Vapor–Liquid Equilibria of Hydrogen Chloride–Sodium Chloride–Water Solutions Below 0 °C

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The vapor–liquid equilibria of HCl–NaCl–H_2O solutions were determined for HCl mole fractions on a salt-free basis of 0.0361–0.2229 and NaCl molalities ranging from 0 to near saturation for the nominal temperature range of 0 to -40 °C. Total pressures were measured by capacitance gauges, vapor compositions by direct vapor-phase sampling into a quadrupole mass filter, and liquid compositions by electric conductivity. Results are compared with data previously obtained for the same temperature range for pure HCl–H_2O solutions. Solubility data for NaCl in the acid solutions at these temperatures suggest the formation of an NaCl–water or NaCl–HCl adduct in equilibrium with the saturated solution.

Introduction

The thermodynamic properties of hydrochloric acid have been investigated more comprehensively than any other strong electrolyte. Specifically, the vapor–liquid equilibria data for HCl–water solutions for 2–46 wt % HCl and temperatures from 0 to 110 °C are compiled in Perry's handbook (*1*) based on Zeisberg's (*2*) evaluation of low-pressure literature data. Fritz and Fuget (*3*) and Othmer and Naphthali (*4*) calculated the vapor–liquid equilibria from the emf data of Harned and Ehlers (*5*, *6*) and Akerlof and Teare (*7*) for 0- to 50 °C and 0.01–15.8 *m* HCl. Rupert (*8*), Thumm et al. (*9*), and Kao (*10*) determined the vapor–liquid equilibria at intermediate to high molalities and pressures for solutions of 0.3–0.5 mole fraction HCl at temperatures from -10 to 70 °C. Miller (*11*) measured the vapor–liquid equilibria for 4–36 wt % HCl solutions between 0 and -40 °C.

Activity data for the HCl–NaCl–H_2O system from 0 to 50 °C in the molality range of 2–10 are given in Harned and Owen (*12*) and Robinson and Stokes (*13*) from which Funk (*14*) calculated the equilibrium vapor composition for a constant molality of NaCl of 3 for a range of liquid solution HCl molalities from about 4.5 to 10.5 at 25 °C. Meyer (*15*) also used these data, extrapolating to 15.8 *m* hydrochloric acid and from 0 to -55 °C for a constant NaCl molality of 6, to calculate vapor pressures. There are unfortunately no experimental vapor–liquid equilibria data available for the HCl–NaCl–H_2O system. The present experimental study fills part of this gap in vapor–liquid equilibria for the nominal temperature range of 0 to -40 °C, HCl concentrations on a salt-free basis of 0.0361–0.2229 mole fraction, and NaCl molalities ranging from 0 to near saturation for the range of acid concentrations cited.

Experimental Section

The experimental method used was previously described in ref 11. As shown schematically in Figure 1, a 2-L Pyrex flask containing the test solution was immersed in an insulated methylene chloride bath cooled by a two-stage mechanical refrigeration system. The temperature of the bath was monitored by a calibrated platinum resistance thermometer and maintained to within ±0.1 °C. The solutions used were made up from ACS reagent grade NaCl, 12-N hydrochloric acid and laboratory distilled water.

Removal of air from the system was effected by a mechanical vacuum pump in series with a liquid nitrogen trap. Equilibrium pressures were measured with two MKS Baratron Type 220 capacitance gauges (10^{-04}–1 torr and 10^{-02}–10^{+02} torr) calibrated by the manufacturer using a transfer standard to ±0.02% of full scale accuracy. Samples of the liquid were analyzed by electroconductivity measurements with a maximum deviation of ±1% at 25 ± 0.1 °C using a Barnstead Model PM-70CB bridge and a Yellowstone Springs YSI 3400 Pyrex cell. Vapor samples were drawn directly from the vapor chamber into a Varian VGA-100 quadrupole mass filter where the composition was derived from the recorded mass spectral areas in the mass number range 34–39 and 15–20 mass numbers for HCl and water, respectively. The spectra were obtained at a nominal pressure of 3.0×10^{-06} torr, sampling continuously from the vapor chamber into the quadrupole mass filter pumped by a Varian 20 L/s Vacion pump. Since the total pressures in the vapor chamber were sufficiently low, the partial pressures of the HCl and water were calculated from the ideal gas law.

All valves, tubing, and fittings were made of AISI 304 or 316 stainless steel. Viton O-rings and copper gaskets were used in the valves and flanges, respectively. All metal parts in continuous contact with the vapor were coated with silicone vacuum grease. No significant corrosion of any of the metals was observed so long as care was taken to avoid contact with liquid acid.

The experimental procedure followed was as follows.

