagent ACS) and sodium bicarbonate (certified ACS) were purchased from Fisher Scientific. Sodium bromide (certified ACS) and potassium iodide (certified ACS) were each dissolved in water to produce 10 mass % solutions. The titration was performed with (1 ± 0.005) mol L^{-1} certified ACS sodium thiosulfate (diluted to 0.1 mol L^{-1}). A simple acid−base titration was utilized to determine the concentration of protons. A (2 ± 0.02) mol L^{-1} certified ACS sodium hydroxide solution (diluted to 0.1 mol L^{-1}) was used as the titrant. Phenolphthalein (certified ACS), prepared from phenolphthalein (solid) and ethanol, was used as the indicator. Distilled water was used for all dilutions.

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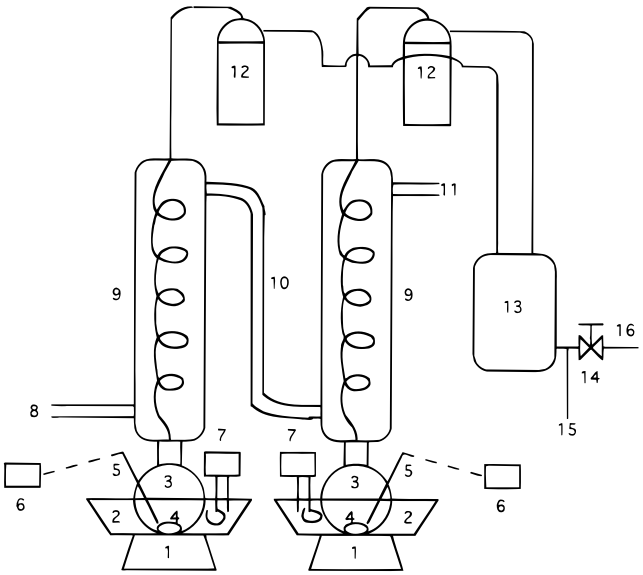

Figure 1. Experimental apparatus: (1) magnetic stirrer; (2) water bath; (3) 250 mL round bottom flask-ground glass embedded (Lab Glass: 7270-138); (4) stirring bar; (5) temperature probe; (6) thermistor; (7) temperature controller; (8) cold water in; (9) condenser; (10) insulated tube; (11) cold water out; (12) trap; (13) ballast; (14) needle valve; (15) to vacuum; (16) air inlet.

Analytical Data. Figure 1 displays the experimental apparatus. This system is based on an ASTM Standard Method (E1719) and is similar to the method employed by Iyoki et al. (1990). Two ebulliometers were employed, one containing the reference fluid (distilled water) and the other containing the test solution. The ebulliometer setup consisted of a 250 mL round bottom flask with ground glass embedded on the interior walls (Lab Glass) to promote boiling and to reduce superheating. The flask was partially submerged in a constant temperature (±0.3 °C) water bath (Fisher Isotemp Immersion Circulator Model 730), and its contents, continuously agitated by a magnetic stirrer (Corning Model PC-351). The solution temperature was measured by a thermistor (Cole Parmer Model 8402-00) which was calibrated against a platinum resistance thermometer and is accurate to ±0.1 deg. The flask was connected to a vertical condenser where the vapor was condensed by 5 °C cooling water and returned to the flask. Vacuum in the system was generated by a water aspirator and was controlled by a needle valve. A 15 L ballast was connected to the vacuum line to correct for minor fluctuations in the pressure. Ice traps were used to collect any vapor which may escape during the boiling process. Preliminary experiments showed this not to be a problem, but the traps were kept as a precautionary measure to protect the ballast.

In each experiment, distilled water and a test solution of known concentration were added to the reference and test flasks, respectively. The pressure in the system was set and the temperature raised until boiling occurred. In order to reduce superheating, the difference between the temperature of the solution and bath temperature was minimized. From the reference fluid temperature, the total vapor pressure could be determined from the vapor pressure tables for water. This pressure corresponded to the pressure above the test solution, as both flasks were connected to the same vacuum system.

