Measurements of the Distribution of Solutes between Liquid Water and Steam

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Direct measurements of the concentration of solutes in both liquid and steam phases in equilibrium with each other have been made in a static mode utilizing a platinum-lined autoclave to a maximum of 350°C. Partitioning constants were derived from these measurements based on existing experimental or estimated values of the stoichiometric mean activity coefficients for the solutes in the liquid phase. Independent measurements of the conductance of some of the solutes in dilute aqueous solutions to 600°C and 300MPa were also made. The combined results are discussed in terms of a speciated model and the implications of these results to industrial and natural hydrothermal processes are presented.

[partitioning constant, ion-association, conductivity, speciation, corrosion]

1. Introduction

Measurements of the partitioning of solutes between aqueous liquid and vapor phases provide not only fundamental information on their thermodynamic properties and speciation, but these measurements also have considerable industrial importance in a wide variety of applications. At the basic scientific level, the distribution of solutes is a function of state variables (temperature, density), solution properties (concentration, activity coefficients, pH, presence of other solutes, etc.), and interactions at the molecular level (ion association, hydration, cluster formation). Parallel experimental programs at ORNL have and continue to yield much of the ancillary thermodynamic information on other thermodynamic properties of electrolytes to supercritical conditions and on the extent of ion association of electrolytes to supercritical temperatures and pressures.

Some of the more obvious applications of this knowledge to industry are control of corrosive "carryover" of impurities and treatment chemicals in power plants, corrosion at the well heads of hydrothermal steam-generating wells, hydrothermal industrial processing, etc. In the United States loss of electrical production from corrosion of low pressure turbines, which is particularly prevalent in the zones where condensation begins, and deposition on high pressure turbines, results in losses of three billion dollars annually [1]. At the Geysers geothermal field, problems have arisen due to declining steam pressures and the appearance of high chloride levels in the north-west end of the field [2].

Over the past six years volatility measurements have been made in our laboratories using a platinum-lined autoclave with a wide variety of solutes (e.g., HCl, H2SO4, H2PO4, H2S, NH4Cl, NaCl, NaOH, NaH2PO4, Na2SO4, Na2HPO4, NH4H2PO4, CH3COOH, and HCOOH) to temperatures of 350°C employing a static two-phase sampling technique [2-5]. These measurements have shown that knowledge of the liquid phase pH is critical in order to account for hydrolysis [4,5]. For example, in the case of dilute aqueous NH4Cl solutions, the dominant species in the steam phase are generally NH3 and HCl, such that the partitioning constant of these "end-member" species must be measured before the contribution of the "hydrolyzable" salt can be assessed. The presence of relatively high levels of HCl in the vapor above solutions containing chloride salts has obvious implications to processes which are affected by corrosive steam.

2. Background

The partitioning of an electrolyte from the liquid to steam can be represented in the simplest case of a 1:1 electrolyte, AB, by the equilibrium:

\[ A^{+}_{\text{aq}} + B^{-}_{\text{aq}} \rightleftharpoons AB^{0}_{\text{vap}} \]  

The partitioning constant for this reaction, \( K_p \), is defined by:

\[ K_p = \frac{m_{AB}^\text{vap}}{m_{A}^\text{aq}m_{B}^\text{aq}} \]  

where \( m_{AB}^\text{vap} \) and \( m_{AB}^\text{aq} \) represent the measured molalities of the assumed associated molecule in the vapor phase and the fully dissociated ions in the liquid phase with the corresponding mean ionic activity coefficient, \( \gamma_{AB} \). Implicit in Eqn. (2) are the assumptions that all species in the steam phase exist as neutral molecules and that in the absence of experimental data at this condition, the activity coefficients of the neutral species are taken to be unity.

