(LIQUID-VAPOR) PHASE EQUILIBRIA OF HCl AND EXCESS THERMODYNAMIC PROPERTIES OF {HCl + NaCl}(aq) MIXTURES AT HIGH TEMPERATURES

J. M. Simonson, D. A. Palmer, and S. L. Marshall
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008, Bldg. 4500S, MS-6110
Oak Ridge, TN 37831-6110

ABSTRACT: Our measurements of the volatility (liquid-vapor partitioning) of HCl from {HCl + NaCl}(aq) mixed brines to 350EC present an opportunity for new developments in the description of excess thermodynamic properties for HCl in these mixtures at high temperatures. A fully-speciated model for HCl(aq) solutions based on the ion-interaction treatment is inappropriate for mixed brines unless a speciated model for NaCl(aq) is also used. As a suitable model for NaCl(aq) is not available, we have adopted a stoichiometric treatment based on a linearized extension of the ion-interaction treatment to describe the effects of association on the activity coefficient for HCl(aq) to high ionic strength in NaCl(aq) media. The model has been extended to {HCl + NaCl}(aq) mixtures with an appropriate mixing parameter describing short-range cation-cation interactions. Values of this parameter based on volatility results at high temperatures are consistent with those extracted previously from our earlier measurements of the enthalpy of mixing of {HCl + NaCl}(aq) to 250EC.

INTRODUCTION

A quantitative understanding of the liquid-vapor phase partitioning of aqueous electrolytes over broad ranges of temperature and solution composition is needed to predict the properties of aqueous systems in a range of applications. These applications include fossil-fired and nuclear steam generator power cycles, production of geothermal steam (either directly or by flashing of brines), and waste mitigation by hydrothermal or supercritical water oxidation processes, among others. Knowledge of the volatility of solutes in solutions of a single electrolyte, while clearly necessary to a quantitative description of the phase partitioning process, is insufficient. Essentially all aqueous fluids encountered in practical applications contain mixtures of solutes, and consideration of the individual contributions to solute partitioning gives only a first approximation to the real behavior of the mixed system.

Here we consider the effects of the mixing of HCl(aq) with NaCl(aq) on the partitioning of the more volatile component (HCl) between liquid and vapor phases over wide ranges of temperature and composition. This mixture is of particular importance as contamination of operating systems (technological or natural) with NaCl is essentially ubiquitous, and the accurate prediction of the acidity (pH) of brines, steam, and condensate in operating cycles is critical to the reliable operation of engineered systems.

EXPERIMENTAL

The experimental basis for the investigation of solute volatilities in mixed electrolytes is the direct measurement of the composition of coexisting liquid and vapor phases through sampling from a high-temperature static equilibration apparatus. The apparatus and techniques used in these experiments have been described in detail previously [1]. The apparatus consists of a high-temperature autoclave of about 600 cm^3 internal volume, equipped with a chemically-inert platinum-alloy liner and sampling tubes which permit samples of the equilibrated liquid and vapor phases to be withdrawn from the system at temperature at carefully-controlled sampling rates. A schematic diagram of the apparatus is shown in figure 1. Molalities of coexisting phases were determined by ion chromatography (for Na^+ or Cl^-) or acidimetric titration, as appropriate.

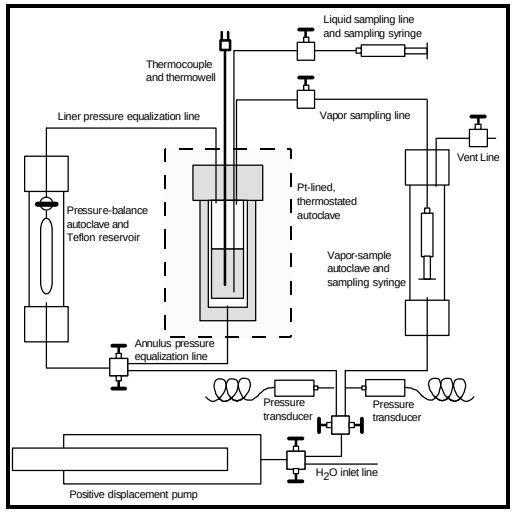


Figure 1. Static volatility apparatus.

