THE VAPOR PRESSURE OF HCL - WATER AND SALT - HCL - WATER SOLUTIONS BELOW. (U) MACKAY SCHOOL OF MINES RENO NV DEPT OF CHEMICAL AND METALLURG. E MILLER JAN 84 UNCLASSIFIED AFOSR-TR-85-0084 AFOSR-77-3333 F/G 7/4 NL
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Final Report Covering Period 1 May 77 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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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 CaCl₂ 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 CaCl₂ for temperatures below 0°C, 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 0°C. 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 CaCl₂-HCl-H₂O solutions for nominal temperatures from 0 to -40°C 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 0°C: 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 -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. 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 0°C: Ref. 7.

The vapor-liquid equilibria of HCl-NaCl-H$_2$O 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 -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$_2$O 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 0°C: 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 -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. 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.
REFERENCES CITED

(8) Miller, E., "The Vapor Pressure of CaCl₂-HCl-Water Solutions Below OC," Annual Report to AFOSR - 1 Dec 82 to 30 Nov 83 (Jan 84)
Addendum to Final Report Covering Period 1-May-77 to 30 Nov 83

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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 CaCl₂ at nominal temperatures ranging from 0 to -40°C. It was found that the CaCl₂-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 CaCl₂ 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 CaCl₂ for temperatures below 0°C, 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 0°C. 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 CaCl₂-HCl-H₂O solutions for nominal temperatures from 0 to -40°C 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, \( p'_{\text{HCl}} \) and \( p'_{\text{H₂O}} \) respectively, molality of CaCl₂ at saturation, \( m_{\text{CaCl₂}} \), vapor phase compositions of HCl and water, \( y'_{\text{HCl}} \) and \( y'_{\text{H₂O}} \) respectively, are given as a function of the molality of the HCl in the liquid phase, \( m_{\text{HCl}} \), and solution temperature, \( T \), in Table I. The original acid composition before the addition of CaCl₂ dihydrate at room temperature is also noted in terms of molality and mol fraction HCl, \( x_{\text{HCl}} \).

The concentration of the CaCl₂ in equilibrium with hydrochloric acid is a complicated function of acid concentration and solution temperature as may be seen from the Table. Since the CaCl₂ was added to the acid solution as a dihydrate, initially the molality of the HCl decreased. However, as the solution temperature was lowered the CaCl₂ precipitated from the solution extracting in most instances more water from the solution than was added by the dihydrate initially i.e. the CaCl₂ evidently formed higher order hydrates, resulting in a higher acid concentration than its
initial concentration at room temperature. There was no excess of CaCl₂ 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. CaCl₂•2H₂O, CaCl₂•4H₂O and CaCl₂•6H₂O are all known to exist in equilibrium with hydrochloric acid at 25°C, ref 5. At low acid molalities the number of water molecules associated with the CaCl₂ 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 -40°C. 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 CaCl₂-HCl-water vapor-liquid equilibria for a range of unsaturated solutions for acid compositions up to mₗHCl = 12.9 at 750 mm constant pressure and boiling temperatures between 50 to 129°C. They noted a minimum pressure azeotrope and found that the azeotrope disappeared for a solution containing 31 wt pct CaCl₂. The present solutions contain from 1.1 to 32.1 wt pct CaCl₂ 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'ₗHCl increases with acid molality at a constant temperature from a value less than to one greater than y'ₗH₂O. Except for the starting acid solution of mₗHCl = 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'ₗHCl and p'ₗH₂O exhibit maxima as acid molality increased at constant temperature. The fact that both p'ₗHCl and p'ₗH₂O 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 CaCl₂ to change with acid composition in order to permit this behavior. The complex solubility behavior of the CaCl₂ 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'ₗHCl 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 CaCl₂ on the formation of secondary smoke in reduced smoke rocket exhausts previously given in ref 4, that CaCl₂ would not cause as serious an effect as NaCl or KCl, is reaffirmed.

REFERENCES CITED


(3) Miller, E., "The Vapor Pressure of CaCl₂-HCl-Water Solutions Below OC," Annual Report to AFOSR - 1 Dec 82 to 30 Nov 83 (Jan 84)


(6) Synowiec, J., Bobrownicki, W., "Investigations of the Desorption of Hydrogen Chloride from Aqueous Solutions. II. The Vapor-Liquid Equilibria in H₂O-HCl-MgCl₂ and H₂O-HCl-CaCl₂ Systems," Chemie Stosowana 4A, 383-403 (1964)

### TABLE I

**VAPOR-LIQUID EQUILIBRIA OF NaCl-HCl-WATER SOLUTIONS**

Smoothed Experimental Data

<table>
<thead>
<tr>
<th>m(\text{NaCl}_1), g mol/kg H(_2)O</th>
<th>T, deg C</th>
<th>m(\text{HCl}_1), g mol/kg H(_2)O</th>
<th>P', torr</th>
<th>Y'(\text{NaCl}_1)</th>
<th>Y'(\text{HCl}_1)</th>
<th>P'H, torr</th>
<th>P'(\text{H}_2)O, torr</th>
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<tr>
<td>5.013</td>
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<td>5.035</td>
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<td>0.6223</td>
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<td>3.824</td>
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<td>0.5960</td>
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<td>7.840</td>
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<td>0.5891</td>
<td>0.132</td>
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<td>7.055</td>
<td>-31.5</td>
<td>1.235</td>
<td>(0.134)</td>
<td>0.4597</td>
<td>0.5403</td>
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</table>

- Initial m\(\text{NaCl}_1\)/X\(\text{NaCl}_1\)
- Interpolated value

*Initial m\(\text{NaCl}_1\)/X\(\text{NaCl}_1\)

*Interpolated value
**Abstract**

Liquid solution analyses were completed. The complete vapor-liquid equilibrium data are tabulated for hydrochloric acid solutions ranging in molality from 0.1 to 15.7, saturated with CaCl_2 at nominal temperatures ranging from 0 to -40°C. 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.