AD-A150 889 THE VAPOR PRESSURE OF HCL - WATER AND SALT - HCL - 1/1
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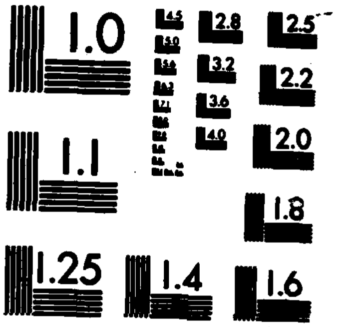

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AD-A150 889

January 1984

Final Report Covering Period 1-~~May 77~~ Dec 81 to 30 Nov 83

THE VAPOR PRESSURE OF HCl - WATER AND SALT - HCl - WATER SOLUTIONS BELOW 0C

Includes addendum

Prepared by: Eugene Miller

Work Performed by: Eugene Miller

Contracts: Grants AFOSR-77-3333, AFOSR-82-0049

Prepared for: AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (NA)
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INTRODUCTION

The vapor pressures of hydrochloric acid solutions are important to the modelling of secondary smoke in reduced smoke ammonium perchlorate solid propellant rocket plumes, ref 1, since the growth of secondary smoke droplets is dependent on their equilibrium behavior. In addition, the behavior of strong electrolytes in aqueous solution is of fundamental theoretical interest. Inorganic salts dissolved in hydrochloric acid will significantly modify its equilibrium behavior due to their effects on the activities of the HCl and water in the liquid phase, ref 2. The resulting change in the solution vapor pressure alters the rate of formation and the chemical composition of the secondary smoke, refs 3, 4. The major contaminants found in ammonium perchlorate are sodium and potassium salts. In addition, tricalcium phosphate added to ammonium perchlorate for ease in processing provides a major source of soluble electrolyte. All these cations are found in the rocket plume in sufficient quantity to nucleate the secondary smoke droplets, and to subsequently dissolve and influence the dynamics of growth and the chemical composition of the smoke, ref 5. If iron and copper combustion modifiers are avoided, none of the others commonly added to propellants will produce salts soluble enough to effect significant changes in the behavior of the hydrochloric acid smoke droplets. The original choices of NaCl and $CaCl_2$ as the salts for study were based on these considerations as well as for interest in studying the effects of their differences in ionic strength. A very limited study of KCl was subsequently added for consideration but time did not permit actual experimental measurements to be made.

Prior to the measurements made by the principal investigator under sponsorship of AFOSR, no vapor pressure data were available for either pure hydrochloric acid or for hydrochloric acid containing dissolved NaCl or $CaCl_2$ for temperatures below 0C, the temperatures of primary interest for secondary smoke formation. Data exist for these solutions, either primary vapor pressure or activities from which the vapor pressure may be predicted, only for temperatures at or above 0C. The low temperature vapor-liquid equilibria measurements for the pure hydrochloric acid and for solutions containing NaCl have been completed and are published in refs 6 and 7. The experimental vapor-liquid equilibria of $CaCl_2$-HCl-H_2O solutions for nominal temperatures from 0 to -40C are given in ref 8, completing the study of the pure and salted hydrochloric acid solutions.

ABSTRACTS OF PUBLISHED RESULTS

(1) VAPOR-LIQUID EQUILIBRIA OF WATER-HYDROGEN CHLORIDE SOLUTIONS BELOW 0C: Ref 6.

The vapor-liquid equilibria of 4-36 wt % (0.0411-0.2145 mole fraction) HCl-water solutions were determined for temperatures between 0 and -40C. 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. Vapor compositions were also predicted thermodynamically from the total pressure and liquid composition data by means of the Gibbs-Duhem equation.

(2) VAPOR-LIQUID EQUILIBRIA OF HYDROGEN CHLORIDE-SODIUM CHLORIDE-WATER SOLUTIONS BELOW 0C: Ref 7.

The vapor-liquid equilibria of $HCl-NaCl-H_2O$ solutions were determined for HCl mole fractions on a salt-free basis of 0.0361 to 0.2229, and NaCl molalities ranging from 0 to near saturation, for the nominal temperature range of 0 to -40C. 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 HCl adduct in equilibrium with the saturated solution.

(3) THE VAPOR PRESSURE OF CALCIUM CHLORIDE-HYDROGEN CHLORIDE-WATER SOLUTIONS BELOW 0C: Ref 8.

Vapor-liquid equilibria data are presented for hydrochloric acid solutions ranging in nominal HCl mol fraction from 0.110 to 0.225, saturated with $CaCl_2$, at nominal solution temperatures between 0 and -40C. 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. The addition of $CaCl_2$ to hydrochloric acid breaks the azeotrope and generally increases the vapor pressures of HCl and water.