(1) The solution was allowed to equilibriate to the selected temperature for at least 18 h. The vapor chamber was then evacuated to a pressure below the range of the gauges. The solution itself was deaerated by slowly opening the flask to the evacuated vapor chamber, allowing the system pressure to rise to the vapor pressure of the solution, shutting off the flask and reevacuating the vapor chamber etc. 5 times.

(2) After deaeration, the flask valve was opened slowly admitting vapor to the vapor chamber and the total pressure measured as a function of time over a minimum of 16 min. Measurements were repeated 4–5 times with five deaeration cycles between runs. Small corrections to the measured pressure for minor leaks and adsorbed gases in the vapor chamber were derived from the slope of the vapor pressure vs. time curve once equilibrium had been achieved.

(3) Subsequently, gas analyses were made by bleeding gases from the vapor chamber continuously into the gas analyzer over a minimum of 2 h to permit the analyzer system to come to equilibrium with the chamber. The gas analyzer was pumped to 1×10^{-08} torr prior to admitting the gas sample. Corrections were made for background water and HCl present in the gas analyzer.

(4) A sample of the liquid solution was taken from the flask as required and the acid separated from the salt by distillation. The acid samples were subsequently diluted with distilled water by 50:1 to 200:1 depending on the sample acid concentration. The diluted sample conductivities were then measured and

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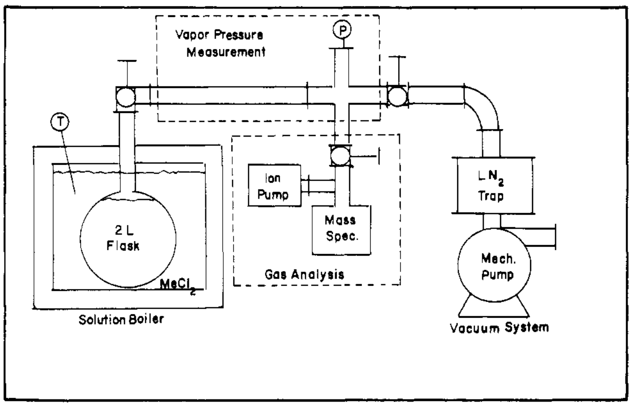

Figure 1. Schematic of experimental apparatus.

compared with certified N/30 and N/10 hydrochloric acid reagent standards. The salt recovered was dissolved in 20 mL of distilled water and generally not diluted further. Salt solution conductivities were compared with standardized 0.0025, 0.0050, 0.0400, and 0.1000 N solutions made up from reagent grade NaCl and distilled water. Densities of the liquid solutions were obtained at room temperature by using calibrated 3- and 10-mL Gay-Lussac pycnometers.

It was necessary to establish the relative sensitivity of the quadrupole mass filter to HCl and water vapor. Details of the procedure are given in ref 11. The filter was found to be more sensitive to water than to HCl. The ratio of sensitivity of water to HCl was found to range from a limiting value of 3.79 at less than 1 × 10^{-08} torr to a maximum of 4.50 at 6.0 × 10^{-07} torr to 4.10 at 3.0 × 10^{-08} torr.

Precision of Experimental Measurements. Total pressure was measured to a standard deviation of 1.7% or better at all acid concentrations and temperatures, and mostly to better than 1.0%. Vapor composition was measured to a maximum standard deviation of 6.5% at low molar concentrations less than 0.04, improving to 1.7% or better at concentrations greater than 0.20. Liquid acid concentrations were measured to a maximum standard deviation of 2.0% and generally to better than 1.0%. Salt molalities were obtained to standard deviations of 0.8% or better and mostly to better than 0.3%.

Results and Discussion

NaCl Molalities at Saturation. Figure 2 illustrates the solubility of NaCl as a function of salt-free mole fraction of HCl, X_{HCl}, and temperature, T. Solubilities at 25 °C were obtained from ref 16. In all the experiments, the solutions were initially saturated with salt at room temperature and were allowed to cool down to temperature over periods ranging from 18 h to several weeks. Generally −10 °C was the first temperature at which a sample was taken. Following the initial sample, usually samples were taken for lower temperatures in approximately 10 °C intervals and then the 0 °C temperature last. The maxima and the trends toward maxima in solubility of NaCl observed in all acid concentrations suggest the formation of an NaCl hydrate or an HCl adduct. This was not confirmed by chemical analysis.

It is not certain that the salt concentrations noted as saturated were truly saturated. In limited experiments evaluating the rate of solution of NaCl in acids at these low temperatures, it was noted that the rate of solution was quite low and that there was hysteresis in the apparent NaCl solubility when temperature cycling back to lower temperatures after dwelling at a higher temperature. It is likely however that the solutions were at saturation or near saturation.

