THE PARTITIONING OF ACETIC, FORMIC, AND PHOSPHORIC ACIDS BETWEEN LIQUID WATER AND STEAM

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Abstract

The chemical carryover of impurities and treatment chemicals from the boiler to the steam phase, and ultimately to the low-pressure turbine and condenser, can be quantified based on laboratory experiments preformed over ranges of temperature, pH, and composition. The two major assumptions are that thermodynamic equilibrium is maintained and no deposition, adsorption or decomposition occurs. The most recent results on acetic, formic and phosphoric acids are presented with consideration of the effects of hydrolysis and dimerization reactions. Complications arising from thermal decomposition of the organic acids are discussed. The partitioning constants for these acids and other solutes measured in this program have been incorporated into a simple thermodynamic computer code that calculates the effect of chemical and mechanical carryover on the composition of the condensate formed to varying extents in the water/steam cycle.

Background

Acetic and Formic Acids

Acetic and formic acids are major breakdown products of morpholine[1] and occur in surface and ground waters. Other sources of carboxylic acids include degeneration of condensate polishing resins and contamination from organic solvents and greases. Salts (principally sodium) of these acids may represent significant components in the liquid phase even at elevated temperatures, but are far less volatile so that their contribution to vaporous carryover can be ignored to a first approximation. The pK_a values for acetic and formic acids are 4.76 and 3.76 at 25°C, but are significantly higher by 350°C, namely 7.97 and 5.23. Taking into account the attendant change in the neutral pH of pure water (7.00 to 6.15) it is clear that the volatile acid forms are substantially more stable with respect to their salts at boiler temperatures.

In addition to affecting the pH of the liquid phase, acetate forms complexes with metals such as iron, producing enhanced dissolution and transport[2]. Acetic acid has also been suspected of contributing to a stress corrosion failure[3]. Another drawback of the acetic acid production from morpholine decomposition is that it limits the utility of cation conductivity measurements for

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detecting low-level contaminant ingress. Acetic and formic acids have been found to behave somewhat differently in some power plants, even though their partitioning behavior is quite similar in magnitude. In one case, formates have been found to concentrate in the moisture separator drains whereas acetates did not[4]. The different tendencies may be a reflection of their markedly different pK_a value at high temperatures, coupled with their widely differing thermal stabilities and complexation abilities. Acetic and formic acids are not thought to accumulate to appreciable extents during normal operation in the boiler, steam, or condensate. However, startup and shutdown may give rise to conditions where the partitioning of acetic acid is very different than under normal operating conditions.

It has long been noted that the vapors of the carboxylic acids (especially formic and acetic acids) diverged widely from the ideal gas law. This has led to models that incorporate dimerization and other low-order molecular clusters in the vapor[5-9]. Liquid vapor equilibria in water-acid mixtures were investigated experimentally by Cruz and Renon[10] (100°C, $2.8 \cdot 10^{-5}$ M to 2.4 M), and Othmer *et al.*[11] (and references therein) at 27 to 150°C in 0.5M to glacial acetic acid. In some of these cases, dimerization in one phase or another was taken into account, sometimes explicitly[10]. However, few of the determinations have considered the full range from very dilute to very concentrated solutions, nor have many covered as broad a temperature range as considered in this study. In interpreting data, previous authors have treated dimerization in the vapor, or the liquid, but not both. There have been numerous attempts to interpret the vibrational spectra (IR and Raman) of acetic and formic acids in terms of linear and cyclic dimers and trimers in concentrated solutions of the acids[12-15].

The kinetics of decomposition (decarboxylation and oxidation) of acetic acid/acetate have been studied in detail and shown to be catalyzed by surfaces in contact with these solutions[16,17]. For example at 300°C (572F), the half lives of acetic acid solutions in contact with magnetite and TiO_2 are approximately 100 days and 10 years, respectively, and this difference increases dramatically at lower temperatures. The products are mainly CO_2 and CH_4, but other [illegible] more rapid oxidation reactions. Formic acid/formate undergo relatively rapid decomposition to either H_2 and CO_2, or H_2O and CO. However, the catalytic effect of metal surfaces, reaction products and rates are controversial. One study measured a reaction half life for dilute aqueous formic acid of only 5.4 seconds at 360°C and 250 bar in a Hastelloy C vessel[18]. On the other hand, extrapolation of these half lives to 150°C yields a value of 4 hours compared with unpublished data from ORNL of 89 days at saturation vapor pressure. Thus the survivability of formic acid in a fossil plant is in question.