Following this reasoning, the overall equilibrium (1) can be broken up into two coupled reactions, namely:

\[ A^{+}_{\text{aq}} + B^{-}_{\text{aq}} \rightleftharpoons AB^{0}_{\text{vap}} \]  

\[ AB^{0}_{\text{aq}} \rightleftharpoons AB^{0}_{\text{vap}} \]
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Therefore, at the critical temperature, the Henry's law constant corresponding to the equilibrium constant for reaction (4) is unity and $K_p = K_A$, where $K_A$ is the ion association constant of the electrolyte corresponding to reaction (3).

Independent conductance measurements carried out in our laboratories of dilute solutions of many of these electrolytes provide the values of $K_A$ at supercritical temperatures and pressures, which can be extrapolated to $T_c$ in order to test this implied agreement [6,7]. These measurements have been performed over the last 35 years in a Udimet 700 tubular autoclave lined with a platinum cylinder, which serves as one electrode with the second electrode extending down the center of the cell in a concentric configuration. The design of this cell, which is operated in a batch mode, limits the effective range of operation to electrolyte concentrations of 0.001 to 0.1 molal. Although the bulk of existing thermodynamic data on ion association equilibria at extreme conditions have been obtained from measurements using cells of this design, recent developments at the University of Delaware have dramatically improved the accuracy of conductance measurements utilizing a flowing cell capable of reaching 400°C and 30 MPa, and extending the concentration range down to 10⁻⁵ molal [8]. A similar cell based on the fundamental design of Zimmerman et al. [8] has been constructed at ORNL with the intention of increasing the working range to higher temperatures and pressures.

High temperature heat-of-mixing calorimetry and a unique isopiestic apparatus at ORNL [9] provide the basis for much of the activity coefficient data required to determine the values of $K_p$ at the finite concentrations employed in the volatility experiments. In many systems studied, relatively high concentrations of solute must be employed in order to obtain analyzable quantities of the solute in the vapor phase, particularly in the case of multicomponent electrolytes where the composition of the steam is determined by the difference between the analyses of cations and anions (e.g., in the case of NH₄Cl solutions, the concentration of this species in the vapor is determined either from the total chloride ion less that due to HCl or the from the total ammonia concentration less that due to NH₃; as the concentrations of the two end member species are large, uncertainties in the NH₄Cl concentration are often high).

\[
K_p = \frac{m_{NH_3}^{vap}}{m_{NH_3}^{liq}}
\]  

Partitioning of ammonia at low molalities between the liquid and vapor phases as represented by Eqn. (5) has been reported to high temperatures by Jones [10] and Edwards et al. [11]. Partitioning constants, which were calculated from the reported data using the assumption of unit activity coefficients for the (uncharged) ammonia in each phase, were fitted as a simple function of temperature and the density of the solvent in the liquid phase [4]:

\[
\log K_p = -0.056 + 458.71/T + 1.3267 \log \rho_{liq}
\]  

where $T$ is in Kelvin and $\rho_{liq}$ corresponds to the density of water in g cm⁻³ along the saturation vapor curve at temperature $T$ [12]. Eqn. (6) is constrained at the solvent critical condition by setting of $\log K_1 = 0$.

Typical of any system involving hydrolyzable solutes, in order to deal with the volatility ammonium chloride solutions, the dependence of the hydrolysis constant $K_r$, for ammonia:

\[
NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-
\]  

in the liquid phase and the ionization constants for water $K_w$:

\[
H_2O \rightleftharpoons H^+ + OH^-
\]  

must be known. Thiessen and Simonson [13] developed an equation for $K_r$, based largely on the potentiometric study of this equilibrium by Hitch and Mesmer [14] and a conductance study by Quist and Marshall [15]:

\[
\log K_r = -5.94455 + 1993.64/T - 7.14031 \times 10^4/T^2 + 6.84111 \times 10^4/T^3 + (2.18977 + 8226.45/T) \log \rho_w
\]  

The international formulation for the water ionization constant, $K_w$, of Marshall and Franck [16] can be used, although it must be noted that recently Lvov [17] has shown that there appear to be systematic deviations in this formalism at low densities with increasing temperature.