Results and Discussion

We tested the apparatus by measuring the vapor pressure of two known systems: 8.9 mass % sodium carbonate (International Critical Tables, 1928) and 30.8 mass % sulfuric acid (Vermeulen et al., 1982). The literature data were fit as ln $P = f(1/T)$ in order to interpolate experimental vapor pressures. From the reference fluid boiling temperature, the vapor pressure was inferred from water vapor pressure data in the CRC Handbook (Weast, 1978). Using this pressure, the literature boiling point was determined from the above mentioned fitted equation. For temperatures ranging from (32−69) °C, the absolute deviation between the measured values and the literature values for 8.9 mass % sodium carbonate was 0.7 deg (observed at 68 °C). For a total of nine runs, the average absolute deviation was 0.3 deg. For 30.8 mass % sulfuric acid in the temperature range of (46−72) °C, the maximum absolute deviation was 0.6 deg. By titration, we determined that the sulfuric acid concentration did not change as a result of the boiling and refluxing. The stock solution of 3.82 mol L^{-1} chloric acid also exhibited no change in concentration due to the boiling and refluxing.

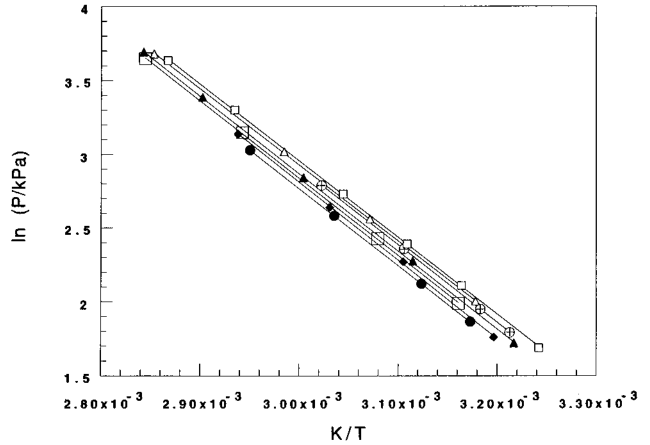

Figure 2. Vapor pressure data for chloric acid solutions. $HClO_3$/mol L^{-1}: (●) 3.82; (◆) 3.42; (□) 2.96; (▲) 2.46; (○) 1.98; (△) 1.5; (□) 1.01.

Chloric Acid Solutions. Table 1 shows the boiling point measurements for chloric acid solutions. The concentrations listed in column 1 were determined at 25 °C by titration. At each experimental concentration, there are 4−6 data sets. Column 2 lists the mass % $HClO_3$ determined from the molarity and density from Crump et al. (1995). Columns 3 and 4 show data for the reference fluid; column 3 is the temperature of the reference fluid, and column 4, that of the reference fluid bath. Likewise, column 5 is the chloric acid solution temperature and column 6 the chloric acid solution bath temperature. Column 7 shows the vapor pressure of the system as determined from the distilled water boiling points listed in column 3.

Column 8 of Table 1 is the boiling point elevation, which is the difference between the boiling point of the chloric acid solution and the reference fluid. As expected, the boiling point elevation increases with increasing chloric acid concentration. The predicted boiling point elevation (column 9), is the total solution ion molality multiplied by an ebullioscopic constant. Atkins (1986) reports the ebullioscopic constant for water as 0.51 K kg mol^{-1}. In using this constant, it was assumed that chloric acid (p$K_a = -2.7$) is completely dissociated (Mendiratta and Duncan, 1993).

The data were modeled as ln(P) versus (1/T) for each concentration, as shown in Figure 2. The lines drawn through the data are linear fits. Moreover, the slopes of all lines appear to be the same, suggesting that the