Vapor–Liquid Equilibria. The unsmoothed experimental data are displayed in Figures 3–5. The logarithms of total equilibrium pressure, P', partial pressure of water, p'_{H_2O}, and the partial pressure of HCl, p'_{HCl}, of the salt solutions at constant salt-free mole fraction of HCl, X_{HCl}, are plotted against the corresponding values of the pure HCl–water solutions, P^0, $p^0_{H_2O}$, and p^0_{HCl}, at the same temperature and X_{HCl} from ref 11. These figures permit a direct comparison of the behavior of the salted and pure solutions. The dashed line represents equality of the pressures of the salt and salt-free solutions. All curves below the dashed line indicate that the salted solutions exhibit lower pressures than the corresponding pure acid solutions, and above the dashed line, higher. Temperatures of the solutions

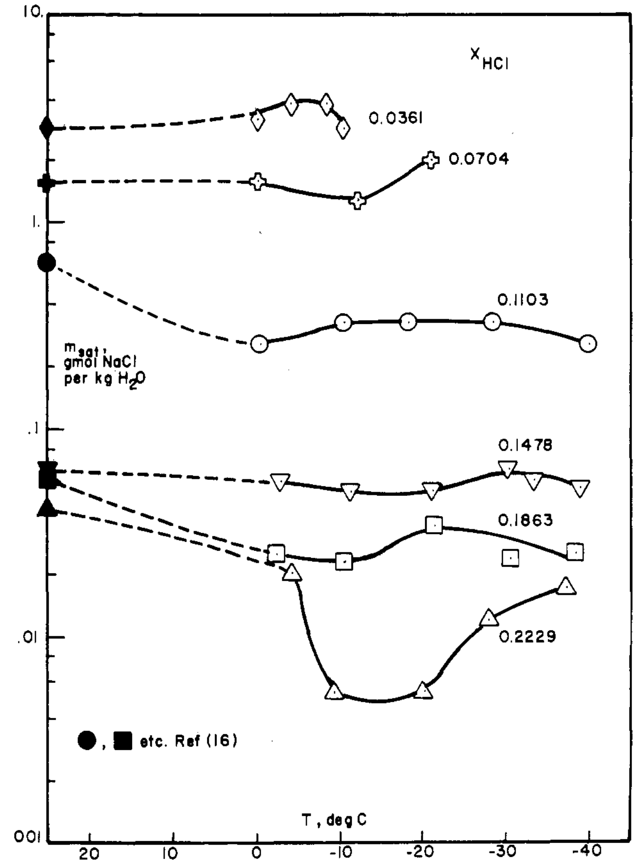

Figure 2. Solubility of NaCl, m_{sat}, as a function of salt-free mole fraction HCl, X_{HCl}, and temperature, T.

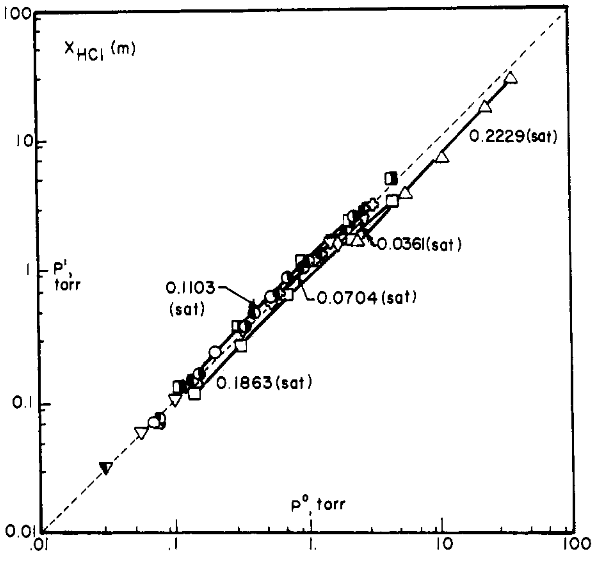

Figure 3. Total vapor pressure of salted acid solution, P', as a function of salt-free mole fraction HCl X_{HCl}, NaCl molality, m, and total vapor pressure of pure acid solution, P^0.