Solubility and solution densities have also been measured. Solution compositions have not been completed to date. These are presently being done. It is probable that the effect of $CaCl_2$ on the formation of secondary smoke in a reduced smoke rocket plume has less an effect than does NaCl.

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Addendum to Final Report Covering Period 1 ~~May 77~~ Dec 80 to 30 Nov 83

THE VAPOR PRESSURE OF HCl - WATER AND SALT - HCl - WATER SOLUTIONS BELOW 0C

Prepared by: Eugene Miller

Work Performed by: Eugene Miller

Contracts: Grants AFOSR-77-3333, AFOSR-82-0049

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ABSTRACT

Liquid solution analyses are presented which supplement the vapor-liquid data previously reported. The complete vapor-liquid equilibria data are tabulated for hydrochloric acid solutions ranging in molality from 5.0 to 15.7, saturated with $CaCl_2$ at nominal temperatures ranging from 0 to -40C. It was found that the $CaCl_2$-HCl-water system exhibits a maximum pressure azeotrope under these conditions. Pure hydrochloric acid and NaCl-HCl-water systems exhibit minimum pressure azeotropes in the same temperature range. At acid molalities greater than about 9, the vapor phase contains about 94% HCl and for all molalities there is an increase in the partial pressures of HCl and water over what is observed with pure hydrochloric acid. Because of these characteristics, it is predicted that the presence of $CaCl_2$ in reduced smoke rocket plumes will not contribute as strongly to secondary smoke as will NaCl.

INTRODUCTION

Prior to the measurements made by the principal investigator under sponsorship of AFOSR, no vapor pressure data were available for either pure hydrochloric acid or for hydrochloric acid containing dissolved NaCl or $CaCl_2$ for temperatures below OC, the temperatures of primary interest for secondary smoke formation. Data exist in the literature for these solutions, either primary vapor pressure or activities from which the vapor pressure may be predicted, only for temperatures at or above OC. The low temperature vapor-liquid equilibria measurements for the pure hydrochloric acid and for solutions containing NaCl have been completed and are given in refs 1 and 2. The experimental vapor-liquid equilibria of $CaCl_2$-HCl-H_2O solutions for nominal temperatures from 0 to -40C are given in ref 3, completing the study of the pure and salted hydrochloric acid solutions.

Ref 3 and the final report on the salt-HCl-water vapor liquid equilibria studies, ref 4, did not include the analyses of the liquid solutions in equilibrium with the vapor phase and the solid phase of precipitated calcium chloride. These have been completed and are reported here together with a tabular summary of the vapor phase compositions and equilibrium pressures. Details of the experimental equipment, experimental methods and analytical procedures are given in ref 1.

RESULTS AND DISCUSSION

Total pressure P', partial pressures of HCl and water, p'_{HCl} and p'_{H_2O} respectively, molality of $CaCl_2$ at saturation, m_{CaCl_2}, vapor phase compositions of HCl and water, y'_{HCl} and y'_{H_2O} respectively, are given as a function of the molality of the HCl in the liquid phase, m_{HCl}, and solution temperature, T, in Table I. The original acid composition before the addition of $CaCl_2$ dihydrate at room temperature is also noted in terms of molality and mol fraction HCl, X_{HCl}.

The concentration of the $CaCl_2$ in equilibrium with hydrochloric acid is a complicated function of acid concentration and solution temperature as may be seen from the Table. Since the $CaCl_2$ was added to the acid solution as a dihydrate, initially the molality of the HCl decreased. However, as the solution temperature was lowered the $CaCl_2$ precipitated from the solution extracting in most instances more water from the solution than was added by the dihydrate initially i.e. the $CaCl_2$ evidently formed higher order hydrates, resulting in a higher acid concentration than its initial concentration at room temperature. There was no excess of $CaCl_2$ present as a solid phase when the solution was transferred to the 2 L boiler except for a small quantity of small particles that may have been in suspension. $CaCl_2.2H_2O$, $CaCl_2.4H_2O$ and $CaCl_2.6H_2O$ are all known to exist in equilibrium with hydrochloric acid at 25C, ref 5. At low acid molalities the number of water molecules associated with the $CaCl_2$ decreases with increasing acid molality. The present data indicate that at higher acid molalities and lower temperatures, the behavior is not the same.