Table 1. Chloric Acid Vapor Pressure Data

$[HClO_3]$/mol L^{-1} at 25 °C	$[HClO_3]$/mass %	t/°C				vap press/kPa	BPE/°C	BPE_{pred}/°C	activity H_2O	act coeff H_2O	P_{calc} from eq 3/kPa	% error	P_{calc} from eq 5/kPa
		ref BP	ref bath	soln BP	soln bath								
3.82	27.29	37.5	40.0	42.0	43.9	6.45	4.5	4.5	0.79	0.85	6.50	0.76	6.45
	27.29	42.3	45.7	47.0	49.9	8.33	4.7	4.5	0.79	0.85	8.42	1.08	8.35
	27.29	51.4	56.0	56.3	59.2	13.21	4.9	4.5	0.79	0.85	13.35	1.04	13.24
	27.29	60.8	63.9	65.8	69.2	20.66	5.0	4.5	0.80	0.86	20.83	0.79	20.64
3.42	24.84	35.6	39.6	39.7	43.6	5.81	4.1	4.0	0.80	0.86	5.91	1.63	5.88
	24.84	45.2	48.3	48.9	52.1	9.68	3.7	4.0	0.83	0.89	9.52	−1.66	9.47
	24.84	63.2	65.6	67.2	68.8	23.05	4.0	4.0	0.84	0.90	22.79	−1.11	22.64
	24.84	52.6	55.3	56.8	59.4	14.01	4.2	4.0	0.82	0.88	14.05	0.24	13.96
2.96	21.92	63.4	65.6	66.7	68.6	23.26	3.3	3.4	0.86	0.92	22.98	−1.22	22.88
	21.92	39.8	42.6	43.2	45.6	7.30	3.4	3.4	0.84	0.89	7.33	0.42	7.31
	21.92	48.3	50.5	51.6	54.8	11.33	3.3	3.4	0.85	0.90	11.24	−0.83	11.20
	21.92	74.9	79.8	78.4	81.2	38.38	3.5	3.4	0.87	0.92	38.35	−0.08	38.15
2.46	18.61	68.8	71.4	71.4	73.4	29.57	2.6	2.8	0.89	0.94	29.31	−0.88	29.25
	18.61	34.9	38.4	37.7	41.1	5.59	2.8	2.8	0.86	0.90	5.66	1.14	5.66
	18.61	45.3	47.4	47.9	51.6	9.73	2.6	2.8	0.88	0.92	9.65	−0.82	9.65
	18.61	56.8	59.4	59.7	62.0	17.15	2.9	2.8	0.87	0.92	17.19	0.27	17.17
	18.61	76.0	78.9	78.6	80.9	40.18	2.6	2.8	0.90	0.94	39.99	−0.49	39.89
1.98	15.3	55.7	59.2	57.7	60.7	16.27	2.0	2.2	0.91	0.94	16.14	−0.79	16.17
	15.3	36.2	39.1	38.1	41.7	6.01	1.9	2.2	0.90	0.94	5.97	−0.65	5.99
	15.3	46.9	49.5	48.8	51.7	10.56	1.9	2.2	0.91	0.94	10.43	−1.22	10.45
	15.3	39.1	42.8	41.0	44.6	7.03	1.9	2.2	0.90	0.94	6.97	−0.86	6.99
1.5	11.85	40.1	43.8	41.5	45.3	7.41	1.4	1.6	0.93	0.96	7.39	−0.34	7.43
	11.85	51.0	53.0	52.4	54.3	12.96	1.4	1.6	0.93	0.96	12.89	−0.55	12.95
	11.85	60.6	63.9	61.9	65.6	20.46	1.3	1.6	0.94	0.97	20.32	−0.70	20.40
	11.85	75.7	78.0	77.3	80.6	39.68	1.6	1.6	0.94	0.96	40.35	1.69	40.47
1.01	8.16	34.3	35.6	35.3	37.6	5.41	1.0	1.1	0.95	0.96	5.47	1.07	5.51
	8.16	47.6	49.8	48.5	51.5	10.94	0.9	1.1	0.96	0.97	10.96	0.20	11.05
	8.16	42.1	44.3	42.9	45.4	8.24	0.8	1.1	0.96	0.98	8.22	−0.30	8.28
	8.16	66.9	69.6	67.6	69.6	27.20	0.7	1.1	0.97	0.99	27.26	0.22	27.44
	8.16	74.5	77.7	75.6	79.1	37.89	1.0	1.1	0.96	0.98	38.76	2.31	38.99
	8.16	54.5	59.1	55.3	59.1	15.37	0.8	1.1	0.96	0.98	15.35	−0.13	15.46

Table 2. Statistical Analysis of Equation 3

predictor	coeff	st dev	*t* ratio	*p*	VIF
constant	18.7179	0.0472	396.8	0.000	
1/*T*, K	−5228.79	15.35	−340.5	0.000	1.0
$[HClO_3]$	−0.066784	0.001895	−35.2	0.000	1.0

$s = 0.0102$ $R^2 =$ 100.0% $R_a^2 =$ 100.0%

Analysis of Variance

source	DF	SS	MS	*F*	*p*
regression	2	12.1784	6.0892	58489.850	0.000
error	28	0.0029	0.0001		
total	30	12.1813			

concentration of $HClO_3$ contributes an additive step to the model equation. Hence, the data were correlated by the following equation:

$$\ln(P/\mathrm{kPa}) = \beta_0 + \beta_1(C_{\mathrm{HClO_3}}/\mathrm{mol\ L^{-1}}) + \beta_2(K/T) \quad (3)$$

