the tie-line data to have the following functional relationship:

$$(X_{2,\mathrm{II}}X_{3,\mathrm{I}}/X_{2,\mathrm{I}}X_{3,\mathrm{II}}) = b(X_{2,\mathrm{I}}X_{3,\mathrm{I}}/X_{1,\mathrm{I}}X_{3,\mathrm{II}})^m \qquad (4)$$

The results of the regression analysis are presented in Figure 6. The probability that the data do not form a straight line is less than 0.01%. The slope m of the regressed line is 0.57. The goodness of the fit confirms the reliability of the experimental LLE data.

Glossary

a_{iL}	activity of component i in phase L
A_{ij}	UNIQUAC binary interaction parameter, k^{-1}
K	distribution coefficient, $K = X_{2,\mathrm{II}}/X_{2,\mathrm{I}}$
T	temperature, K
x_{iL}	experimental weight percent concentration of component i in phase L
X_{iL}	experimental mole percent concentration of component i in phase L
rmsd	mole percent root mean square deviation, eq 3

Subscripts

i,j	components (i,j = 1, 2, 3)
L	phases (I, aqueous; II, organic)
k	tie lines (1, 2, 3, ..., M)

Registry No. Acetone, 67-64-1; isooctane, 540-84-1.

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Vapor–Liquid Equilibria below 0 °C of Hydrogen Chloride Solutions Saturated with Calcium Chloride

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The vapor-liquid equilibria of HCl-H_2O solutions saturated with $CaCl_2$ were determined for HCl molalities of 5.031–15.691 g-mol of HCl/kg of H_2O for the nominal temperature range of 0 to -40 °C. Total pressures were measured by means of capacitance gauges, vapor compositions by direct vapor-phase sampling with a quadrupole mass filter, and liquid-phase compositions by electric conductivity measurements. Solubilities of $CaCl_2$ in the hydrochloric acid at these temperatures are also reported.

Introduction

The thermodynamic properties of hydrochloric acid and acid solutions containing salts, specifically the vapor–liquid equilibria, have been investigated more thoroughly than for any other strong electrolyte. However, relatively few studies have been reported for hydrochloric acid solutions below 0 °C, possibly because of the experimental difficulties involved. Kao (*1*) reported data for HCl–H_2O down to −10 °C. For the temperature range of 0 to -40 °C, Miller (*2*, *3*) measured the vapor–liquid equilibria of pure HCl-H_2O solutions and of acid solutions containing unsaturated to near-saturated NaCl concentrations.

The present experimental study is a continuation of the effort to fill the gap in data for hydrochloric acid solutions containing dissolved salts, in this case $CaCl_2$, in the temperature range of 0 to -40 °C. Vapor–liquid equilibria are reported for solutions with HCl molalities of 5.013–15.691 g-mol of HCl/kg of H_2O saturated with $CaCl_2$. $CaCl_2$ is an important industrial additive used in the recovery of waste hydrochloric acids by extractive distillation (*4*). The design analysis in ref 4 was based on the vapor–liquid equilibria data of Synowiec and Bobrownicki (*5*) for HCl–$CaCl_2$–H_2O solutions with 0–39 wt % HCl and unsaturated concentrations of $CaCl_2$ of 0–50 wt %. These data were for higher boiling temperatures at a constant pressure of 750 mmHg.

Experimental Section

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 maintained to within ±0.1 °C of the desired temperature, monitored by a calibration platinum resistance thermometer.

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 the liquid acid.

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^{-4}–1 and 10^{-2}–10^{2} Torr) calibrated by the manufacturer using a transfer standard to ±0.02% of full-scale accuracy. Samples of the liquid solution were analyzed for acid and $CaCl_2$ content, after their separation as described below, by electroconductivity measurements made by using a Barnstead Model PM-70CB bridge and a Yellowstone Springs YSI 3400 Pyrex cell with a maximum deviation of ±1% at 25 ± 0.1 °C. Vapor samples were drawn directly from the vapor chamber into a Varian VGA-100 quadrupole mass filter, and the composition was derived from the recorded mass spectral areas in the mass number ranges 34–39 and 15–20 for HCl and water, respectively. The spectra were obtained at a nominal pressure of 3.0 × 10^{-6} Torr, sampling continually from the vapor chamber into the quadrupole mass