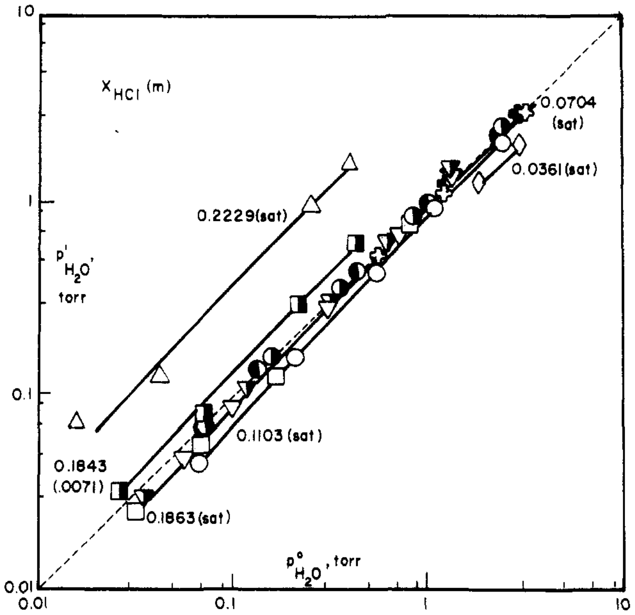

Figure 4. Partial pressure of water of salted acid solution, p'_{H_2O}, as a function of salt-free mole fraction HCl, X_{HCl}, NaCl molality, m, and partial pressure of water of pure acid solution, $p^0_{H_2O}$.

are not shown since there is no unique temperature scale for these overall plots. They cover the range of temperatures from 0 to −45 °C depending on the acid concentration. Similar plots were used by Othmer and Naphthali (*4*) to correlate partial pressures, total pressures, and vapor compositions of pure hydrochloric acid solutions with the corresponding values of water at the same temperature. They noted that the logarithm of the pressures of the hydrochloric acid solutions yielded straight lines when plotted against the logarithm of the corresponding pressures at the same temperature. There is no fundamental reason why the lines should be straight, however. In figures 3–5, curved lines in general correlate the data.

***Total Pressure Data*.** The NaCl–HCl–H_2O system displays a minimum pressure azeotrope at about $X_{HCl} = 0.147$ for all salt molalities. The pure HCl–H_2O system at these temperatures (ref 11) also exhibits a minimum pressure as a function of X_{HCl} but at a higher value of X_{HCl} of about 0.1545. In the range $X_{HCl} = 0.07$–0.11, the total pressures of the salted solutions were close to what is observed for pure hydrochloric acid solutions. This was also true for the unsaturated salt solution at an X_{HCl} of 0.1843. At the extremes in HCl mole fractions studied for salt-saturated solutions, X_{HCl} values of 0.0361, 0.1863, and 0.2229, the total pressures measured were lower than for the pure acid solutions over the temperature range studied. Generally there is only a modest effect on total vapor pressure that can be attributed to the dissolved salt.

***Water Partial Pressure Data*.** For $X_{HCl} < 0.1863$, the water partial pressures for the salted solutions were close to or less than the corresponding values for pure HCl solutions, generally the suppression of P'_{H_2O} relative to p_{H_2O} increasing with a decrease in temperature. For saturated salt solutions, the effect of NaCl in depressing the partial pressure of water was greatest for the most dilute acid solution studied, $X_{HCl} = 0.0361$. The saturated salt solution water partial pressures exceeded the partial pressures for the pure acid solutions for an X_{HCl} of 0.2229. In all cases, at constant X_{HCl} the water partial pressure decreased with increasing salt concentration. At an X_{HCl} of 0.1843 and an intermediate salt molality of 0.0071_9, the p'_{H_2O} was higher than $p^0_{H_2O}$ for pure acid of the same HCl concentration, approaching the pure acid values at the lower temperatures. At $X_{HCl} = 0.1863$ for the saturated salt solution, p'_{H_2O} was lower than $p^0_{H_2O}$ of the pure hydrochloric acid solution.