Best subsets and stepwise regression algorithms of Minitab (Version 8) confirmed the validity of eq 3 as the "best" model for the data. Least squares estimates for the parameters in the regression equation are $\beta_0 = 18.7$, $\beta_1 = -0.0668$, and $\beta_2 = -5229$. Table 2 reports the details of the regression. Each estimated parameter is significant as well as the equation itself. An adjusted coefficient of multiple determination (R_a^2) of 1.00 indicates that the model explains all of the scatter in the data. The model equation assumes that the error components are normally and independently distributed with constant variance. Residual analysis shows that the model assumptions hold for this regression (Neter et al., 1990). The calculated vapor pressures and percent prediction errors in Table 1 (columns 12 and 13, respectively) were computed from 3.

Equation 3 takes the same form as the Clausius−Clapeyron equation:

$$\ln(P^*) = -\Delta_{vap}H/RT + B \quad (4)$$

if we set $\Delta_{vap}H/R = \beta_2$ and $B = \beta_0 + \beta_1(C_{\mathrm{HClO_3}}/C_o)$, where $C_o = 1$ mol L^{-1}. In eq 4, P^* is the vapor pressure, $\Delta_{vap}H$ is the enthalpy of vaporization, *R* is the ideal gas constant, and *B* is a constant of integration. The lines represented in Figure 2 indicate that the enthalpy of vaporization for this system is in the range (43.1−43.9) kJ/mol. Within experimental error, this range of enthalpies corresponds to that of water. This observation led to the assumption that the vapor phase in these experiments consisted either solely of water or of water with only a trace concentration of other components. This assumption was confirmed in vapor characterization experiments described in a later section.

On the basis of this assumption, and by applying Raoult's law, water activity was calculated as the ratio of solution vapor pressure to the saturated vapor pressure of water at the temperature of the chloric acid solution. These values are shown in Table 1, column 10. Column 11 lists the activity coefficients of water determined by dividing activity by water mole fraction.

Sodium Chlorate + Chloric Acid Solutions. Table 3 displays vapor pressure data for solutions containing both chloric acid and sodium chlorate. The solution molarities (columns 1 and 2) at 25 °C were calculated from proton and chlorate (column 3) concentrations determined by titration. Chloric acid concentration is assumed equal to the proton concentration, and sodium chlorate concentration is determined as the difference between chlorate and proton concentration. The titration procedures are listed in Crump et al. (1995). As reported, the absolute deviation