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Table I. Experimental Vapor–Liquid Equilibria of HCl–Water Solutions Saturated with $CaCl_2$

T, °C	m_{HCl}, g-mol/kg of H_2O	m_{CaCl_2}, g-mol/kg of H_2O	P,[a] Torr	y_{HCl}	y_{H_2O}	P_{HCl}, Torr	y_{HCl}
	6.798[b]						
−2.5	5.013	5.035	2.216*	0.3777	0.6223	0.837	1.379
−2.8			2.16				
−10.8	7.420	3.824	0.993*	0.4040	0.5960	0.401	0.592
−10.3			1.048				
−22.5	7.840	2.076	0.320*	0.4109	0.5891	0.132	0.188
−22.7			0.306				
−31.5	7.055	1.235	0.134*	0.4597	0.5403	0.062	0.072
−31.8			0.135				
−42.6	8.644	0.893	0.046*	0.5174	0.4826	0.024	0.022
−43.7			0.041				
	8.128[b]						
−0.8	14.718	3.458	34.60*	0.9417	0.0583	32.58	2.02
−0.7			34.86				
−12.8	15.016	0.833	13.71	0.9440	0.0560	12.94	0.77
−22.3	13.682	0.573	6.22	0.9431	0.0569	5.87	0.35
−31.5	15.387	0.286	2.765*	0.9382	0.0618	2.594	0.171
−30.8			2.94				
−38.6	15.691	0.160	1.449*	0.9494	0.0506	1.376	0.073
−39.7			1.31				
	9.561[b]						
−0.7	9.218	2.923	44.20*	0.9376	0.0624	41.442	2.758
0.0			47.30				
−2.8	12.866	3.845	35.61*	0.9509	0.0491	33.862	1.749
−3.2			34.77				
−9.7	14.077	1.376	18.33*	0.9246	0.0754	16.948	1.382
−10.0			17.49				
−24.0	13.471	0.519	5.740*	0.9324	0.0676	5.352	0.388
−22.7			6.38				
−31.2	12.524	0.300	3.579*	0.9441	0.0559	3.379	0.200
−31.3			3.54				
	16.062[b]						
−1.9	14.519	2.020	55.62*	0.9491	0.0509	52.789	2.831
−1.4			56.10				
−11.4	14.070	1.422	29.29	0.9467	0.0533	27.73	1.56
−25.4	11.468	0.530	10.05*	0.9395	0.0605	9.442	0.608
−25.5			9.71				
−36.0	12.004	0.248	4.643*	0.9473	0.0527	4.398	0.245
−35.8			4.73				

[a] Values marked with an asterisk are interpolated values. N.B. To convert pressures in torr to pascals, multiply by 133.322. [b] Initial acid concentration.

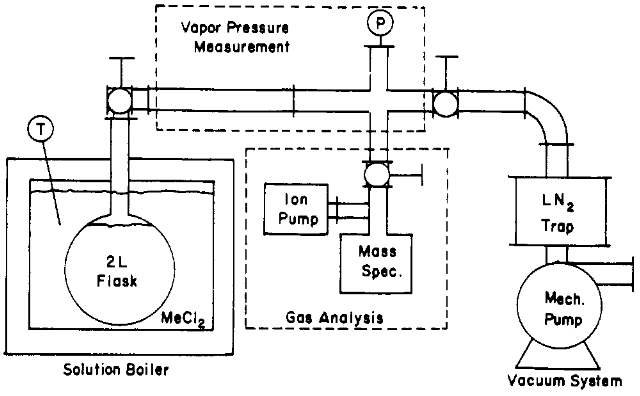

Figure 1. Schematic of experimental apparatus.

filter. The mass filter was 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.

