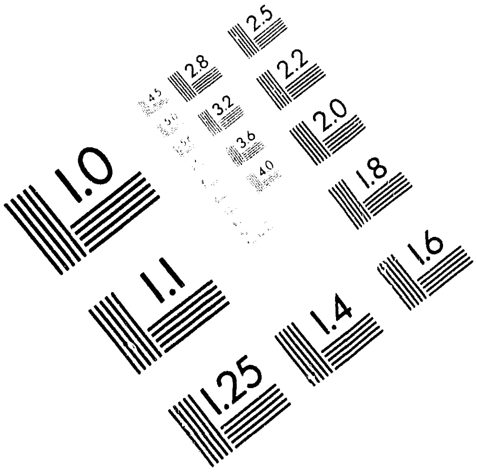

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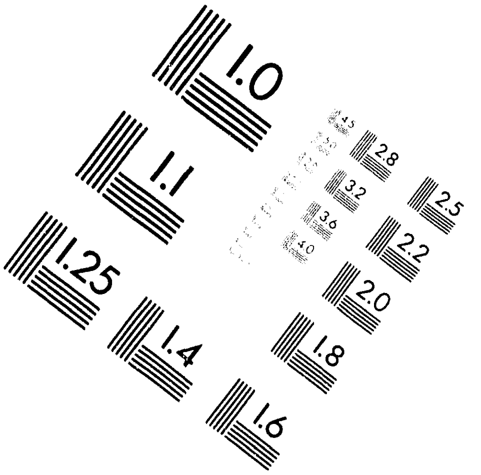

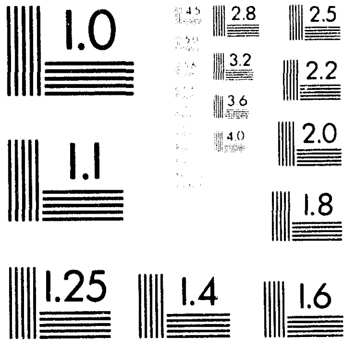

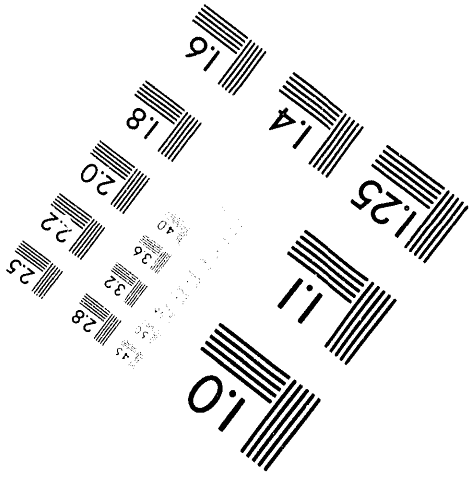

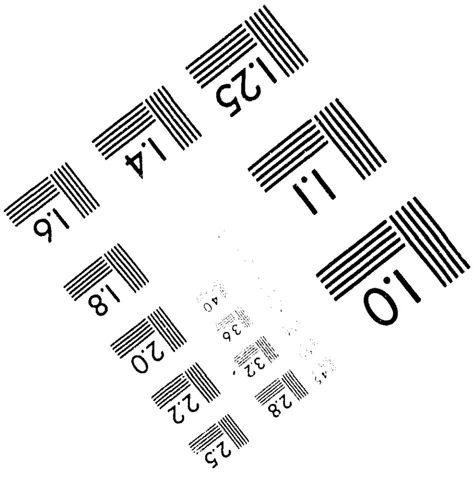

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LIQUID-VAPOR PARTITIONING OF NaCl(aq) FROM CONCENTRATED BRINES AT TEMPERATURES TO 350°C

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ABSTRACT

Compositions of coexisting liquid and vapor phases have been determined at temperatures from 250 to 350°C for brines containing NaCl and either HCl or NaOH by direct sampling of both phases from a static phase-equilibration apparatus. In these experiments, NaCl concentrations in the liquid phase ranged to 6.5 mol·kg^{-1}, with corresponding vapor-phase NaCl concentrations varying strongly with temperature and brine composition. Acid or base was added to the brines to suppress unknown contributions of NaCl(aq) hydrolysis products to the observed volatilities. Thermodynamic partitioning constants for NaCl have been determined from the observed compositions of the coexisting phases combined with the known activity coefficients of NaCl(aq) in the liquid phase. An apparent dependence of the values of these partitioning constants on brine concentration is explained by considering the effect of decreasing pressure on the density of the vapor phase. Concentrations of HCl and NaCl in steam produced from various natural brines may be calculated as functions of temperature and brine composition based on these new results coupled with our previous determinations of the partitioning constants for HCl(aq). Application of these results to The Geysers will be discussed in terms of the composition of postulated brines which could be in equilibrium with observed steam compositions at various temperatures.