Work aimed at determining the relative volatility of organic acids with specific reference to power plant steam cycles includes the results of Petrova *et al.*[19] obtained at the Moscow Power Institute. In this work the authors noted that these impurities in steam have a strong influence on erosion-corrosion wear of the low pressure turbines and may largely be responsible for a sharp decrease of the pH of early condensate discovered in one survey of power plants. The results from the present work are in qualitative agreement with the results from this earlier study.

Phosphoric Acid

Phosphoric acid in power plant water/steam cycles originates from hydrolysis of the phosphate treatment chemicals added to drum boilers. Phosphoric acid is a relatively weak inorganic acid[20], which like all neutrally-charged acids[21,22], becomes weaker with increasing temperature so that

phosphate are still being evaluated.

A number of utilities have experienced serious corrosion and related boiler tube failures while operating under congruent phosphate treatment. These problems were ascribed to acid phosphate corrosion occurring under deposits[23]. The effects of various phosphate treatments and recommendations to reduce additions of more acidic sodium phosphates have been discussed in detail[24]. Jonas and Reiger[25] summarized the carryover results of 40 utility drum units operating on phosphate chemistry; in only three cases did the phosphate weight percent in the steam generated in the drum exceed or almost equal that of either chloride or sulfate. In most cases the phosphate level was only given as an upper limit. Large-scale loop experiments by Goodstine[26] yielded up to 10 ppm in steam generated from 1000 ppm "tri-sodium" phosphate solutions at *ca.* 368°C. These levels decrease systematically with decreasing temperature (pressure) and concentration in the liquid phase. However, based on the preliminary results from experiments that are not reported here, it is thought that the dominant species in the vapor may be phosphoric acid and lower order sodium phosphates in both cases.

Experimental Method

The experimental technique employed at ORNL was first described by Simonson and Palmer[27] in the study of HCl volatility, although minor modifications have been made subsequently[28-30]. Basically, an equilibrated two-phase aqueous solution is contained in a platinum alloy liner seated in a one liter pressure vessel and samples are withdrawn under controlled conditions for analysis by ion chromatography, potentiometic titration, or atomic-adsorption, graphite-furnace spectroscopy. The partitioning constants obtained by this method for NaOH and H_2SO_4 were shown to be in good agreement with those from various larger scale, flow-through systems[26,31,32]. In the study of acetic and formic acids the platinum liner was replaced by a glass cup, in order to reduce the rate of decarboxylation, which was catalyzed very effectively by the platinum surface. An advantage of our experimental technique, apart from ease of use, reliability and cost, is that corrosive solutions can be studied and adsorption of the solutes dissolved in steam onto the tubing walls is not a factor. On the other hand, only relatively small volumes of either phase can be sampled so that for relatively low volatile solutes, high concentrations are required in the liquid phase to produce measurable levels in the vapor. High concentrations necessitate knowledge of the activity coefficients and careful control of pressure in order to prevent aerosol formation and hence mechanical carryover. The static nature of the apparatus is conducive to minimizing mechanical carryover, which has been monitored by adding traces of potassium salts to the liquid phase[28].

Approach

In any experimental study of the partitioning of electrolytes, including their neutrally charged precursors, it is essential to know the pH of the liquid phase. For example, in the study[28] of NH_4Cl, at any given temperature the vapor contains varying concentrations of HCl, NH_3, and NH_4Cl depending on pH. Therefore, the volatility of NH_4Cl can only be measured by subtraction of the contributions of HCl to the total chloride and/or NH_3 from the total ammonia/ammonium concentrations; hence the pure solutes must be measured independently. In this case and many others, the two "end members" exhibit much higher volatilities than their salt, so that K_D for NH_4Cl can only be determined with much lower certainty. The example of ammonium bisulfate is even more extreme[30].