The solutions used were prepared from ACS reagent grade $CaCl_2$–$2H_2O$, 12 N hydrochloric acid, and laboratory-distilled water. Sufficient salt was added to the hydrochloric acid at room temperature to saturate the solution. The water added to the acid initially by the addition of the hydrated salt, and the subsequent removal of water by precipitation of $CaCl_2$–water adducts as the solution was cooled to the selected experimental temperature, significantly modified the HCl and $CaCl_2$ molalities of the solutions. The solution was allowed to equilibrate to the selected temperature for a minimum of 18 h, and generally 72–108 h, before any pressure and composition measurements were made. A sample of the liquid solution was taken from the flask for each test and the acid separated from the $CaCl_2$ salt by distillation. The residue salt was heated to 210–220 °C for several hours to assure that all the water of hydration was transferred to the recovered acid solution. 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 compared with the conductivities of certified N/30 and N/10 hydrochloric acid reagent standards. The recovered solid $CaCl_2$ was dissolved in 10–20 mL of distilled water for the electroconductivity analysis. Salt sample solution conductivities were compared with the conductivities of M/10 and M/30 solutions prepared from reagent grade $CaCl_2$–$2H_2O$. The latter solutions were standardized by Mohr titration to ±0.2% and ±0.1% precision,

Table II. Interpolated Vapor-Liquid Equilibria of HCl-Water

T, °C	m_{HCl}, g-mol/kg of H_2O	m_{CaCl_2}, g-mol/kg of H_2O	P, Torr	y_{HCl}	y_{H_2O}	p_{HCl}, Torr	p_{H_2O}, Torr
-2.5	5.013	5.035	2.216	0.382	0.618	0.847	1.369
	12.420	3.792	36.713	0.941	0.059	34.537	2.176
	14.559	1.996	53.242	0.962	0.038	51.218	2.024
	15.031	2.587	30.600	0.941	0.059	28.795	1.805
-5.0	5.843	4.707	1.740	0.385	0.615	0.669	1.071
	14.626	1.870	44.380	0.961	0.039	42.640	1.740
	14.904	3.396	28.591	0.936	0.064	26.758	1.833
	15.535	1.780	25.226	0.948	0.052	23.916	1.307
-10.0	7.249	3.952	1.072	0.391	0.609	0.419	0.653
	13.973	1.302	17.815	0.929	0.071	16.554	1.261
	14.278	1.530	30.837	0.958	0.042	29.553	1.284
	15.351	1.019	17.085	0.951	0.049	16.244	0.841
-15.0	7.995	3.149	0.661	0.400	0.600	0.265	0.396
	13.175	0.722	11.508	0.926	0.074	10.662	0.846
	13.364	1.142	21.426	0.956	0.044	20.483	0.943
	14.609	0.749	11.429	0.948	0.052	10.834	0.595
-20.0	8.025	2.405	0.407	0.413	0.587	0.168	0.239
	12.287	0.800	14.887	0.954	0.046	14.197	0.690
	13.333	0.586	7.707	0.928	0.072	7.149	0.558
	13.770	0.632	7.551	0.943	0.057	7.118	0.433
-25.0	7.578	1.783	0.251	0.429	0.571	0.108	0.143
	11.836	0.546	10.344	0.951	0.049	9.839	0.505
	13.441	0.495	5.351	0.933	0.067	4.991	0.360
	13.965	0.486	4.927	0.938	0.062	4.620	0.307
-30.0	7.115	1.333	0.155	0.448	0.552	0.086	0.069
	11.987	0.377	7.187	0.949	0.051	6.820	0.367
	12.793	0.340	3.852	0.942	0.058	3.627	0.225
	15.073	0.325	3.175	0.936	0.064	2.972	0.203
-35.0	7.147	1.064	0.095	0.472	0.528	0.045	0.050
	11.425*	0.184*	2.874*	0.955*	0.045*	2.744*	0.13*
	12.054	0.265	4.994	0.946	0.054	4.727	0.267
	15.795	0.213	2.020	0.941	0.059	1.900	0.120
-40.0	7.900	0.927	0.059	0.501	0.499	0.029	0.029

[a] Values marked with an asterisk are interpolated values. N.B. To convert pressures in torr to pascals, multiply by 133.322.

respectively. Densities of the saturated liquid acid samples were obtained at room temperature with calibrated 3- and 10-mL Gay-Lussac pycnometers.