INTRODUCTION

The production of acidic, chloride-containing steam from wells at The Geysers has resulted in corrosion of well casings and steam piping through attack by corrosive condensed fluids. In extreme cases corrosion has forced wells to be taken out of production. While the incidence of acid-chloride steam was originally considered a problem in the hotter producing regions of the northwest portion of The Geysers, recently the possible production of acid-chloride steam from the lower-temperature regions of the central portion of the field has received renewed attention. While the subject of acid-chloride steam chemistry has been modeled and discussed (Truesdell *et al.*, 1988; Hirtz *et al.*, 1991), little new experimental information has been obtained on the partitioning of electrolytes between liquid and vapor phases over the temperature range commonly found in steam at The Geysers. The relative lack of reliable experimental values in this temperature range limits our ability to predict steam compositions over brines of varying pH and salinity. Conversely, given the observed composition and temperature of produced steam, the ability to predict a brine composition which would be in equilibrium with that steam phase is limited for many systems by a lack of data.

A number of aspects of the basic physical chemistry of geothermal systems are under investigation at ORNL, including solubility and speciation of aluminum in aqueous solutions, thermodynamics and phase relations in granitic melts, liquid-vapor distribution of stable isotopes in brines, and liquid-vapor distribution of HCl including the production of acid-chloride-containing steam. We have previously reported (Simonson and Palmer, 1993) measured values obtained in this program for the partitioning of HCl over HCl(aq) from 50 to 350°C. In a similar experimental study sponsored by the Electric Power Research Institute, we have measured liquid-vapor partitioning of NH_4Cl over acidic and buffered aqueous solutions from 120 to 350°C (Palmer and Simonson, 1993) Ammonia and ammonium salts have been found in steam from The Geysers (Hirtz *et al.*, 1991). Our recent experimental studies have addressed possible sources of acidity in steam from hydrolysis of alkaline-earth chlorides (Mg and Ca) at high temperatures through extensive series of measurements on brines containing NaCl. These latter experiments were performed both to determine quantitatively the effects of NaCl concentration on HCl partitioning, and to reinvestigate the partitioning of NaCl to steam from multicomponent brines. These new measurements of NaCl partitioning, coupled with experimental values for HCl partitioning from pure aqueous acid and from acidic NaCl brines, may be used to provide new estimates of steam composition above {NaCl + HCl}(aq) at temperatures ranging to the solvent critical temperature.

EXPERIMENTAL

The apparatus and techniques used to equilibrate and analyze the samples taken in these equilibrium studies have

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been described in detail previously. (SIMONSON and PALMER, 1993; PALMER and SIMONSON, 1993) The experimental method is based on the static equilibration of liquid and vapor phases at temperature in a chemically-inert, platinum-lined autoclave system (Figure 1).