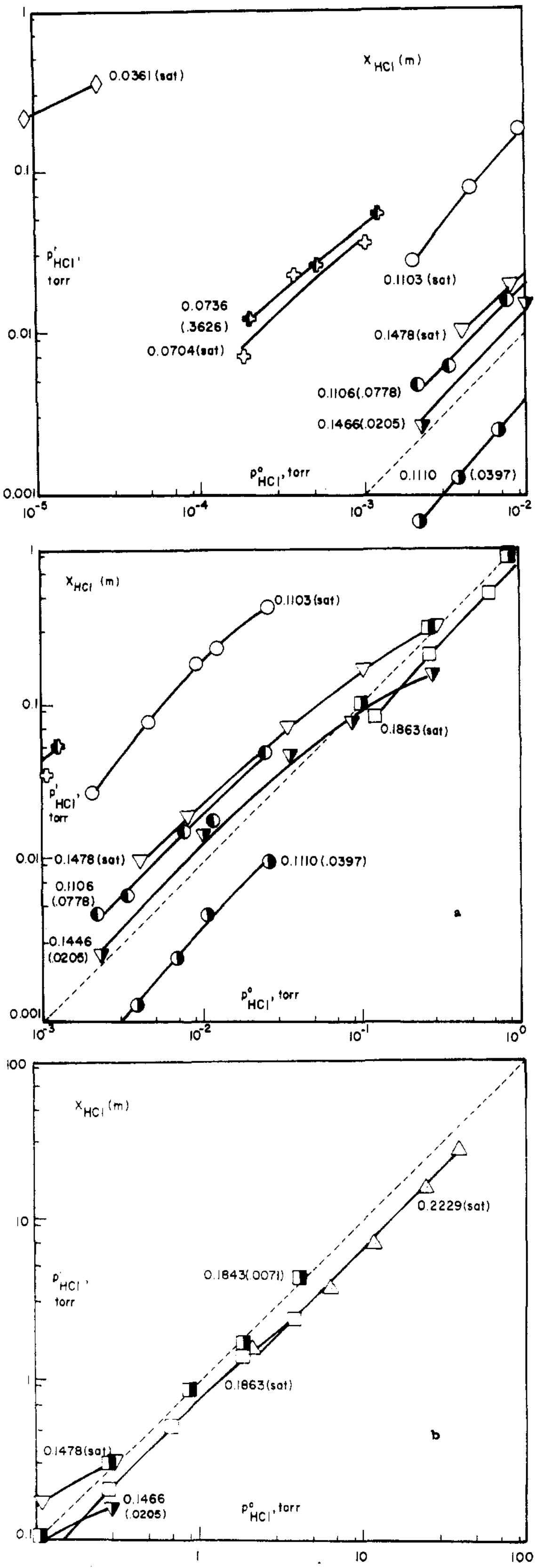

Figure 5. Partial pressure of HCl of salted acid solution, p'_{HCl}, as a function of salt-free mole fraction HCl, X_{HCl}, NaCl molality, m, and partial pressure of HCl of pure acid solution, p^0_{HCl}.

***HCl Partial Pressure Data*.** For saturated salt solutions at $H_{HCl} \le 0.1478$, the p'_{HCl} values were higher than the corresponding values for pure hydrochloric acid, p^0_{HCl}, and lower for $X_{HCl} \ge 0.1863$. At an X_{HCl} of 0.1478 for a saturated salt solution, the p'_{HCl} is about the same as p^0_{HCl} near 0 °C, and

Table I. Vapor-Liquid Equilibria of NaCl-HCl-Water Solutions[a]

X_{HCl}	T, °C	m, g mol/kg H_2O	P', torr	y'_{HCl}	y'_{H_2O}	p'_{HCl}, torr	p'_{H_2O}, torr
0.0361[b]	0	3.15	3.49	0.148	0.852	0.51_7	2.97
	−10	3.15	1.61	0.139	0.861	0.22_3	1.38
0.0704[b]	0	1.545	3.18	0.011	0.989	0.03_6	3.24
	−10	1.285	1.48	0.017	0.983	0.02_5	1.45
	−20	1.795	0.628	0.014	0.986	0.008_7	0.619
0.1103[b]	0	0.2537	2.70	0.154	0.846	0.41_4	2.28
	−10	0.3199	1.28	0.201	0.799	0.27_0	1.02
	−20	0.3225	0.535	0.259	0.741	0.139	0.396
	−30	0.3205	0.207	0.334	0.666	0.069	0.138
	−40	0.2550	0.073	0.385	0.615	0.028	0.045
0.1106	0	0.0778	2.72	0.020	0.980	0.05_4	2.66
	−10	0.0778	1.27	0.025	0.975	0.03_1	1.23
	−20	0.0778	0.476	0.036	0.964	0.017	0.458
	−30	0.0778	0.203	0.044	0.956	0.008_9	0.194
	−40	0.0778	0.067	0.066	0.934	0.004_4	0.063
0.1110	0	0.0397	2.80	0.003_7	0.996	0.010	2.79
	−10	0.0397	1.24	0.005_0	0.995	0.006_3	1.23
	−20	0.0397	0.505	0.006_4	0.994	0.003_2	0.502
	−30	0.0397	0.192	0.007_6	0.992	0.001_5	0.190
	−40	0.0397	0.061	0.009_8	0.990	0.000_6	0.060
0.1478[b]	0	0.0573	2.24	0.178	0.822	0.39_9	1.84
	−10	0.0495	0.986	0.190	0.810	0.187	0.799
	−20	0.0485	0.410	0.196	0.804	0.080	0.330
	−30	0.0550	0.154	0.187	0.813	0.029	0.125
	−40	0.0500	0.051	0.184	0.816	0.009_3	0.041
0.1466	0	0.0205	2.31	0.085	0.915	0.19_6	2.12
	−10	0.0205	1.00	0.104	0.896	0.10_4	0.89_6
	−20	0.0205	0.394	0.121	0.879	0.048	0.347
	−30	0.0205	0.145	0.121	0.879	0.018	0.128
	−40	0.0205	0.047	0.095	0.905	0.004_5	0.042
0.1863[b]	0	0.0261	3.95	0.742	0.258	2.93	1.02
	−10	0.0226	1.81	0.769	0.231	1.39	0.41_9
	−20	0.0335	0.761	0.788	0.212	0.600	0.161
	−30	0.0235	0.278	0.787	0.213	0.219	0.059
	−40	0.0256	0.094	0.769	0.231	0.072	0.022
0.1843	0	0.0070_9	6.80	0.797	0.203	5.42	1.38
	−10	0.0070	2.73	0.760	0.240	2.08	0.65_7
	−20	0.0070	1.07	0.748	0.252	0.80_3	0.27_0
	−30	0.0070	0.411	0.761	0.239	0.313	0.098
	−40	0.0070	0.139	0.762	0.238	0.106	0.033
0.2229[b]	0	0.0259	32.44	0.942	0.058	30.57	1.87
	−10	0.0050	17.03	0.942	0.058	16.04	0.99_0
	−20	0.0051	7.96	0.947	0.053	7.54	0.41_9
	−30	0.0125	3.34	0.956	0.044	3.19	0.14_8
	−40	0.0165	1.33	0.965	0.035	1.28	0.04_6