Table 3. Sodium Chlorate/Chloric Acid Solution Vapor Pressure Data

$[HClO_3]$/ mol L^{-1}	$[NaClO_3]$/ mol L^{-1}	$[ClO_3^-]$/ mol L^{-1}	t/°C	BPE/ °C	BPE_{pred}/ °C	activity H_2O	act coeff H_2O	P/kPa	P_{calc}/kPa	%/error in P
0.89	1.48	2.37	37.6	1.7	2.6	0.91	0.95	5.91	5.83	−1.34
0.89	1.48	2.37	51.6	2.0	2.6	0.91	0.95	12.09	12.03	−0.52
0.89	1.48	2.37	67.0	2.1	2.6	0.91	0.95	24.90	24.91	0.01
0.89	1.48	2.37	77.2	2.3	2.6	0.91	0.95	38.36	38.94	1.52
0.79	2.69	3.48	39.4	3.2	4.0	0.84	0.90	6.01	6.07	1.00
0.79	2.69	3.48	47.9	3.1	4.0	0.85	0.91	9.48	9.44	−0.45
0.79	2.69	3.48	58.1	3.5	4.0	0.85	0.91	15.44	15.58	0.91
0.79	2.69	3.48	68.6	3.5	4.0	0.86	0.92	25.13	25.28	0.61
0.79	2.69	3.48	77.0	3.6	4.0	0.86	0.92	36.02	36.48	1.26
0.73	4.07	4.80	40.3	4.3	5.8	0.79	0.88	5.94	5.94	0.01
0.73	4.07	4.80	54.0	4.5	5.8	0.80	0.89	12.03	11.94	−0.78
0.73	4.07	4.80	68.0	4.7	5.8	0.81	0.89	23.14	22.98	−0.72
0.73	4.07	4.80	81.9	5.2	5.8	0.81	0.89	41.40	41.83	1.06
1.34	1.48	2.82	38.2	2.6	3.2	0.87	0.92	5.81	5.83	0.28
1.34	1.48	2.82	51.6	2.5	3.2	0.88	0.93	11.79	11.64	−1.28
1.34	1.48	2.82	60.8	2.6	3.2	0.89	0.94	18.31	18.13	−0.95
1.34	1.48	2.82	81.5	3.0	3.2	0.88	0.93	44.46	45.16	1.56
1.24	2.89	4.13	39.0	3.8	4.9	0.81	0.88	5.65	5.69	0.59
1.24	2.89	4.13	55.3	4.1	4.9	0.82	0.89	13.09	13.04	−0.36
1.24	2.89	4.13	70.2	4.1	4.9	0.83	0.91	26.21	26.00	−0.79
1.24	2.89	4.13	81.6	4.8	4.9	0.82	0.89	41.52	42.39	2.10
1.14	4.25	5.39	38.5	5.1	6.8	0.76	0.85	5.14	5.19	0.89
1.14	4.25	5.39	56.6	5.4	6.8	0.77	0.86	13.09	13.02	−0.57
1.14	4.25	5.39	68.0	5.5	6.8	0.78	0.88	22.30	22.10	−0.94
1.14	4.25	5.39	82.5	6.1	6.8	0.78	0.87	40.85	41.24	0.95
1.85	1.24	3.09	35.1	2.6	3.5	0.87	0.92	4.89	4.81	−1.73
1.85	1.24	3.09	52.6	2.8	3.5	0.87	0.93	12.21	11.94	−2.22
1.85	1.24	3.09	71.3	2.7	3.5	0.89	0.95	29.32	28.50	−2.78
1.85	1.24	3.09	80.2	2.6	3.5	0.90	0.96	42.93	41.76	−2.74
1.66	2.55	4.21	36.0	4.1	5.1	0.80	0.87	4.73	4.78	1.02
1.66	2.55	4.21	50.1	4.2	5.1	0.81	0.88	10.03	9.98	−0.57
1.66	2.55	4.21	69.7	3.9	5.1	0.84	0.92	25.90	25.12	−3.03
1.66	2.55	4.21	81.5	4.6	5.1	0.83	0.91	41.74	41.69	−0.12
1.52	3.52	5.04	36.9	5.0	6.2	0.76	0.84	4.73	4.81	1.81
1.52	3.52	5.04	57.1	4.9	6.2	0.79	0.88	13.75	13.48	−1.91
1.52	3.52	5.04	71.4	5.3	6.2	0.79	0.88	26.21	25.99	−0.86
2.30	1.13	3.43	55.0	3.9	4.0	0.83	0.89	7.41	7.41	−0.04
2.30	1.13	3.43	55.0	3.9	4.0	0.83	0.89	13.03	13.07	0.35
2.30	1.13	3.43	69.7	4.1	4.0	0.84	0.89	25.68	25.86	0.70
2.30	1.13	3.43	79.8	3.6	4.0	0.86	0.92	40.50	39.98	−1.29
2.18	2.23	4.41	42.7	4.5	5.3	0.79	0.86	6.70	6.69	−0.05
2.18	2.23	4.41	46.4	4.6	5.3	0.79	0.86	8.11	8.11	−0.10
2.18	2.23	4.41	68.2	4.4	5.3	0.82	0.90	23.69	23.01	−2.86
2.18	2.23	4.41	80.9	4.5	5.3	0.83	0.91	40.85	39.84	−2.48
2.08	3.32	5.40	43.7	5.6	6.9	0.74	0.83	6.66	6.71	0.66
2.08	3.32	5.40	55.5	5.4	6.9	0.77	0.86	12.41	12.12	−2.39
2.08	3.32	5.40	72.4	6.0	6.9	0.77	0.86	26.60	26.35	−0.93
2.08	3.32	5.40	81.4	6.8	6.9	0.76	0.85	37.89	38.67	2.06
2.70	1.13	3.83	42.4	4.0	4.5	0.81	0.87	6.77	6.73	−0.63
2.70	1.13	3.83	52.7	3.8	4.5	0.83	0.90	11.68	11.35	−2.80
2.70	1.13	3.83	72.1	4.7	4.5	0.82	0.88	27.81	27.92	0.41
2.70	1.13	3.83	79.8	4.8	4.5	0.82	0.89	38.54	38.84	0.77
2.47	2.30	4.77	44.1	5.6	5.9	0.74	0.82	6.81	7.02	3.22
2.47	2.30	4.77	53.0	5.4	5.9	0.77	0.85	10.94	11.01	0.62
2.47	2.30	4.77	71.1	6.0	5.9	0.77	0.85	25.13	25.54	1.63
2.47	2.30	4.77	81.5	6.5	5.9	0.77	0.85	38.54	39.85	3.38
3.15	0.97	4.12	41.7	4.7	4.9	0.78	0.85	6.28	6.33	0.87
3.15	0.97	4.12	68.4	5.0	4.9	0.80	0.87	23.26	23.14	−0.53
3.06	2.00	5.06	46.3	6.2	6.3	0.72	0.81	7.41	7.66	3.32
3.06	2.00	5.06	53.8	5.4	6.3	0.77	0.85	11.39	11.14	−2.14
3.06	2.00	5.06	69.1	5.9	6.3	0.77	0.86	23.05	22.76	−1.28
3.59	0.85	4.44	47.4	5.9	5.4	0.74	0.81	7.99	8.29	3.77
3.59	0.85	4.44	63.0	5.8	5.4	0.76	0.84	17.47	17.65	1.04
3.59	0.85	4.44	77.8	6.4	5.4	0.77	0.84	33.09	33.97	2.67
3.59	0.85	4.44	83.4	6.5	5.4	0.77	0.84	41.74	42.92	2.81