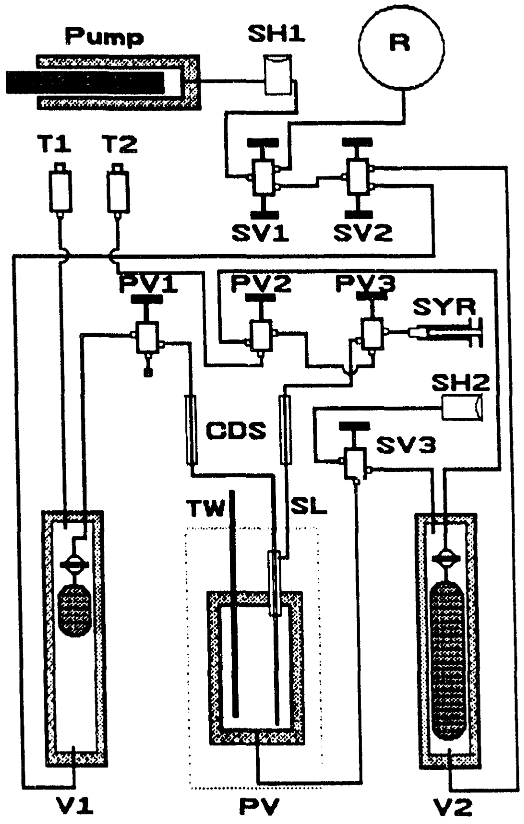

Figure 1. Static liquid-vapor equilibration apparatus and sampling equipment for partitioning measurements.

A stainless-steel pressure vessel PV of ca. 600 cm^3 internal volume, equipped with a platinum liner, is thermostated at the desired experimental temperature. The liquid phase is sampled into a syringe via platinum tubing and PEEK valve V3. Vapor-phase samples are drawn into a preweighed Teflon sample bag contained in the ambient-temperature pressure vessel V1 at a controlled rate (between 0.5 and 6 $cm^3\ h^{-1}$) by withdrawing water from the annular space of the pressure vessel using a positive-displacement pump. A second ambient-temperature pressure vessel V2 contains a large Teflon bag, connected to the platinum liner through capillary tubing and filled with the same solution as in the liner. The annular space of this pressure vessel contains distilled water, and is connected to the annular space surrounding the platinum liner; fluid transfer in this subsystem serves to equalize the pressure across the thin platinum liner.

Samples of the two phases were analyzed for chloride and sodium by ion chromatography, and for proton or hydroxide by acidimetric titration. The general procedure was to fill the liner approximately half-full with the desired solution and allow time for equilibration at the experimental temperature. Due to the preferential extraction of water from the system during vapor-phase sampling the liquid-phase molality increases over a series of samples for a particular loading of the system. Liquid-phase samples were taken both before and after obtaining a given vapor-phase sample, with the liquid-phase composition assumed to be the average of the two liquid samples. The overall increase in liquid-phase molality due to water extraction from a given set of samples was no more than a factor of two for any series of equilibrations. A tabular summary of the experimental conditions is given in Table 1.

Table 1. Summary of NaCl Partitioning Measurements.

{NaCl + HCl}(aq) Runs

t(av)/°C	{m(Na)/m(H)}(aq)	$I/(mol\cdot kg^{-1})$
297.5	5 - 14	0.1 - 0.3
322.6	7 - 25	0.1 - 0.3
347.5	15 - 59	0.2 - 0.5
297.5	90 - 170	1.6 - 2.5
322.5	100 - 230	1.4 - 1.9
346.8	200 - 620	2.0 - 3.6
247.2	140 - 470	3.3 - 6.3
249.4	42	0.9
298.6	32 - 70	0.6 - 0.9
244.3	150 - 290	3.0 - 4.1
294.9	140 - 520	2.1 - 3.6
318.1	300 - 800	3.2 - 4.5
345.4	50 - 340	1.1 - 3.0

{NaCl + NaOH}(aq) Runs

t(av)/°C	{m(Cl)/m(OH)}(aq)	$I/(mol\cdot kg^{-1})$
197.3	29	3.1- 4.6
248.4	30	2.5 - 3.1
297.5	30	2.8 - 3.7
321.5	30	2.8 - 4.4
343.9	30	2.7 - 4.8

{NaCl + $MgCl_2$}(aq) Runs

t(av)/°C	{m(Na)/m(Mg)}(aq)	$I/(mol\cdot kg^{-1})$
248.1	16	1.0 - 1.4
297.8	16	0.9 - 1.3
322.7	16	1.0 - 2.2
347.4	16	0.9 - 2.2

Measurements of NaCl volatilities were carried out over the mixed brines {NaCl + HCl}(aq), {NaCl + NaOH}(aq), and {NaCl + $MgCl_2$}(aq). The runs with excess acid or base were designed to eliminate the possibility of apparent transport of NaCl to the vapor phase as products of a hydrolysis reaction of unknown extent; i.e., addition of either acid or base to a predominantly NaCl brine suppresses any appreciable hydrolysis of NaCl, with the vapor-phase molality of sodium ion indicating NaCl transport in the acidified experiments, and the chloride ion molality indicating NaCl partitioning in the basic runs. It should be noted from Table 1 that under the conditions of these measurements, HCl partitions preferentially to the vapor phase, resulting in 'stripping' of HCl from the liquid and a corresponding shift in the ratio m(Na)/m(H).