Knowledge of the equilibrium expressions for (7) and (8) allows calculation of the ionization of ammonium ion:

\[
NH_4^+ \rightarrow NH_3 + H^+
\]  

i.e., $(K_{10} = K_r/K_c)$:

\[
\log K_{10} = 1.847 - 5233.8/T + 9.3765 \times 10^4/T^2 - 1.0825 \times 10^6/T^3 + (11.767 - 9488.8/T + 8.5641 \times 10^3/T^2) \log \rho_w
\]  

and hence determination of the pH of the solution from a knowledge of the relative molalities of NH₃ and NH₄⁺. As will be demonstrated in this discussion, the pH of the liquid phase is a critical variable in determining speciation and concentration in the steam phase.

The third element of this system is HCl, which due to its covalent nature, is a relatively volatile strong acid, particularly at high temperatures approaching the critical condition where it becomes a weaker acid. In fact the partitioning of HCl was the...
The value of \( K_A \) (= \( K_p \)) for the molal ion association constant of HCl(aq) at the critical temperature of water calculated from the conductance measurements of Frantz and Marshall \([22]\) is \(10^{63}\), which compares favorably with that calculated from Eqn. (12) of \(10^{66}\). In making this comparison based on the results of these two independent experimental methods it must be noted: (1) the conductance measurements, which were made at ORNL, are fraught with large uncertainties due to the corrosive nature of HCl solutions at extreme conditions (100 - 700°C to 400 MPa), the design of the cell itself and the use of the simple Ostwald method to treat the results; and (2) the steep extrapolation of the log \( K_p(\text{HCl}) \) values from Eqn. (12) between the highest measured temperature of 350°C and the critical temperature of water. The conductance measurements of HCl solutions will be repeated in the near future with the improved apparatus of Zimmerman et al. \([8]\) and inclusion of the resulting ion association constant at the critical temperature in the fit of the partitioning constant data should then lead to an even more reliable representation of log \( K_p(\text{HCl}) \) over the entire temperature range.

Given knowledge of the partitioning constants of \( \text{NH}_3 \) (Eqn. 6) and HCl (Eqn. 12), and the ionization constant for \( \text{NH}_4^+ \) (Eqn. 11) as functions of temperature, two series of volatility experiments were initiated to determine the contribution of \( \text{NH}_4\text{Cl} \) to the vapor phase composition from 125 to 350°C \([4,5]\). The first series was conducted in \( \text{NH}_4\text{Cl}/\text{HCl} \) mixtures where the pH was controlled and estimable from the stoichiometric concentration of "free acid" and the vapor phase concentration of \( \text{NH}_4\text{Cl} \) was determined from the excess chloride present over that which was predicted for HCl at that temperature and activity (approximations were also necessary to estimate the activity coefficients of the ions in this mixture). In the second series, the pH was buffered by the \( \text{NH}_4\text{Cl}/\text{NH}_3 \) mixture (i.e., pH was calculated from Eqn. 11) and \( \text{NH}_4\text{Cl} \) concentrations in the vapor were estimated from the excess of total \( \text{NH}_3 \) present above that attributable to \( \text{NH}_3 \) alone (Eqn. 6).

The large uncertainties in the values of \( K_p(\text{NH}_4\text{Cl}) \) derived by this difference method at low temperatures (<300°C), compounded by the fact that the individual end members are far more volatile than \( \text{NH}_4\text{Cl} \), two equations (13 and 14) can be fit to these data leading to substantially different results at temperatures below 150°C as illustrated in Fig. 2.

\[
\log K_p(\text{NH}_4\text{Cl}) = -1.875 - 1248.65/T - 23.401 \log \rho_w \quad (13)
\]

\[
\log K_p(\text{NH}_4\text{Cl}) = -16.063 - 15203.4/T - 9.3301 \log (\rho_b/\rho_w) \quad (14)
\]