about the average is 0.5% for proton analysis and 1.0% for chlorate analysis. Column 4 displays the sodium chlorate + chloric acid solution sample temperature. Columns 5 and 6 show the boiling point elevation and the predicted boiling point elevation, respectively, based on the ebullioscopic constant, 0.51 K kg mol^{-1}, and the assumption that both chloric acid and sodium chlorate were completely dissociated. As expected, the boiling point elevation increases with increasing total solution ionic concentration. Water activity and activity coefficient are displayed in columns 7 and 8, respectively. The vapor pressure calculated from the distilled water boiling temperature is given in column 9.

The solutions listed in Table 3 were prepared from the same chloric acid solutions studied in the previous section. To each chloric acid concentration sample were added two to three known amounts of sodium chlorate (each under the saturation limit). For each sodium chlorate + chloric

Table 4. Statistical Analysis of Equation 5

predictor	coeff	st dev	*t* ratio	*p*	VIF
constant	18.7076	0.0363	515.9	0.000	
1/*T*, K	−5221.2	11.68	−446.9	0.000	1.0
[$HClO_3$]	−0.072332	0.001954	−37	0.000	1.3
[$NaClO_3$]	−0.052957	0.001306	−40.5	0.000	1.3
$s = 0.01523$		$R_2 =$ 100.0%		$R_a^2 =$ 100.0%	

Analysis of Variance

source	DF	SS	MS	*F*	*p*
regression	3	46.527	15.509	66830.700	0.000
error	92	0.021	0.000		
total	95	46.548			

acid sample, two to five separate vapor pressure experiments were performed. These solutions range in concentration from (0.73−3.59) mol L^{-1} $HClO_3$ and (0.85−4.25) mol L^{-1} $NaClO_3$. The sodium chlorate + chloric acid boiling temperatures range from (35−83) °C. Species molalities and mass percents (not listed) were determined from solution densities (Crump et al., 1995).

The data in Table 3 were combined with the chloric acid vapor pressure data from Table 1 in an attempt to correlate all of the data by a single equation. Several variables were used as potential parameters for this system (e.g. species mass percents, molalities, molarities, total chlorate ion concentration, etc.). Stepwise regression and best subsets algorithms (Minitab, Version 8) suggest that an equation of the form

$$\ln(P/\mathrm{kPa}) = \beta_0 + \beta_1(C_{\mathrm{HClO_3}}/\mathrm{mol\ L^{-1}}) + \beta_2/(T/\mathrm{K}) + \beta_3(C_{\mathrm{NaClO_3}}/\mathrm{mol\ L^{-1}}) \quad (5)$$

correctly models the system. This is the same form of the equation utilized to correlate the chloric acid vapor pressure data, with an additional term to account for the effect of sodium chlorate. Least squares estimates of the parameters are $\beta_0 = 18.7$, $\beta_1 = -0.0723$, $\beta_2 = -5221$, and $\beta_3 = -0.053$. The estimates of the intercept and the independent variable, 1/*T*, are statistically the same as those determined for eq 3.