At high temperatures, {NaCl + $MgCl_2$} solutions are slightly acidic due to the hydrolysis of magnesium ion. While these measurements were performed primarily to determine the extent of hydrolysis of magnesium ion in NaCl(aq) at high temperatures, measurement of vapor-phase sodium ion molalities gave additional information on the partitioning of NaCl from acidic solutions.

RESULTS AND DATA ANALYSIS

Following the procedure used in our analysis of liquid-vapor partitioning results for HCl and NH_4Cl (SIMONSON and PALMER, 1993; PALMER and SIMONSON, 1993) it was assumed that NaCl was fully associated (unionized) in the vapor phase, and predominantly dissociated in the liquid. These assumptions lead to an expression for the equilibrium constant K_D for the liquid-vapor phase distribution

$$K_D(\mathrm{NaCl}) = \frac{m_v(\mathrm{NaCl})\gamma_v(\mathrm{NaCl})}{m_l(\mathrm{Na}^+)m_l(\mathrm{Cl}^-)\gamma_l(\mathrm{Na}^+)\gamma_l(\mathrm{Cl}^-)} \qquad (1)$$

where m_l and γ_l are the molality and activity coefficient of a given species in the liquid phase; the corresponding quantities subscripted 'v' refer to the vapor phase. It should be noted that no speciation of solute is considered in the liquid phase, or equivalently, that the activity coefficients γ_l in the liquid phase are stoichiometric values. On this basis it is not necessary to consider explicitly the formation of ion pairs in the liquid phase, provided that values of the stoichiometric activity coefficients are available. While this approach makes it unnecessary to assign speciation of electrolytes in the aqueous phase where such assignments are often poorly known or ambiguous, some additional uncertainty in the calculation of K_D is introduced through neglect of speciation in common-ion systems where one component (e.g. HCl) may by strongly associated while the other (e.g. NaCl) is much less associated. This point will be discussed in further detail below.

The present experimental results give directly the compositions (molalities) of the coexisting liquid and vapor phases. In order to calculate K_D using equation (1) it is necessary to calculate activity coefficients of NaCl(aq) in the aqueous medium of interest at the experimental temperature. Values of the stoichiometric mean-ionic activity coefficient $\gamma_\pm$(NaCl) approriate to pure NaCl(aq) media along the saturation vapor-pressure curve at temperatures to 350°C are available from the compilations of PITZER, PEIPER, and BUSEY (1984) and ARCHER(1992) at temperatures to 300 and 325°C, respectively, and are tabulated at 350°C by BUSEY, HOLMES and MESMER (1984). Noting that the former two compilations give values of $\gamma_\pm$ in good agreement with each other at temperatures to 300°C (the upper limit of applicability of the representation of PITZER *et al.*), we have adopted values for $\gamma_\pm$ from ARCHER for this work. At temperatures above 325°C, $\gamma_\pm$(NaCl) were interpolated from the 325°C values of ARCHER and the 350°C values reported by BUSEY *et al.*

Experimental studies leading to values of $\gamma_\pm$ for NaCl in mixed-electrolyte media at the temperatures of interest here are not available. To a reasonably good approximation the stoichiometric mean-ionic activity coefficient of NaCl(aq) in the mixture may be taken as $\gamma_\pm$ in pure NaCl(aq) media at the ionic strength of the mixture. This approximation has been used here for calculating $\gamma_\pm$(NaCl) in {NaCl + $MgCl_2$}(aq) mixtures, where reliable values of excess thermodynamic properties for $MgCl_2$(aq) solutions at high temperatures are not available. For the {NaCl + HCl}(aq) and {NaCl + NaOH}(aq) mixtures, excess thermodynamic properties for HCl(aq) are available to 375°C from SIMONSON *et al.* (1990). NaOH(aq) excess thermodynamic properties to 250°C are available from SIMONSON, MESMER, and ROGERS (1989); values at higher temperatures were calculated from extrapolated differences in NaOH(aq) and NaCl(aq) properties following the procedure adopted for NH_4Cl(aq) by PALMER and SIMONSON (1993). NaCl(aq) properties in the mixed-electrolyte media were then calculated from the approximate relation

$$\ln\gamma_\pm(\mathrm{NaCl}) \approx \ln\gamma_\pm^*(\mathrm{NaCl}) + y\Delta\phi^* \qquad (2)$$