In order to overcome the limitations of the ray diagram[33] for representing the partitioning of solutes from liquid water to steam, a thermodynamic approach has been adopted in this program[27-30]. For weak electrolytes such as acetic, formic and phosphoric acids, the partitioning equilibrium may be considered as a simple Henry's law equation:

$$K_D = m_{HA,vap}\gamma_{HA,vap}/m_{HA,liq}\gamma_{HA,liq} \qquad (1)$$

where m and γ represent the measured molalities and corresponding activity coefficients in each phase, respectively. In the studies to date[27-30], $\gamma_{HA,vap}$ has been assumed to be unity due to the low concentrations observed in sampled steam and the absence of reliable experimental measurements of $\gamma_{HA,vap}$. Similar expressions may be written for the partitioning of ammonia, or other neutrally-charged solutes, for which either the liquid phase thermodynamics are known (e.g., hydrolysis, dimerization, etc.), or at conditions where this specie is dominant (albeit that its activity coefficient is either known or very low concentrations are employed). In the case of acetic and formic acids, for example, the hydrolysis quotients have been measured[21,22] and dimerization in both phases was taken into account.[34] The partitioning constants for these neutrally-charged solutes are shown in Fig. 1 as a function of reciprocal temperature (Kelvin). As these constants were all defined by Eq. 1, the volatilities may be compared directly. In other words at temperatures <200°C, the order of decreasing volatility is $NH_3 > SO_2 > CH_3COOH > HCOOH >> H_3PO_4$. The value of K_D in this case must approach unity at the critical temperature and hence the difference in volatilities decreases with increasing temperature. However, it must be remembered that the actual concentration in the vapor phase will also depend on the pH of the liquid as the acids will tend to dissociate with increasing pH and decreasing concentration into their constituent ions, which are invariably less volatile than the acids themselves. For bases such as ammonia, concentration in the vapor will decline as the parent molecule is protonated to

can be effectively ignored in normal water/steam cycles, unless concentrations build up in crevices or films.

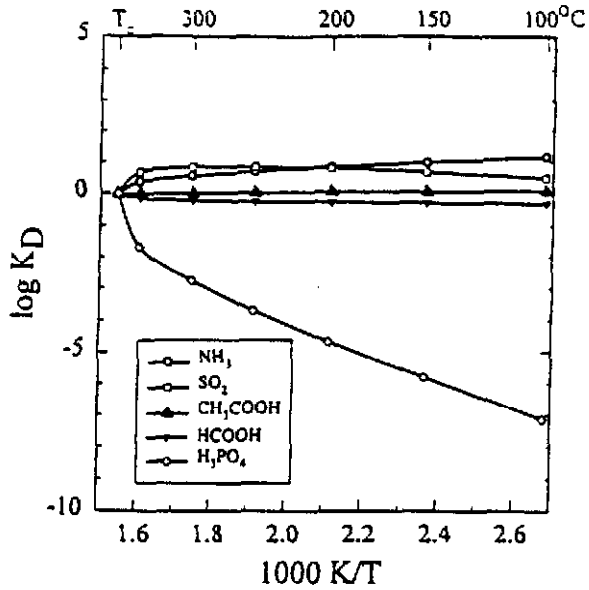

Figure 1. The logarithm of the partitioning constants for neutral solutes as a function of reciprocal temperature in Kelvin.

Dissociation constants for molecular hydrochloric and sulfuric acids are not known with any certainty and therefore these solutes must be treated as 1:1 electrolytes (H^+,Cl^- and H^+,HSO_4^-), together with their salts (e.g., Na^+,Cl^-; NH_4^+,HSO_4^-, etc.) and strong bases (e.g., Na^+,OH^-). For this class of electrolytes the partitioning constant is defined as:

$$K_D = m_{HA,vap}\gamma_{HA,vap}/m_{H+,liq}\, m_{A-,liq}\, \gamma_{\pm\, HA,liq}^{\ 2} \qquad (2)$$

where $\gamma_{\pm\, HA,liq}$ is the mean ionic activity coefficient of HA. Fortunately $\gamma_{\pm\, HA,liq}^{\ 2}$ is a measurable quantity and many of these values have been measured to high temperatures at ORNL by dilution calorimetry and isopiestic measurements[27-30]. Isopiestic measurements yielding the activity coefficients for phosphoric acid and its sodium salts are now available[35,36]. As indicated above, $\gamma_{HA,vap}$ is set to unity by necessity. The partitioning constants for a series of 1:1 electrolytes are shown in Fig. 2 as a function of temperature, including phosphoric acid (H^+,$H_2PO_4^-$), which was converted from the form defined in Eq. 3 using the measured first acid dissociation constant (K_1)[20] for H_3PO_4, Eq. 4, to that represented by Eq. 5.