Details of the experimental procedure for measurement of vapor pressures and gas-phase composition may be found in ref 2. Also, a description of the procedure used to establish the relative sensitivity of the quadrupole mass filter to HCl and water vapor may be found in ref 2. The mass filter was found to be more sensitive to water than to HCl. The ratio of the sensitivity of water to HCl was found to range from a limiting value of 3.79 at less than 1×10^{-8} Torr to a maximum of 4.5 at 6.0×10^{-7} Torr to 4.10 at 3.0×10^{-6} Torr.

Precision of Experimental Measurements. Total pressure was measured to a mean square maximum deviation of 2.9% for pressures of about 0.04 Torr and 1.7% for pressures of about 55 Torr. Mostly, the pressure mean square deviations were in the range 0.2-1.6%. Water vapor composition results showed maximum mean square deviations of 7.0% for mole fractions ≤ 0.11 and 1.9% for mole fractions ≥ 0.6. HCl composition measurements were found to have a maximum mean square deviation of 3.2% for mole fractions ≤ 0.38 and 0.2% for mole fractions ≥ 0.95. Liquid acid molalities were determined with a maximum mean square deviation of 0.5%; mostly, the mean square deviation was 0.2% or less. The maximum mean square deviation of the $CaCl_2$ molalities was found to be 0.2%, but for most determinations it was less than 0.1%.

Results and Discussion

Unsmoothed Experimental Results. Table I summarizes the measured values of HCl molality, m_{HCl} (g-mol of HCl/kg of H_2O); $CaCl_2$ molality, m_{CaCl_2} (g-mol of $CaCl_2$/kg of H_2O); total pressure, P (Torr), vapor-phase HCl mole fraction, y_{HCl}; vapor-phase water mole fraction, y_{H_2O}; and P_{HCl} (Torr) and P_{H_2O} (Torr), the partial pressures of HCl and H_2O, respectively, at the experimental temperatures, T (°C). The conversion factor from pressure units of Torr to pascals is noted in the table. The data are given in four groups, each group based on the initial acid molality of the solution at room temperature prior to saturation with $CaCl_2$-$2H_2O$. Note that the acid molality changed significantly, first from the water in the $CaCl_2$ salt added at room temperature and second when the $CaCl_2$ precipitated out of solution with its adduced water as the solution temperature was decreased.

In most cases, the temperatures at which the total pressure and the vapor composition were measured were slightly different. Hence, in order to calculate the partial pressures of HCl and water, the total vapor pressure at the temperature at which the vapor compositions were measured was interpolated to the same temperature from the data by linear regression.

Interpolated Data. The logarithms of P, p_{HCl}, and p_{H_2O} for each group of data were correlated by linear regression with T, since an examination of the data indicated that, for each group of data, T was the dominant variable. The standard deviation about the regression for P for each of the groups was 2.8%, 0.5%, 2.1%, and 4.6%; for p_{HCl}, 3.0%, 0.7%, 1.0%, and 2.0%; and for p_{H_2O}, 2.0%, 7.1%, 16.0%, and 3.6%, respectively. Except for the first group of data where the magnitudes of p_{HCl} and p_{H_2O} are about the same, the deviations for p_{H_2O} are larger than for p_{HCl}. An error in measurement in y_{HCl} was amplified in a much smaller value of y_{H_2O} because of the greater relative sensitivity of the quadrupole mass filter for water. Hence, for the data in which y_{HCl} is of the order of 0.95, the error in p_{H_2O} in larger than at lower values of y_{HCl}.

m_{HCl} and m_{CaCl_2} varied in a much more complicated fashion with temperature; the logarithms of each were correlated with T by using a spline fit. The spline fit does not smooth out any experimental data variations. The results of the interpolation computations are given in Table II, combining the data from