ANALYSIS OF RESULTS

At temperatures below the solvent critical point (374EC) the equilibrium partitioning of electrolyte MX between liquid and vapor phases can be described quantitatively with the equilibrium constant

$$K_D \; ' \; m_v(MX)\,(_v(MX)/m_l(M^{\%})\,m_l(X^{\&})\,(_{\pm}(MX) \qquad (1)$$

The assumption inherent in equation (1) is that the solute is essentially completely associated in the (low density) vapor phase. Under the conditions of the experimental determination of coexisting-phase compositions (i.e., t # 350EC; m_v \$ 10^{-7} mol‰kg^{-1}) this assumption appears reasonable; a more complete analysis of the fully-speciated case has been given previously [2]. Similarly, under these conditions it is generally assumed the the activity coefficient $(_v(MX)$ for the neutral species in the vapor phase is equal to unity. Given a set of measurements of the compositions of coexisting phases at a particular temperature, values of $(_{\pm}(MX)$ can in principle be calculated through a consistent fitting of a value of the equilibrium constant and values of an appropriate composition-dependent model for the liquid-phase activity coefficient. In practice it is preferable to use available values of the activity coefficient of the pure aqueous solutions available from independent measurements or estimations, in order to reduce the overall uncertainty in the determination of the equilibrium constant from the partitioning data. For the {HCl + NaCl}(aq) system values of $(_{\pm}(NaCl)$ are available from Archer [3] and from Busey et al. [4]; corresponding values for $(_{\pm}(HCl)$ have been reported by Holmes et al. [5] and Simonson et al. [6]. Activity coefficients from these references have been used to determine K_D for NaCl(aq) [7] and for HCl(aq) [1] from liquid-vapor equilibrations of the single-solute aqueous solutions.

The first step in developing a quantitative treatment for the partitioning of solutes in the mixed electrolyte {HCl + NaCl}(aq) is to insure consistency in the models adopted for the treatment of the composition dependence of the activity coefficients for the single-solute solutions. In this case this consistency is not immediately attained from adopting directly the available literature treatments. The treatments for NaCl(aq) of Archer [3] and Busey et al. [4] are strictly stoichiometric; that is , no explicit account is taken of the possible formation of ion pairs at high temperature, and the effect of the reaction on the thermodynamic properties of the solution. This poses no fundamental problem for analysis of the mixture data, as the activity coefficients in equation (1) are the stoichiometric quantities. However, the use of a stoichiometric model for NaCl(aq) activity coefficients requires that a stoichiometric model be used for the corresponding HCl(aq) system. The treatment for HCl(aq) given by Holmes et al. [5] is consistent with the NaCl(aq) models, but gives values of $(_{\pm}$(HCl) at temperatures above 300EC which are significantly different from those obtained by Simonson et al. [6] using a speciated model. These latter values were used in determining the original equilibrium constant for the partitioning of HCl(aq) at high temperatures. Therefore a consistent application of the available activity coefficients for NaCl(aq) and HCl(aq) to volatility data for the mixed electrolyte system requires the development of either a stoichiometric model for HCl(aq) which is consistent with the activity coefficients of Simonson et al. used to derive K_D(HCl), or a model for NaCl(aq) which incorporates ion pairing. In the interest of a simple and useful treatment we have expanded the Pitzer ion-interaction treatment to develop a stoichiometric model for HCl(aq) valid at high temperatures.

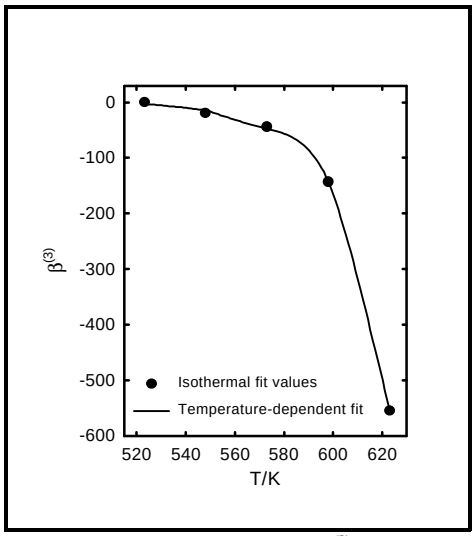


Figure 2. Values of the parameter $\$^{(3)}$ for HCl(aq)

The Pitzer model of aqueous electrolyte thermodynamics includes a linearized approximation for the effect of ion association as an additional term in the ionic-strength-dependent second virial coefficient [8], which for the osmotic coeffient expression appears as:

$$B^{N} = \$^{(0)} + \$^{(1)}\exp(-\alpha_1 I^{1/2}) + \$^{(2)}\exp(-\alpha_2 I^{1/2}) \qquad (2)$$

This expression for the second virial coefficient is appropriate when ion association is modest. For HCl ion association at high temperatures is relatively strong, with log K ≈ 2.5 at 350EC. In order to make a linear approximation to the model which is appropriate for association at this level, another term can be added to the second virial coefficient having the same form as equation (2):

$$B^{N} = \$^{(0)} + \$^{(1)}\exp(-\alpha_1 I^{1/2}) + \$^{(2)}\exp(-\alpha_2 I^{1/2}) + \$^{(3)}\exp(-\alpha_3 I^{1/2}) \qquad (3)$$