A maximum pressure azeotrope occurs for this system at all temperatures from 0 to -40C. This is surprising since pure hydrochloric acid and saturated NaCl-hydrochloric acid exhibit minimum pressure azeotropes in the same temperature range. Refs 6 and 7 report on the $CaCl_2$-HCl-water vapor-liquid equilibria for a range of unsaturated solutions for acid compositions up to $m_{HCl} = 12.9$ at 750 mm constant pressure and boiling temperatures between 50 to 129C. They noted a minimum pressure azeotrope and found that the azeotrope disappeared for a solution containing 31 wt pct $CaCl_2$. The present solutions contain from 1.1 to 32.1 wt pct $CaCl_2$ but an azeotrope was found for all the temperatures studied. The presence of the azeotrope is also evidenced by the vapor phase mol fractions given in Table I.

y'_{HCl} increases with acid molality at a constant temperature from a value less than to one greater than y'_{H_2O}. Except for the starting acid solution of $m_{HCl} = 6.798$, for more concentrated starting acid compositions the liquid phase acid composition increased rapidly to a high acid molality and the vapor phase composition increased also to a value greater than 0.94.

Both p'_{HCl} and p'_{H_2O} exhibit maxima as acid molality increased at constant temperature. The fact that both p'_{HCl} and p'_{H_2O} increase and decrease together as acid molality is increased at constant temperature requires some interpretation. The Gibbs-Duhem equation requires the solid state of the $CaCl_2$ to change with acid composition in order to permit this behavior. The complex solubility behavior of the $CaCl_2$ with acid molality and temperature suggests that this does indeed occur. Unfortunately, the quadrupole mass filter used for vapor analysis is most inaccurate at the higher y'_{HCl} values and the changes in partial pressure could be explained by experimental error as well. Without additional experimental data and an improved analytical device, the question cannot be resolved.

The data from the experiments does not show the planned variation of the independent variables that is desirable for ease in correlation of the results. Efforts to correlate the results by statistical analysis have been modestly successful but the question of possible experimental errors cannot be so resolved.

The conclusion concerning the effects of $CaCl_2$ on the formation of secondary smoke in reduced smoke rocket exhausts previously given in ref 4, that $CaCl_2$ would not cause as serious an effect as NaCl or KCl, is reaffirmed.

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(1) Miller, E., "Vapor-Liquid Equilibria of Water-Hydrogen Chloride Solutions Below 0C," J. Chem. Eng. Data 28, 363-367 (Oct 83)

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TABLE I
VAPOR-LIQUID EQUILIBRIA OF NaCl-HCl-WATER SOLUTIONS

Smoothed Experimental Data

m_{HCl}, gmol/kg H_2O	T, deg C	m_{CaCl_2}, gmol/kg H_2O	P', torr	y'_{HCl}	y'_{H_2O}	p'_{HCl}, torr	p'_{H_2O}, torr
[6.798/ 0.110]+							
5.013	- 2.5	5.035	(2.20)*	0.3777	0.6223	0.83	1.37
	- 2.8		2.16				
7.420	-10.8	3.824	(1.02)	0.4040	0.5960	0.40	0.60
	-10.3		1.04				
7.840	-22.5	2.076	(0.321)	0.4109	0.5891	0.132	0.189
	-22.7		0.3057				
7.055	-31.5	1.235	(0.134)	0.4597	0.5403	0.062	0.072
	-31.8		0.1351				
8.644	-42.6	0.893	(0.046)	0.5174	0.4826	0.024	0.022
	-43.7		0.0405				
[8.128/ 0.128]							
14.718	- 0.8	3.458	(34.80)	0.9417	0.0583	32.77	2.03
	- 0.7		34.86				
15.016	-12.8	0.833	13.71	0.9440	0.0560	12.94	0.77
13.682	-22.3	0.573	6.22	0.9431	0.0569	5.87	0.35
15.387	-31.5	0.286	(2.72)	0.9382	0.0618	2.55	0.17
	-30.8		2.94				
15.691	-38.6	0.160	(1.46)	0.9494	0.0506	1.39	0.074
	-39.7		1.31				
[9.561/ 0.147]							
9.218	- 0.7	2.923	(44.26)	0.9376	0.0624	41.50	3.76
	0.0		47.30				
12.866	- 2.8	3.845	(36.23)	0.9509	0.0491	34.45	1.78
	- 3.2		34.77				
14.077	- 9.7	1.376	(18.17)	0.9246	0.0754	16.80	1.37
	-10.0		17.49				
13.471	-24.0	0.519	(5.81)	0.9324	0.0676	5.42	0.39
	-22.7		6.38				
12.524	-31.2	0.300	(3.56)	0.9441	0.0559	3.36	0.20
	-31.3		3.54				
[16.062/ 0.225]							
14.519	- 1.9	2.020	(54.00)	0.9491	0.0509	51.25	2.75
	- 1.4		56.10				
14.070	-11.4	1.422	29.29	0.9467	0.0533	27.73	1.56
11.468	-25.4	0.530	(9.75)	0.9395	0.0605	9.16	0.59
	-25.5		9.71				
12.004	-36.0	0.248	(4.00)	0.9473	0.0527	3.88	0.22
	-35.8		4.73				

+Initial m_{HCl}/X_{HCl}
*Interpolated value

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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