[a] Smoothed experimental data. The original experimental data is incorporated in supplementary Table IA. [b] Saturated or near-saturated salt solutions; see text.

for an intermediate salt molality of about 0.0205 (X_{HCl} = 0.1466) drops below p^0_{HCl} as the temperature decreases below about −10 °C. For acid concentrations, $X_{HCl} < 0.1863$, the solutions containing intermediate salt molality concentrations exhibited lower HCl partial pressures than the saturated solutions. The p'_{HCl} values for $X_{HCl} = 0.0704$–0.0736 for saturated and intermediate salt concentrations are probably the same within the accuracy of the measurements in this composition range. In addition, for a hydrochloric acid concentration, X_{HCl} = 0.1110, at an intermediate salt molality of 0.0397 the p'_{HCl} values measured were lower than the corresponding partial pressures for the pure HCl solution but were higher for a salt molality ≥ 0.0778.

It is noteworthy that the salted solutions exhibit minima in p'_{HCl} and the y'_{HCl} values. At 0 to −10 °C, the minima occur at approximately X_{HCl} = 0.0704 and with a decrease in temperature at X_{HCl} = 0.1478. Correspondingly, p'_{H_2O} and y'_{H_2O} exhibit maxima over the same range of acid mole fractions and temperatures. Although all intermediate salt molalities for the acid solutions were not completely explored, it appears that the minima in p'_{HCl} and y'_{HCl} remain near an X_{HCl} = 0.11 or less for all temperatures. This behavior is very different from that observed for pure hydrochloric acid solutions. In the latter system p^0_{HCl} and y^0_{HCl} increase and $p^0_{H_2O}$ and $y^0_{H_2O}$ decrease continuously with an increase in X_{HCl}.

The behavior of the solutions is consistent with the Gibbs–Duhem equation. It may be shown that

$$[X_{HCl}/(1 - X_{HCl})]\,d \ln p'_{HCl} + [X_{NaCl}/(1 - X_{HCl})]\,d \ln a_{NaCl} = -d \ln p'_{H_2O}$$

where $X_{NaCl} = x_{NaCl}/(1 - x_{NaCl})$, x_{NaCl} is the mole fraction of salt in the liquid phase, and a_{NaCl} is the salt activity in the liquid phase. Note that the equation given for the Gibbs–Duhem equation is based on the salt-free mole fraction of HCl, X_{HCl}. For the special case in which X_{NaCl} is equal to zero, i.e., pure hydrochloric acid solution, it is clear that if p_{HCl} increases p_{H_2O} must decrease as x_{HCl} increases. Similarly, if the second term on the left-hand side of the equation remains constant as X_{HCl}, increases, the same is true. Depending on the magnitude of the change of this term with X_{HCl}, it is possible for p'_{H_2O} to increase or decrease with p'_{HCl} as X_{HCl} increases.

For the solutions saturated with NaCl both p'_{HCl} and p'_{H_2O} increase as X_{HCl} increases from 0.1863 to 0.2229. The activity of the NaCl, a_{NaCl}, in equilibrium with the solid salt would be constant if the state of the solid salt remained the same as X_{HCl}

changed. However as described above, the solubility data suggest the formation of a water or HCl adduct in the solid phase. If therefore there is a change in the state of the solid salt with an increase in X_{HCl}, the activity term on the left-hand side of the equation would change as X_{HCl} increased. A sufficient decrease would result in an increase in p'_{H_2O}, as observed. It is also possible that the increase in p'_{H_2O} is due to experimental error in measuring the vapor composition. Only a couple of percent increase in y'_{HCl} would reverse the trend observed for p'_{H_2O}. Therefore the partial pressure data for X_{HCl} = 0.2229 should be used with caution.