Quantities marked with an asterisk represent pure-electrolyte values at the ionic strength of the mixture, $\Delta\phi^* = \phi^*(\mathrm{NX}) - \phi^*(\mathrm{NaCl})$ and $y = m(\mathrm{NX})/\{m(\mathrm{NX})+m(\mathrm{NaCl})\}$ where NX is HCl or NaOH. It is clear from Table 1 that m(NX) is never large relative to m(NaCl) in the present experiments, and that equation (2) should therefore provide a suitable approximate representation for the activity coefficient of NaCl(aq) in the mixed electrolyte.

The partitioning equilibrium constants K_D calculated from the observed partitioning of NaCl between liquid and vapor phases for the various media considered here are shown graphically in Figures 2 and 3. The scatter in the experimental values, which may be as large as ±0.5 log units, particularly at lower temperatures, is indicative of the difficulty in determining quantitatively the very low levels of NaCl in the vapor phase in the measurements at lower temperatures. As an example, at 250°C the liquid phase NaCl molality is more than six orders of magnitude greater than that of the vapor phase, leading to the possiblity of significant contamination of the vapor samples due to even a small amount of entrained liquid in the vapor phase. However, the consistency of the results as functions of sampling rate in the various media implies that contamination of the vapor samples with entrained liquid was not a significant problem in these experiments.

Within the precision of the experimental determinations, the approximations used to calculate activity coefficients in the liquid phase, and the assumption of unit activity coefficient for low levels of NaCl in the vapor phase, the values of K_D shown in Figures 2 and 3 should be independent of solution composition, as indicated by the horizontal dashed lines on these figures. However, linear regressions of the data (solid lines) show an apparent dependence of log K_D on ionic strength which is larger than the experimental uncertainty. It is possible that the observed dependence is due to a failure of one or both of the assumptions concerning the value of the activity coefficients of NaCl in the liquid phase and the state of the solute in the vapor (associated NaCl with unit activity coefficient), or to systematic errors in the determination of equilibrium molalities of the two phases. However, K_D decreases by approximately one order of magnitude on increasing ionic strength from infinite dilution to about 5 mol·kg^{-1}. If small amounts of the liquid phase were systematically entrained in the vapor-phase samples, it is expected that the calculated K_D would increase with increasing liquid-phase molality. An error of 0.5 log units in calculating $\gamma_\pm$ is unlikely due to the precise information available for NaCl(aq) solutions and the relatively small effect of the other constituents of the mixed brines considered here. Significant dissociation of NaCl in the vapor phase, which could lead to an apparent decrease in K_D with increasing ionic strength as calculated from equation (1) through overestimation of the molality of the associated molecule in steam at lower total vapor-phase molalities, seems unlikely due to the low density and dielectric constant of the vapor phase even at the highest temperatures considered here. Neglecting the presence of dissociated ions in the vapor phase is supported by calculations of the association constant of NaCl in steam as extrapolated from electrical conductance measurements at high temperatures (QUIST and MARSHALL, 1968). Finally, although little is known about the activity coefficient of the [assumed] associated NaCl in the vapor phase, it should be noted that the total vapor-phase NaCl molality near 347°C increases by only about a factor of five between the lowest (ca. 0.2) and highest (ca. 4.5) ionic strengths investigated in this work. Thus the activity coefficient of NaCl in the vapor phase would have to decrease quite strongly with increasing molality to give log K_D values which are independent of ionic strength.