Choosing a large value of α_3 = 50 with the other parameters of equation (3) fixed by the fits of Holmes et al. [5] permits a representation of the excess thermodynamic properties of HCl(aq) which is consistent with the osmotic coefficients calculated at high temperatures by Holmes et al.

in the concentration range of the experimental results, and with the activity coefficients of the AI model reported by Simonson et al. [6] as used to fit the original HCl(aq) volatility data [1]. The $^{(3)} parameter is dependent on temperature as shown in Figure 2. As would be expected for a parameter which approximates ion-pairing ben

$$\ln(_{MX} ' \ln(^{(}_{MX} \% y) N^{(} \% y \frac{m}{mE} \left\{ 2_{MN} \% \frac{m}{mE} \left(1 \& \frac{y}{2} \right) R_{MNX} \right\} \quad (4)$$

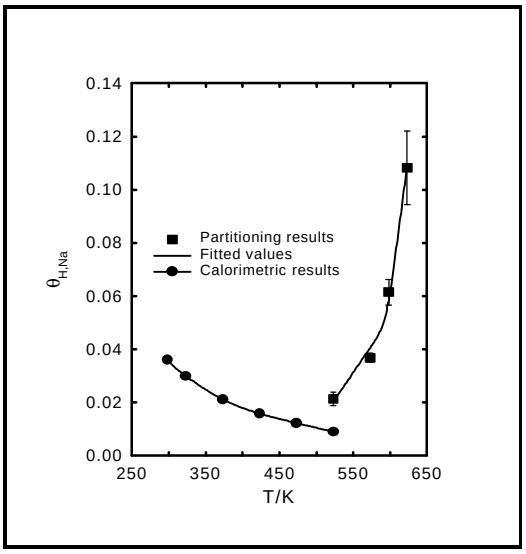
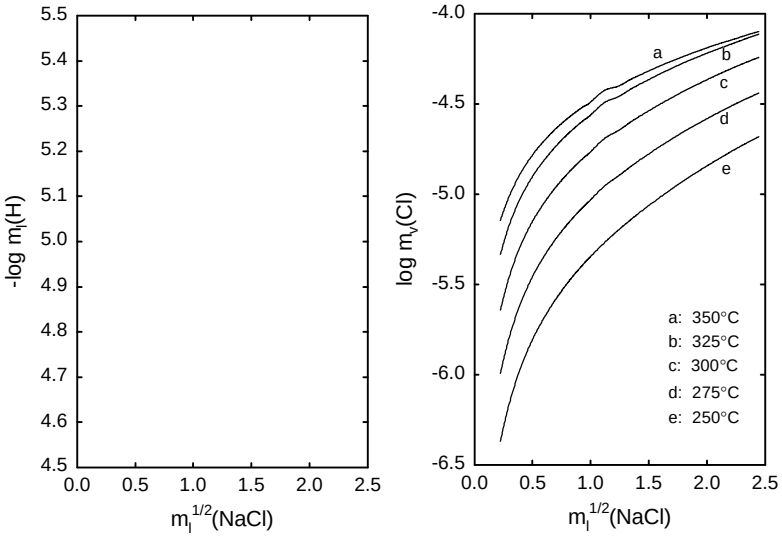


Figure 3. Values of the parameter $2_{H, Na}$


5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
-log m_l(H)
0.0
0.5
1.0
1.5
2.0
2.5
m_l^1/2(NaCl)
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
log m_v(Cl)
a
b
c
d
e
a: 350°C
b: 325°C
c: 300°C
d: 275°C
e: 250°C
0.0
0.5
1.0
1.5
2.0
2.5
m_l^1/2(NaCl)

The right-hand plot of figure 4 shows the predicted molality of chloride in the vapor phase over NaCl(aq) at the neutral pH values shown in the left-hand panel. Values of the equilibrium constant for HCl partitioning at these temperatures were taken from Simonson and Palmer [1]. The trend with temperature is somewhat counterintuitive; the value of the partitioning constant K_D increases strongly with increasing temperature, but the curves at regular temperature intervals are spaced more closely at higher temperatures. Again the effect of NaCl(aq) on the activity coefficient of HCl(aq) is influencing strongly the calculated quantities for this reaction at finite molalities, with the depression of $\gamma_{\pm}$(HCl) at higher temperatures leading to the near-coincidence of the predicted volatilities at 325 and 350EC. Finally, it should be noted that the partitioning of NaCl to the vapor phase under these conditions has no effect on the calculated molalities of chloride ion in the vapor phase; that is, the contribution of NaCl(aq) volatility is negligible at temperatures to 350EC. This observation points out the need for a knowledge of the pH of experimental solutions in determining the liquid-vapor partitioning equilibria for such nonvolatile solutes as NaCl.

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