In Eqn. (14), \( \rho_b \) represents the density of the vapor phase as calculated from the Steam Tables of Haar et al. \([12]\). An alternative method of representing the partitioning equilibrium involves the use of the so-called "isocoulombic" approach \([23]\), Eqn (15), which simplifies the temperature dependence of ionic equilibria by combining the partitioning equilibrium with that for the dissociation of water, Eqn. 8, which is known with reasonable accuracy over the entire

\[
\log K_p(\text{HCl}) = -13.4944 - 934.466/T + 5.4847 \log T - 11.0029 \log \rho_w \quad (12)
\]
temperature range, particularly below 300°C:

\[ \text{NH}_4^+ + \text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{Cl}_\text{w} + \text{OH}^- + \text{H}^+ \]  \hspace{1cm} (15)

The form of this equation, which effectively contains equally-charged ions on both sides, minimizes changes in solvation and thereby tends to simplify the temperature and ionic strength dependencies of the reaction (i.e., \(\Delta C_p\) approaches zero). This approach has been used successfully for a number of partitioning equilibria, including that for HCl, so that from Fig. 2 one might conclude Eqn. (13) provides the more realistic representation of the temperature dependence of log \(K_p(\text{NH}_4\text{Cl})\), because of the virtual linear dependence of the isocoulombic constant below 300°C. Accurate partitioning constants at low temperatures are needed when calculating the composition of the condensate formed under these conditions, e.g., in a low pressure turbine of a power plant, because solutes in steam will naturally partition to the liquid phase as the least volatile forms.

Fig. 2. Partitioning constants for \(\text{NH}_4\text{Cl}\) derived from Eqns. (13) (heavy curve) and (14) (dashed curve) treated according to the generalized equilibrium represented by Eqn. (1) (left hand axis) and in an isocoulombic form (Eqn. 15, right hand axis), shown as functions of the reciprocal temperature in Kelvin.

In order to illustrate the chemistry implied from the discussion outlined above, consider the artificial example of a fossil-fired, drum-boiler power plant operating under AVT (all volatile treatment), which in effect means adding a volatile pH buffer to the feed water to the boiler, in this case ammonia, to control the pH of the water/steam circuit and inhibit the dissolution of magnetite. For a feed water composition (in this simple model the feed water and boiler water must be considered to have identical compositions) at 25°C of:

\[ [\text{Cat*}]=278\text{ppb}; \quad [\text{H}^+] = 0.075\text{ppb}; \quad [\text{Na}^+] = 0.03\text{ppb}; \quad [\text{H}^+] = 0.03\text{ppb}; \quad [\text{Cl}^-] = 0.7\text{ppt}; \quad [\text{OH}^-] = 350\text{ppb}; \quad [\text{SO}_4^{2-}]= 0.001\text{ppt}; \quad [\text{NaOH}] = 0.004\text{ppt}; \quad [\text{NH}_3] = 449\text{ppb}; \quad [\text{NH}_4^+] = 0.75\text{ppb}; \quad [\text{Na}^+] = 2\text{ppb}; \quad [\text{H}^+] = 0.075\text{ppb}; \quad [\text{Cat*}]=278\text{ppb}; \quad \text{and pH}=7.13. \]

Steam in equilibrium with this solution has the composition: [HCl]=0.7ppb; [NH4Cl]=0.04ppb; [NaCl]=0.00 ppt; [NaOH]=0.004ppt; [NH3]=1146ppb; and [H2SO4]=0.001ppt, as estimated from the respective partitioning constants. It is immediately apparent that HCl is the dominant chloride-containing (transporting) component in the steam, despite the relatively high pH and concentration of ammonium ion in the liquid phase. Sulfuric acid plays a similar role, although this is less apparent from this example. Note that these thermodynamic calculations do not take into account non-equilibrium effects, nor are solubility limitations in the steam phase incorporated into the calculations. Therefore, these results probably represent the maximum carryover of chemicals into the steam and as such are well suited for setting guidelines for the safe operation of power plants. Other considerations such as the entrainment of liquid droplets can be accounted for in these calculations and the partial condensation of steam can be treated explicitly within the framework of the thermodynamic model. For example in the present case, if 4% of the steam is condensed at 100°C the condensate will have a predicted composition of: [Cl]=0.7ppt; [OH]=350ppb; [SO4]=0.001ppt; [Na+] = 0.03ppt; [H+] = 0.03ppt; [NH3] = 900ppb at a pH=7.57.