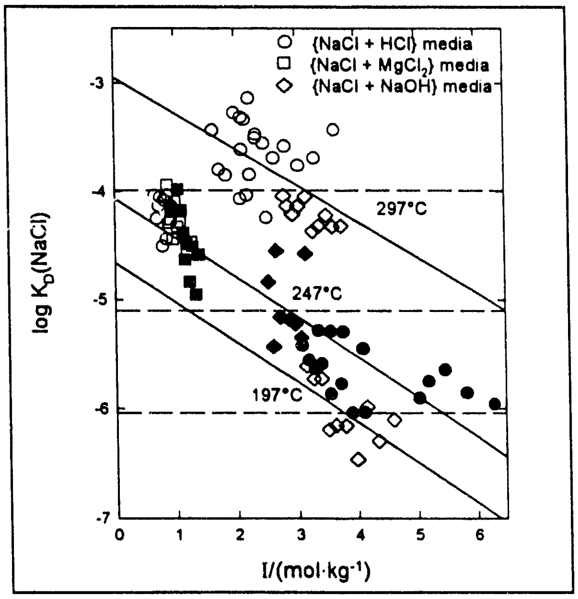

Figure 2. Liquid-vapor distribution constants for NaCl at low temperatures calculated from equation (1).

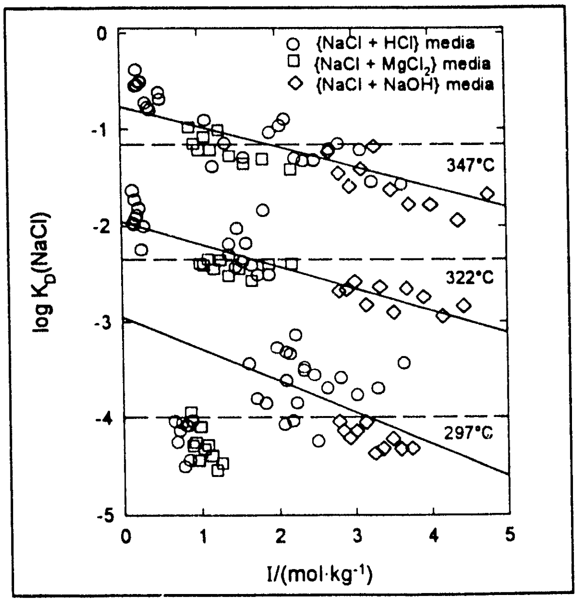

Figure 3. Liquid-vapor distribution constants for NaCl at high temperatures calculated from equation (1).

Equilibrium constants on a Gibbs free energy basis, such as those calculated for the partitioning of NaCl, are appropriate to conditions of constant temperature and pressure. As the ionic strength in these experiments increases the pressure decreases significantly, particularly at the higher temperatures. For example, at 347°C the observed experimental pressures decrease by more than 10% on increasing ionic strength from 0.2 to 4 mol·kg^{-1}. The effect of this pressure decrease on the liquid-phase activity coefficient of NaCl is small, but may in principle lead to a significant change in K_D depending on the magnitude of the volume change $\Delta V°$ for the reaction.

Recently PITZER and PABALAN (1986) have addressed the question of the thermodynamics of NaCl in steam, considering the formation of multiple hydrates of the neutral NaCl molecule in steam and including interparticle interactions based on statistical mechanical models of imperfect gases. Their working equation for the ratio of the total [volumetric] NaCl concentration in steam to the gas-phase NaCl concentration over pure NaCl(cr) was given in terms of a power series in the fugacity of water vapor, with coefficients given by the equilibrium constants for steam-phase hydrate formation. A somewhat similar but much less rigorous approach was adopted by STRYKOVICH *et al.* (1965) to describe both NaCl solubility in supercritical steam and liquid-vapor partitioning under subcritical conditions. These investigators used the density of water and steam as an independent variable in their representation of the data available to them, reflecting the assumed degree of hydration of NaCl.

The observed behavior of log K_D values obtained in this study as illustrated in Figures 2 and 3 was represented with the fitting equation:

$$\log K_D = a + b/T + c \log \rho_l + d \log \rho_v \qquad (3)$$

where a = -33.31, b = 33829, c = 7.152, and d = 20.728; ρ_l and ρ_v are the densities of liquid water and steam respectively at the experimental conditions as calculated from the equation of state of HAAR, GALLAGHER, and KELL (1984).