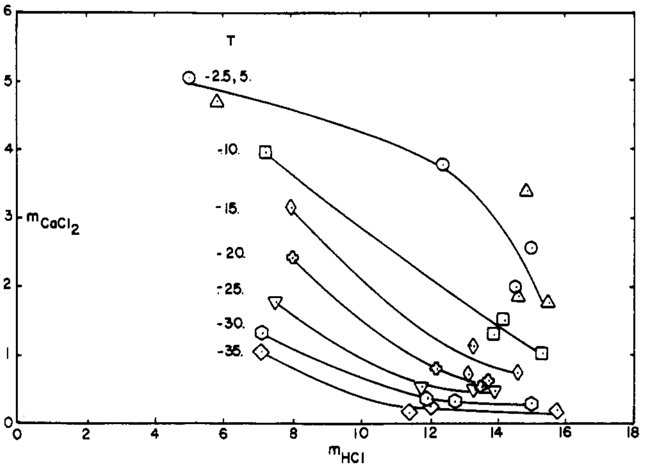

Figure 2. Solubility of $CaCl_2$, m_{CaCl_2} (g-mol of $CaCl_2$/kg of H_2O), as a function of HCl molality, m_{HCl} (g-mol of HCl/kg of H_2O), and temperature, T (°C). See Figures 3, 4, or 5 for legend for T values of -2.5 and -5.0 °C.

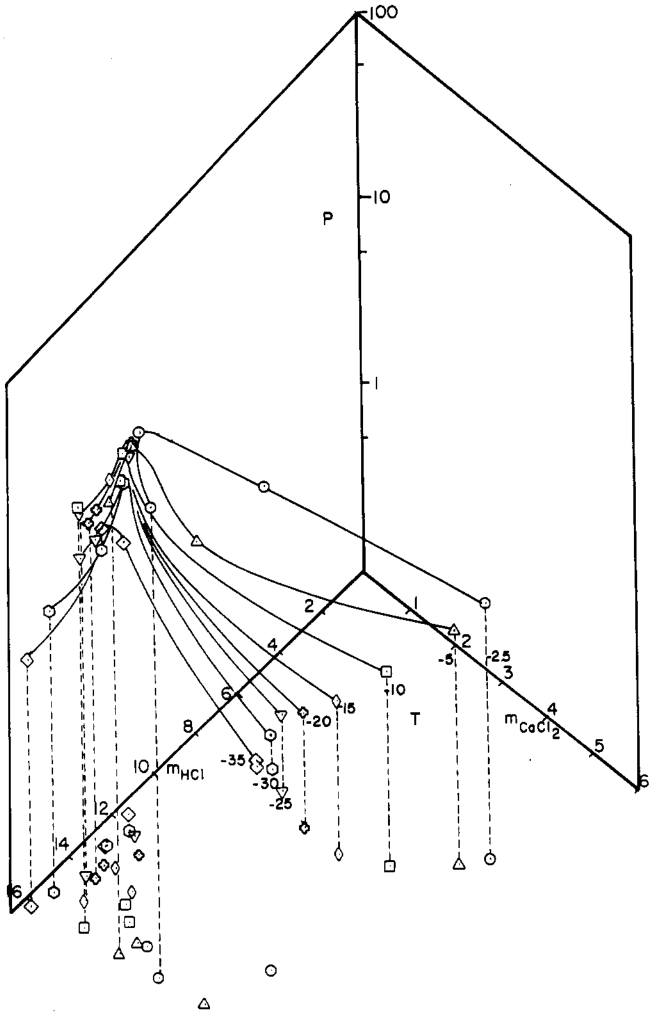

Figure 3. Total vapor pressure of solution, P (Torr), as a function of HCl molality, m_{HCl} (g-mol of HCl/kg of H_2O), m_{CaCl_2} (g-mol of $CaCl_2$/kg of H_2O), and temperature, T (°C).