Consider the example of the Geysers geothermal system in northern California where corrosive HCl-containing steam is being produced in the north-west end of the field from deep saline pore fluid. In the absence of definitive analyses of these fluids, the combination of field observations and the results of the laboratory experiments presented here, Simonson and Palmer [24] concluded the following: (1) the superheated steam probably deposits halite in the producing wells as the steam cools while traveling to the surface; (2) ammonia, which is known to be present in relatively high concentrations at depth, accounts of a significant portion of the chloride, as ammonium chloride, present in the steam at the surface, together with HCl, (3) the hydrolysis of other constituents of the liquid phase, such as magnesium and calcium, is insufficient to lower the pH to a degree where HCl alone would dominate the vapor phase.

The final electrolyte to be considered here is sodium hydroxide. Apart from the intrinsic interest in this important base, there exist a number of volatility studies of aqueous NaOH, all of which have used dynamic sampling equipment, rather than the static apparatus described here. Therefore, these results provide an opportunity to test the comparative reliability of the various approaches. Similarly, there have been a number
of high temperature conductance studies, which show considerable disparity when used to derive the association constant for NaOH, which as shown above, is an integral part of the mechanism generalized in Eqns. (3) and (4), and provides a reference point for the partitioning constant at the critical temperature. The results of the conductance study carried out recently at ORNL for dilute NaOH solutions are shown in Fig. 3 [7].

![Graph of log K_a(NaOH) vs. 1000/K/T](image)

Fig. 3. Molal ion association constants for NaOH shown as a function of reciprocal temperature (Kelvin) at various solution densities [7], where the solid lines result from the fit according to Eqn. (16).

The best-fit equation used to describe the molal association constants over the range 400 to 600°C at pressures to 300 MPa from Ho and Palmer [25] at 75, 100 and 150°C, is as follows:

\[
\log K_a(\text{NaOH}) = 1.648 - 370.31/T - (13.215 - 6300.5/T) \log \rho_w
\]  

(16)

The recent results of Bianchi et al. [26], who utilized a dc method for their conductance measurements, provide some insurance for the extrapolation to subcritical conditions appropriate to the volatility study. However, the new conductance cell design of Zimmerman et al. [8], which is better suited to low density measurements than the traditional configuration employed at ORNL, indicates that for densities \(\leq 0.35 \text{g/cm}^3\), Eqn. (16) may have greater uncertainty. A new cell modification based on the Zimmerman et al. [8] concept has now been constructed and successfully tested at ORNL in collaboration with Professor Robert H. Wood (University of Delaware, USA) with the intent of extending these measurements into the supercritical region of water [26].

Nevertheless, a fit of the combined partitioning constant data from ORNL and from three independent sources resulted in a value for log \(K_a(\text{NaOH})\) at the critical temperature (i.e., \(= \log K_a(\text{NaOH})\)) of 3.2 compared with 2.8 from Eqn. (16). Considering the uncertainties in both sets of measurements, this level of agreement is very satisfactory and attests to the validity of the treatment of the volatility data for NaOH.

Moreover, the agreement between four sets of independent partitioning experiments involving the static (inert) approach outlined here [27], and three larger scale flow methods [28-30], verifies the validity of the current measurements and their applicability to industrial settings.

This article has concentrated on two energy-related technologies that can benefit directly from basic thermodynamic information on the volatility and solution properties of electrolytes generated in the laboratory. Other applications of these data include the fields of geochemistry and industrial processing, as well as contributing to the molecular level understanding of solutes at extreme conditions.

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