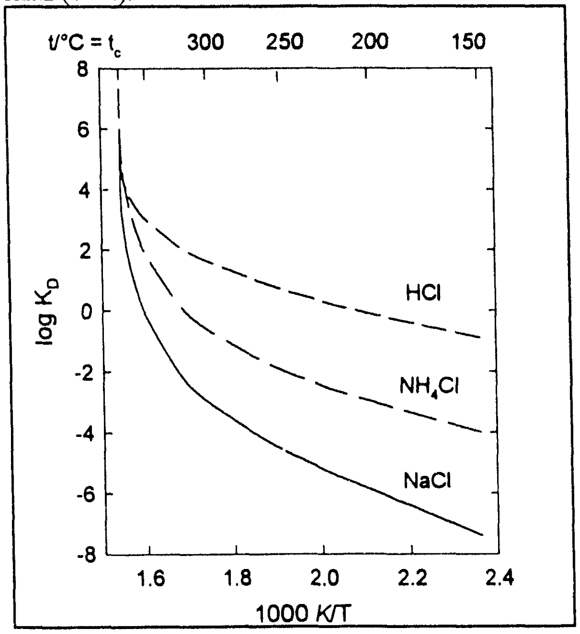

Figure 4. Comparison of liquid-vapor distribution constants of HCl, NH_4Cl, and NaCl at the saturation vapor pressure of pure water.

The parameters are based solely on a preliminary fit of the results of this study; the overall fit of the available subcritical partitioning data is expected to change somewhat as additional experimental results in the literature are incorporated fully into the data analysis. However, even with this provisional representation, it is possible to make comparisons of the results of this study with recent measurements on HCl and NH_4Cl under similar conditions. Such a comparison is shown in Figure 4, where it is clear that HCl is significantly more volatile than NH_4Cl, which is in turn more volatile than NaCl at the same temperature.

Due to its fundamental importance the NaCl(aq) system is the most thoroughly investigated aqueous electrolyte at elevated temperatures and pressures. It is not possible here to review the extensive literature data on this system, nor to present detailed comparisons of the present measurements with previously available values. Of the previous studies of compositions of coexisting liquid and vapor phases in NaCl(aq), the work of Khaibullin and Borisov (1966) provides the most direct comparison with the present results. Among other studies the work of ÖLANDER and LIANDER (1950) and GOODSTINE (1974) include measurements at subcritical temperatures slightly above those considered here, and STEPHAN and KUSKE (1983) measured NaCl partitioning at constant pressures (120 and 160 bars) within the ranges of the present work. BISCHOFF, ROSENBAUER and PITZER (1986) reported steam compositions along the three-phase line near 300, 325, and 350°C, and have referenced the numerous other studies of NaCl(cr) solubility in steam. While detailed comparisons are still in progress, a comparison of the present results with those of KHAIBULLIN and BORISOV (1966) shows systematic differences at all temperatures. Above 300°C, K_D calculated from the measurements reported here are higher by 1 log unit than those calculated from the results of KHAIBULLIN and BORISOV, with very similar trends as a function of liquid-phase ionic strength. This difference increases with decreasing temperature, with values calculated from equation (3) higher by nearly 2 log units at 200°C than those of KHAIBULLIN and BORISOV. Comparisons with the results of STEPHAN and KUSKE (1983) show somewhat smaller systematic deviations, with the present results again higher. These differences might indicate a systematic error in the present measurements due to the presence of small amounts of entrained liquid in the vapor-phase samples, or to some contamination of the vapor-phase samples with excess solute. The wide range of solution compositions and sampling rates used in this study was intended to minimize the possibility of unrecognized systematic errors, but this possibility cannot be completely discounted. Nevertheless, systematic sample contamination seems unlikely due to the observed agreement among the studies in the various media: ion-chromatographic analysis for sodium ion was used to determine the NaCl vapor-phase molality in the runs with excess HCl, whereas analysis for chloride ion was the indicator used in the experiments with excess NaOH. Mass balance among all components of the vapor and liquid phases was observed in all experiments within the precision of the ion-chromatographic determinations. In their development of an equation of state for near-critical NaCl-H_2O, TANGER and PITZER (1989) noted that "the vapor compositions reported by KHAIBULLIN and BORISOV (1966) at or below 350°C are much too small to be consistent with the measurements of BISCHOFF *et al.* (1986)", which Tanger and Pitzer adopted along the three-phase curve. A full analysis of the available experimental results at temperatures below 350°C, which clearly is needed to address the discrepancies noted above, is currently in progress.