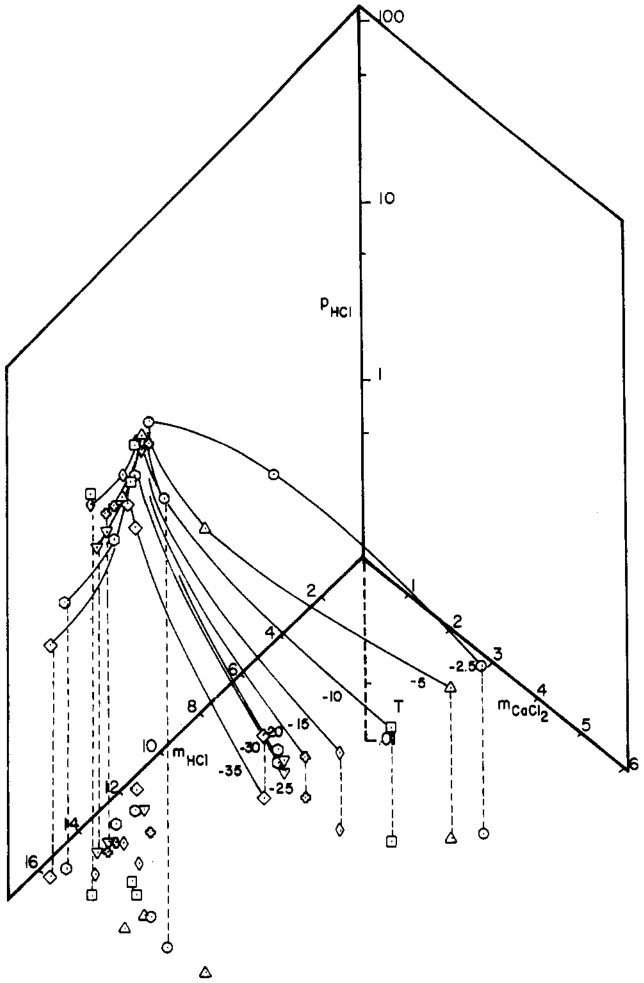

Figure 4. Partial pressure of HCl of solution, p_{HCl} (Torr), as a function of HCl molality, m_{HCl} (g-mol of HCl/kg of H_2O), m_{CaCl_2} (g-mol of $CaCl_2$/kg of H_2O), and temperature, T (°C).

all the groups for each interpolated temperature. Again, the conversion factor from pressure units of Torr to pascals is noted in the table.

The resultant relation between m_{HCl} and m_{CaCl_2} at constant temperature is displayed in Figure 2. For a given temperature, m_{CaCl_2} decreases with an increase in m_{HCl}. The decrease in the solubility of $CaCl_2$ in the acid decreases most markedly with m_{HCl} at the higher temperatures of -2.5 and -5.0 °C. The curves illustrate the variations of the HCl and $CaCl_2$ concentrations, but they are drawn in a somewhat arbitrary manner since the data are concentrated at the extreme values with few data points in between.

Figures 3-5 display the variation of P, p_{HCl}, and p_{H_2O} as a function of m_{HCl}, m_{CaCl_2}, and T for the values taken from Table II. At every temperature, as m_{HCl} increases and m_{CaCl_2} decreases, P, p_{HCl}, and p_{H_2O} increase to maximum values and then decrease. In addition, as p_{HCl} increases or decreases, p_{H_2O} does likewise. As seen from Table II, there is also a marked increase in y_{HCl} (and a decrease in y_{H_2O}) as m_{HCl} is increased at a given temperature.

In a binary system of $HCl-H_2O$, the comovement of p_{HCl} and p_{H_2O} with m_{HCl} would be in violation of the thermodynamic consistency rule of the Gibbs-Duhem equation. However in a ternary system, such behavior is possible. The Gibbs-Duhem equation is written as follows:

$$[X_{HCl}/(1 - X_{HCl})]\ d\ln p_{HCl} + [X_{CaCl_2}/(1 - X_{HCl})]\ d\ln a_{CaCl_2} = -d\ln p_{H_2O}$$

where X_{HCl} is the salt-free mole fraction of HCl in the liquid phase. $X_{CaCl_2} = x_{CaCl_2}/(1 - x_{CaCl_2})$; x_{CaCl_2} is the mole fraction of salt in the liquid phase, and a_{CaCl_2} is the salt activity in the liquid phase. For the special case in which X_{CaCl_2} is equal to zero, i.e., pure hydrochloric acid solution, if p_{HCl} increases, p_{H_2O} must decrease (and vice versa) as x_{HCl} increases. Similarly, if a_{CaCl_2} in the second term on the left-hand side of the equation remains constant as X_{HCL} increases, the same is true. The equilibrium phase diagram of $HCl-H_2O-CaCl_2$ is available only for 25 °C (*6*). These data and the equilibrium diagram for