$$H_3PO_4(liq) \rightleftharpoons H_3PO_4(vap) \qquad K_D\ (Eq.\ 1) \qquad (3)$$

$$H^+(liq) + H_2PO_4^-(liq) \rightleftharpoons H_3PO_4(liq) \qquad 1/K_1 \qquad (4)$$

$$H^+(liq) + H_2PO_4^-(liq) \rightleftharpoons H_3PO_4(vap) \qquad K_D\ (Eq.\ 2) \qquad (5)$$

The curves in Fig. 2 result from fitting available data obtained over different temperature ranges with differing accuracies according to the general equation:

$$\log K_D = a + b/T + \log \rho_w \qquad (6)$$

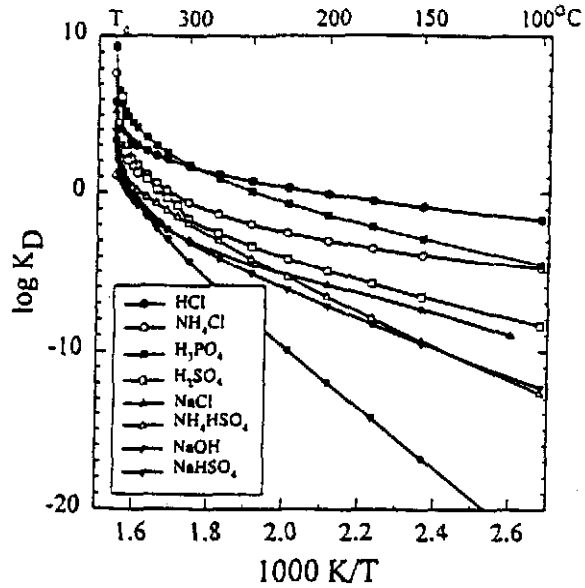

Figure 2. The logarithm of the partitioning constants for 1:1 solutes as a function of reciprocal temperature in Kelvin.

where ρ_w is the density of water. Extrapolation of these results to temperatures beyond the measured temperature range (i.e., typically 250 – 350°C) with this expression is tenuous as log K_D increases sharply as the critical temperature of water is approached (see Fig. 2). However, this problem is alleviated to some extent, because examination of Eqs. 3-5, indicates that at the critical temperature, K_D for Eq. 3 is unity and therefore K_D (Eq. 5) = $1/K_i$ (Eq. 4), where the latter is known from independent measurements[20]. In the case of other 1:1 electrolytes, $1/K_i$ (the ion association constant) is often known from independent conductance measurements. Indeed, it is the increasing tendency of electrolytes of associate, particularly at the approach to supercritical conditions, that drives the values of K_D to high values under these conditions.

It is clearly apparent from Fig. 2 that the volatilities of these 1:1 solutes vary over many orders of magnitude. This is particularly true at lower temperatures and dictates their relative concentrations in the early condensate, as will be discussed below in some detail. Phosphoric acid is surprisingly volatile at high temperatures when compared in this manner, even surpassing that of hydrochloric acid at high temperatures.

It should be noted that the partitioning constant for Na_2SO_4 (1:2 electrolyte) was also measured by conducting experiments in solutions of dominantly Na_2SO_4 supported by the addition of NaOH[29]. Contributions to the steam phase from H_2SO_4, $NaHSO_4$, and NaOH where subtracted, thereby establishing the expected low volatility of Na_2SO_4. Note that in the excellent experimental study of Goodstine[26] in 1974, pure Na_2SO_4 solutions were used and as a result the vapor was dominated by $NaHSO_4$ according to our analysis[29]. The volatility of $(NH_4)_2SO_4$ could not be measured[30], presumably due to its intrinsic low volatility compounded by the hydrolysis of NH_4^+ to ammonia in strongly basic solutions.

Modeling the Water/Steam Circuit on an Equilibrium Basis

[redacted] Windows based computer code that simulates equilibrium processes within an idealized water/steam circuit. The predictions resulting from this algorithm are idealized in the sense that: (1) chemical equilibrium is assumed to be maintained throughout the circuit; (2) neither precipitation nor adsorption of solutes occurs; and (3) neither decomposition nor redox transformations of the solutes occurs. Thus, this treatment should predict the maximum vaporous carryover. The following steps in the calculation are similar to those described previously by Jensen *et al.*[37] with some additional features and a unified fitting procedure that is robust and simplifies the addition of new solutes:

a. input the solutes of interest and their concentrations (and pH) in the boiler water at 25°C
b. allow the program to adjust the concentration of a designated cation or anion (or pH) to achieve charge balance
c. the concentrations are then calculated at 25°C and recalculated at a designated boiler temperature (activity coefficients are determined from the NaCl model substance approach)
d. species distributions and concentrations in the coexisting steam are determined from the partitioning constants
e. contributions to the species in the steam from mechanical carryover (or attemperation sprays) are calculated; if set at 100% this would simulate a once-through unit
f. composition of the steam at a given condensate temperature is calculated
g. composition of the condensate formed is calculated for a given percentage condensation; total and cation conductances are estimated (these calculations assume that sufficient steam passes to permit equilibration with highly concentrated condensate droplets or films)
h. finally, the composition corresponding to complete condensation at 25°C is calculated as well as the cation and total conductivities

Test Cases

As the analysis of the sodium phosphate partitioning constants is not complete, analysis of plant data using phosphate treatments can not be made at this time. Some examples of AVT treatment are given below to indicate the main features of the equilibrium approach understanding the speciation and relative concentrations around an idealized water/steam cycle.

AVT without Carboxylic Acids. The initial conditions were chosen more or less at random, based loosely on the action 1 guidelines for AVT treatment for drum boilers without reheat operating at 2300 psi, which is approximately equivalent to 346.7°C.[38]

Table 1.
Concentrations given in ppb: initial conditions: pH = 9.4; Cl = 68; Na = 2100; S = 63
(charge balanced by nonvolatile anion)

Species	Boiler, 25°C	Boiler, 347°C	Steam, 347°C	Cond., 100°C 10%	Cond., 25°C 100%*
Na^+	2100	2100	0.0051 NaOH	0.039	0.0040
Cl^-	68	68	0.0024 NaCl	0.038	0.0038
SO_4^{2-}	63	23		0.0055	0.00055
HSO_4^-		40	0.0007 $NaHSO_4$		
NH_3	316	529	1263	98	782
NH_4^+	226	1	0.0001 NH_4Cl	158	509
pH	9.40	7.30	0.0023 HCl	7.21	9.44

* specific conductivity = 7.6 $\mu S/cm^2$

AVT with Carboxylic Acids. The initial conditions are essentially the same as in the previous case with the addition of acetic and formic acids.

Table 2.
Concentrations given in ppb: initial conditions: pH = 9.4; Cl = 68; Na = 2100; S = 63;
CH_3COOH (HAc) = 100; HCOOH (HFo)= 100 (charge balanced by nonvolatile anion)

Species	Boiler, 25°C	Boiler, 347°C	Steam, 347°C	Cond., 100°C 10%	Cond., 25°C 100%*
Na^+	2100	2100	0.0055 NaOH	0.055	0.0054
Cl^-	68	68	0.0024 NaCl	0.036	0.0036
SO_4^{2-}	63	24		0.0054	0.00054
HSO_4^-		39	0.00066 $NaHSO_4$		
NH_3	316	529	1263	97	773
NH_4^+	226	1	0.00009 NH_4Cl	302	519
HAc		64	64	6.2	0.0014
Ac^-	100	37		581	63

* specific conductivity = 7.6 $\mu S/cm^2$

The presence of acetic and formic acid in the boiler water, given the assumptions described above concerning their survivability around the circuit, has the anticipated effect of lowering the pH of the "early condensate". The possibility of partial condensation allows a build up in the concentrations of organic acids. The use of lower ammonia concentrations exacerbates this effect. On the other hand lowering the concentrations of sodium, chloride and sulfate to ≤10 ppb in the boiler water has an insignificant effect on the pH of either condensate. The addition of

0.2% mechanical carryover has little effect on the final pH and condensate compositions under at these prevailing conditions.

Preliminary calculations at similar compositions as those used in the previous two examples with phosphate replacing ammonia at *ca.* 2 ppm (i.e., corresponding to action level 1 with equilibrium phosphate chemistry[24]) predict that the dominant specie in the steam would indeed be phosphoric acid.

Comparisons of these model calculations with plant data are now needed in order to determine the practical application of these results. Nevertheless, as indicated above the equilibrium approach does establish the maximum vaporous carryover and therefore provides a benchmark in establishing operating guidelines. Moreover, these laboratory scale measurements conducted under carefully controlled conditions establish the chemical speciation in both the liquid and steam phases and thereby improves our understanding of the chemistry occurring within the cycle.

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