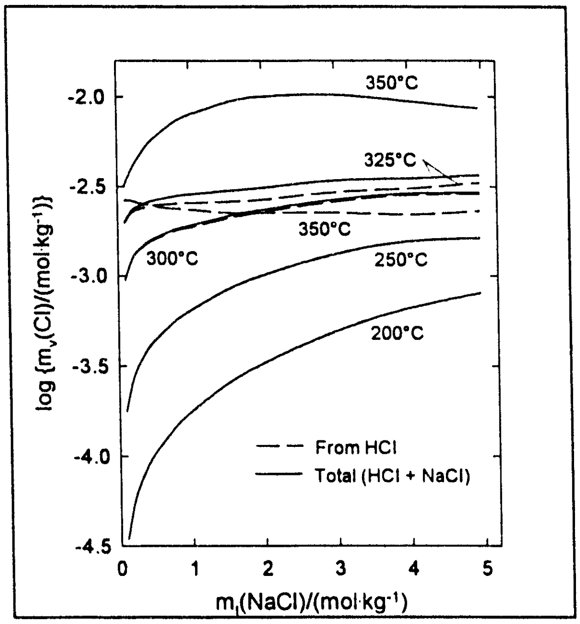

Figure 5. Molality of chloride in steam as a function of temperature and NaCl(aq) molality for brines with pH = 3.

The representation for the partitioning constant K_D given in equation (3) may be combined with activity coefficients for NaCl(aq) to calculate the NaCl molality in steam in equilibrium with NaCl(aq) over wide ranges of temperature and liquid-phase molality. Partitioning constants and activity coefficients for other solutes may also be combined with the NaCl data to permit calculation of the steam composition over mixed electrolyte brines. As an example, the composition of steam in equilibrium with acidic NaCl(aq) solutions was calculated from the results of this study, combined with the equation for K_D for HCl given by SIMONSON and PALMER (1993). Activity coefficients in the aqueous mixture were calculated from equation (2) using values for the pure-electrolyte activity and osmotic coefficients taken from BUSEY *et al.* (1984) for NaCl(aq), and from SIMONSON *et al.* (1990) for HCl(aq).

The calculated molalities of chloride in steam are shown in Figure 5. The total chloride molality in steam is indicated in this figure by the solid lines, while the contribution from HCl partitioning is indicated by the dashed curves. At a pH of 3 the contribution of NaCl partitioning to the total chloride molality in the steam is negligible at temperatures to 300°C, as indicated by the coincidence of the HCl-contribution and total-chloride curves at these temperatures. At higher temperatures the calculated vapor-phase chloride molality due to HCl partitioning decreases with increasing temperature even though the partitioning constant for HCl increases strongly (SIMONSON and PALMER, 1993). This behavior, which is due to the very low values of the activity coefficient for HCl in these media at high temperatures, has been verified experimentally (SIMONSON and PALMER, in preparation). At these higher temperatures the partitioning of NaCl contributes significantly to the total chloride molality in steam, increasing to near 0.01 mol·kg^{-1} over a wide range of liquid-phase ionic strength at 350°C. This high chloride molality in steam, corresponding to *ca.* 350 ppm, indicates the importance of NaCl partitioning to the total molality of chloride in steam at the highest temperatures encountered at The Geysers.

The presence of even low levels of solutes in the vapor phase may lead to the production of quite concentrated, and hence potentially corrosive, brines on condensation of a small percentage of the steam. This concentration process can also be accompanied by significant shifts in pH from that of the original brine. Calculation of the composition of condensates has been discussed in detail for geothermal brines by HIRTZ *et al.* (1991), and for the limiting case of infinitessimal condensate formation in all-volatile-treated steam generators by PALMER and SIMONSON (1993). These calculations are dependent on the process conditions of interest (steam formation and condensation temperatures; liquid-phase composition) and will not be discussed in detail here. However, it should be noted that equilibrium liquid and steam compositions may now be calculated for Na - H - NH_4 - Cl brines to 350°C based on experimental results from this laboratory, and that experiments currently in progress on sulfates, bisulfates and hydroxides should contribute significantly toward a description of liquid-vapor equilibria of "nonvolatile" components in a wide variety of mixed brines of importance in natural systems.

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