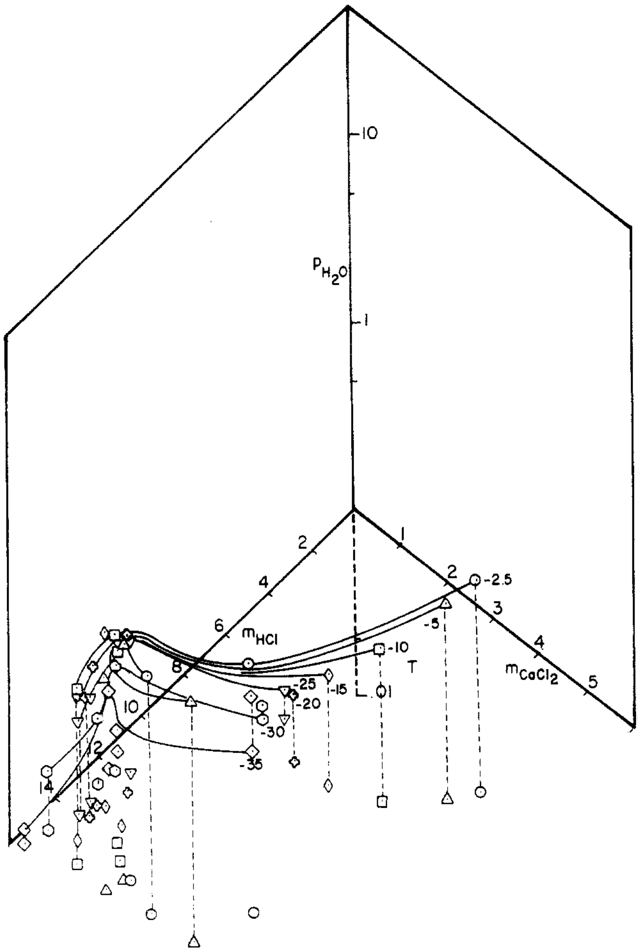

Figure 5. Partial pressure of H_2O of solution, p_{H_2O} (Torr), as a function of HCl molality, m_{HCl} (g-mol of HCl/kg of H_2O), m_{CaCl_2} (g-mol of $CaCl_2$/kg of H_2O), and temperature, T (°C).

$CaCl_2$–H_2O (*7*) however, suggest marked changes in the state of the salt in equilibrium with the acid solution as a function of composition and temperature. They indicate that the precipitated $CaCl_2$ could have six, four, two, and possibly no water molecules of hydration as a function of X_{HCl}. A change in the state of the $CaCl_2$, and hence in a_{CaCl_2}, with a variation in X_{HCl} would permit the observed variations in p_{HCl} and p_{H_2O}. With the same argument, the observed maximum in P is consistent with the permitted behavior of a ternary system. There is a need for experimental determination of the phase diagram of the HCl–H_2O–$CaCl_2$ system for the conditions of these measurements to verify these arguments.

It was noted that at high values of y_{HCl}, the errors in y_{H_2O} increase due to the higher relative sensitivity of the quadrupole mass filter for water. In refs 2 and 3, it was found that the mass filter gave low values for y_{HCl} when y_{HCl} was about 0.95. Special care was taken in the present studies to ensure that the mass filter was at equilibrium when measurements were made. For y_{H_2O} of about 0.05, a maximum deviation of 16% was found and 3–6% maximum deviations for most of the measurements. It is estimated that the reported p_{H_2O} variation with m_{HCl}, m_{H_2O}, and T may be too high by as much as 16%, but more likely 3–6%. The reported p_{HCl} variation with m_{HCl}, m_{H_2O}, and T could be low by as much as 3%, and more likely 1–1.5%. The P variation is not affected by any possible error in the vapor composition measurements.

At higher temperatures, above 50 °C, a minimum pressure azeotrope was reported by ref 5 for acid solutions with low concentrations of $CaCl_2$. The azeotrope disappeared at concentrations of $CaCl_2$ in the range 30–50 wt %. The saturated solutions studied here do not exhibit an azeotrope either, as might be expected.

Glossary

a	activity
m	molality, g-mols/kg of water
p	partial pressure, Torr
P	total pressure, Torr
T	temperature, °C
x	liquid-phase mole fraction
X	liquid-phase mole fraction, salt-free basis
y	gas-phase mole fraction

Subscripts

$CaCl_2$	calcium chloride
HCl	hydrogen chloride
H_2O	water

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