Table 4 shows the regression details for eq 5. Although the regression contained 96 total data points, the generated equation accounts for all of the scatter in the data ($R_a^2 =$ 100.0%). Each estimated parameter is highly significant and uncorrelated, judging by the low variance inflation factors (VIFs). The variance inflation factor is a measure of multicollinearity. Residual analysis showed that the model assumptions hold for this regression (Neter et al., 1990). Table 3, column 10, displays the predicted vapor pressures from eq 5. The percent errors, column 11, are based on deviations of pressure from the experimental values and not on natural logs of pressure. Column 14 of Table 1 displays the predicted solution vapor pressures from eq 5.

Some solutions with high total chlorate concentrations at high temperatures developed a yellow, and sometimes pink, color. This phenomenon generally did not occur in solutions until heated to 65 °C, although a few solutions developed a light yellow color at 50 °C. The yellow color can be attributed to chlorine dioxide which may form as a result of decomposition of the chlorate or perhaps by reaction of chlorate and chloride ions, present as an impurity in the sodium chlorate. The formation of chlorine dioxide was not enough to alter the chlorate ion concentration, as solutions examined both before and after the experiment yielded the same concentration (within the titration error). We are unsure at this time what accounted for the pink hue. Solutions with this pink color did exhibit an odor characteristic of chlorine dioxide. One unstable compound that has been reported as having a reddish-brown color in the pure state is chlorine trioxide (Masschelein, 1979). Dilute aqueous solutions are expected to have a light red or pink color.

Vapor Phase Characterization. The color change associated with some of the solutions suggested that components other than water may be present in the vapor phase, such as chloric acid, chlorine dioxide, or another component. A simple one-stage distillation apparatus was constructed to elucidate the contents of the vapor phase. A known volume (usually 110 mL) of a chloric acid + sodium chlorate mixture was charged to a flask submerged in a constant temperature bath. The flask was carefully monitored to ensure that the solution did not boil. The vapors from the liquid surface were condensed and collected in a separate flask submerged in an ice-water bath to prevent evaporation. An average of 15 mL was collected for pH determination and further analysis.

This system accurately duplicated literature partial pressure data for 70.1, 40.8, and 26.9 mass % HNO_3 (Taylor, 1928). Solutions containing chloric acid and sodium chlorate with a total chlorate ion concentration between (1.0−5.7) mol L^{-1} were examined in this system from (33−75) °C. The pH of the condensate ranged from 2.4−4 (0.0037−0.0001 mol L^{-1} H^+). This corresponds to a mol fraction of H^+ in the range $10^{-5}-10^{-6}$ and a partial pressure of ($10^{-2}-10^{-4}$) mmHg. Distilled water (initial pH = 5.3), subjected to distillation in the same system at 61 °C, produced a condensate pH of 4.0. This confirmed that the measured pressures were that of water with a trace amount of another component in the vapor phase. Attempts to classify this other component as chloric acid were unsuccessful as our method of evaluating chlorate ion concentration is not sensitive enough to detect these trace concentrations. This analysis confirms the observation that the enthalpy of vaporization of these solutions (43.1−43.9 kJ/mol) is essentially that for pure water.

Conclusions

The apparatus for this work was validated by reproducing vapor pressure data for 8.9 mass % sodium carbonate and 30.8 mass % sulfuric acid. The maximum deviation from the reported literature boiling points for these systems was 0.7 deg. The concentration of species in solution did not change as a result of boiling and refluxing. The data for chloric acid solutions ranging in concentration from (1.01−3.82) mol L^{-1} over the temperature range (35−79) °C were well correlated by a simple equation of the form $\ln(P) = f(1/T)$ with an additive term for chloric acid concentration. By applying the Clausius−Clapeyron equation, the enthalpy of vaporization for this system was found to be between (43.1−43.9) kJ/mol.

Vapor pressures of sodium chlorate + chloric acid solutions over the ranges (0.73−3.59) mol L^{-1} chloric acid, (0.85−4.25) mol L^{-1} sodium chlorate, and (35−83) °C were correlated by the same equation form as above with the addition of a term to account for sodium chlorate concentration. Some solutions with high chlorate ion concentrations at high temperatures developed a yellow or pink color. Vapor phase composition measurements showed that the vapor pressure was that of water with a trace contribution from another component. The trace component of the vapor was not identified.

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