Similar thermodynamic arguments can be given in the case of nonsaturated salt solutions relative to the complexity of the variation of the partial pressures for a given X_{HCl} with a change in salt molality. It is interesting to note for example the variation of p'_{HCl} with salt molality for X_{HCl} = 0.111 in Figure 5a. p'_{HCl} first decreases as salt is added to the pure hydrochloric acid solution and then increases. There is little change in p'_{H_2O} until near saturation where p'_{H_2O} decreases. Reference 17 studied the vapor pressures of HCl and water over 5.0 M hydrochloric acid containing 0.0–1.5 M $CuCl_2$. They found similar behavior for temperatures between 60 and 90 °C—p'_{H_2O} decreased and p'_{HCl} first decreased and then increased with increasing salt molality.

Smoothed Data. The experimental data for total and partial vapor pressures and vapor mole fraction were smoothed graphically for a given X_{HCl} and salt molality by weighting the data within the group, and by maintaining consistency in variation of the dependent variables for all the other acid compositions and salt molalities with temperature. Pressure and mole fraction data were taken at four to five temperatures for each X_{HCl} and for each case in which salt molality was held constant except for X_{HCl} = 0.0361 and 0.0704 where freezing point considerations limited the data to two and three temperatures, respectively. Salt molalities were measured for the saturated solutions at a minimum of three temperatures for X_{HCl} = 0.0704 to four to six temperatures at the other acid mole fractions.

A summary of all the smoothed experimental results interpolated to 0 to −40 °C in 10 °C intervals is given in Table I. The average and maximum percent deviations of the experimental total pressure, vapor compositions, and partial pressures from their respective smoothed values are given in Table II for the X_{HCl} compositions and salt molalities studied. The average deviation of the experimental from the smoothed total pressure data is 0.5% and the maximum deviation +1.7% for an X_{HCl} of 0.1863. The average and maximum deviations are 0.2% and +4.0% respectively for X_{HCl} = 0.1478. For all other compositions, the smoothed and the experimental total pressure data are the same within the precision of the measurements. The largest deviations between experimental and smoothed gas composition measurements occur for X_{HCl} values at which the water or the HCl is at its lowest concentration. Thus for water the average and maximum deviations are highest, 7.8% and +22.5%, respectively, at an X_{HCl} of 0.2229 when y'_{H_2O} = 0.04. For HCl the average and maximum deviations are 7.6% and +32.7%, respectively, at X_{HCl} = 0.1106 for y'_{HCL} = 0.03. In general, as the gas concentration increases in water or HCl content the average and maximum deviations of the respective gas mole fraction decrease. The maximum deviation between experimental and smoothed HCl partial pressures is seen at X_{HCl} = 0.1105 where the errors in measurement and total pressure combine to produce an average deviation of 13.7% and a maximum deviation of +33.3%. The average and maximum deviations for p'_{H_2O} are greatest, 1.7% and +23.4%, respectively, at X_{HCl} = 0.2229 where the deviation in y'_{H_2O} is the greatest. The higher deviations for HCl are a reflection of the greater sensitivity of the quadrupole mass filter for water than for HCl.

Table II. Percentage Deviation of Experimental from Smoothed Data

	P, torr	
X_{HCl}	AD[a]	MD[a]
0.0361		
0.0704		
0.0736		
0.1103	0	0
0.1106	0	0
0.1110	0	0
0.1466	0	0
0.1478	0.2	+4.0
0.1843	0	0
0.1863	0.5	+1.7
0.2229	0	0

	vapor composition			
	y'_{H_2O}		y'_{HCl}	
X_{HCl}	AD	MD	AD	MD
0.0361				
0.0704				
0.0736				
0.1103	1.3	+4.0	3.5	−11.5
0.1106	0.3	−0.9	7.6	+32.7
0.1110	0	0	1.1	+4.5
0.1466	0	0	0	0
0.1478	0	0	0	0
0.1843	5.6	+10.2	1.8	−3.2
0.1863	1.0	+4.1	3.0	−8.8
0.2229	7.8	+22.5	1.0	−3.2

	partial pressure, torr			
X_{HCl}	p'_{H_2O}		p'_{HCl}	
0.0361				
0.0704				
0.0736				
0.1103	0.3	+2.8	5.2	+13.0
0.1106	0	0	13.7	+33.3
0.1110	0	0	0.8	+4.3
0.1466	0	0	0	0
0.1478	0	0	0	0
0.1843	1.0	+11.0	4.2	+11.3
0.1863	0.7	+5.1	2.0	+9.2
0.2229	1.7	+23.4	0	0

[a] AD = average deviation; MD = maximum deviation.

Since there are no experimental vapor–liquid equilibria data reported in the literature for the NaCl–water–HCl system, it is not possible to compare the present results with any other. The calculated results (ref 14 and 15) are at either higher temperatures or different acid or salt concentrations.

Glossary

a_{NaCl}	activity of NaCl in solution
m	molality of NaCl in solution, g mol NaCl per kg water
m_{sat}	solubility of NaCl in solution, g mol NaCl per kg water
p_{HCl}	partial pressure of hydrogen chloride, torr
p_{H_2O}	partial pressure of water, torr
P	total pressure, torr
T	Temperature, °C
x_{NaCl}	mole fraction of NaCl in solution
X_{NaCl}	equal to $x_{NaCl}(1 - x_{NaCl})$
X_{HCl}	liquid-phase mole fraction of hydrogen chloride, salt-free basis
y_{HCl}	gas-phase mole fraction of hydrogen chloride
y_{H_2O}	gas-phase mole fraction of water

Superscripts

′	respective variable of acid solution containing NaCl
0	respective variable of pure acid solution

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Registry No. HCl, 7647-01-0; NaCl, 7647-14-5.

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Supplementary Material Available: The original, unsmoothed experimental data incorporated in Table IA, 3 pages. Ordering information is given on any current masthead page.

Densities and Refractive Indices of Aqueous Zinc Nitrate Solutions

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Densities and refractive indices of aqueous zinc nitrate solutions (0.01–21.6 *m*) have been measured as a function of temperature over the range 20–60 °C. Thermal expansivity (α) for the system shows a maximum near a concentration of 10 *m*, which corresponds to a water:salt mole ratio (*R*) of 6, and tends to attain a limiting value at higher salt concentrations. From the density measurements, apparent molal volumes (ϕ) and partial molal volumes of zinc nitrate ($\bar{V}_2$) and water ($\bar{V}_1$) have been calculated. The refractive indices at all compositions vary linearly with temperature and have negative temperature coefficients. An increase in the salt content increases the refractive index of the system, leading to a limiting value beyond ≈15 *m*, which corresponds to $R = 4$. The molar refractions have been calculated by using the Lorentz and Lorenz equation and are found to depend upon temperature. The expansivity estimated from the temperature coefficient of the refractive index and the differential forms of the Gladstone–Dale and Lorentz–Lorenz equations agrees well with that estimated from the density data.

Introduction

Continuing our work concerning the measurement of refractive index in molten hydrates and concentrated electrolytic solutions (*1–4*), we present some results for aqueous zinc nitrate solutions over an extended range of temperature and concentration.

Experimental Section

Zinc nitrate hexahydrate (AR) was used in the present study. The solutions were prepared by weighing the hexahydrate and then making up the solutions with distilled water. Melts with lower water content were prepared by removing calculated amounts of water from weighed quantities of the hydrate melts by continuous evacuation at ≈50 °C. All the solutions or melts were transparent.

The densities were measured with a modified manometric densitometer as described earlier (*5*). The refractive indices were measured on an Abbê-type refractometer. The experimental technique and the precision of measurement were essentially similar to those described earlier (*4*).

Results and Discussion

The mole fraction (X) is not a convenient unit for describing the composition of solutions such as those studied here because of the variation in its magnitude by a factor of about 10^6 over the composition range studied in the present work. Therefore, for the present study the compositions are expressed in terms of molality (m) and water-to-salt mole ratio (R).

The densities (ρ) for 0.01–21.6 m aqueous solutions of zinc nitrate presented in Table I show a quadratic temperature dependence and have been fitted to eq 1. The coefficients A,

$$\rho(\text{g cm}^{-3}) = A + Bt + Ct^2 \qquad (1)$$

B, and C are presented in Table II. The composition dependence of density across the entire concentration range at 60 °C is shown in Figure 1. The data of Jain and Tamamushi (*2*) for $Zn(NO_3)_2 \cdot xH_2O$ where $2 \le x \le 6$ have been included for a facile comparison. The agreement between the two independent studies is better than ±0.5%. The expansivity (α) determined from eq 2 passes through a maximum at a concentration of approximately 10 m (Figure 1), which corresponds to a water-to-salt mole ratio of six, and tends to acquire a limiting value at higher salt concentrations. The expansivity

$$\alpha_t = -\frac{1}{\rho_t}\left[\left(\frac{d\rho}{dT}\right)\right]_t \qquad (2)$$

values are presented in Table II.

The apparent molal volumes of zinc nitrate (ϕ) were calculated (*6*, *7*) from each individual density value using eq 3, where

$$\phi = \frac{1}{d}\left[M_2 - \frac{1000(d - d_1)}{md_1}\right] \qquad (3)$$

d is the density of the solution, M_2 is the molar mass of zinc

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