

Accurate Prediction of Deprotonation and pH value of Acids in Aqueous Solutions over the Whole Concentration Range

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Abstract

The pK_a of an acid is important for determining the dissociation and thermodynamic properties of solutions containing it. However, the value of pK_a is typically determined at dilute limit and cannot be used to describe properties of the solution at high concentrations. In this work, we propose an approach to determine the concentration independent equilibrium constant K_{eq} based on pK_a and predicted activity coefficients. The equilibrium constant thus determined is applied to predict the degree of dissociation over whole concentration range for weak to strong acids. The proposed method is capable of capturing the redissociation phenomenon observed in sulfuric acid aqueous solutions. Furthermore, the pH of acid aqueous solution is predicted over whole concentration range, showing a good agreement with experiments. Based on this approach, we found that the vapor pressures of acid aqueous solutions strongly depend on the degree of dissociation of acids. The proposed model provides useful insights to link the macroscopic properties of acid aqueous solutions to its microscopic dissociation phenomena over the whole concentration ranges.

Keywords: Degree of Dissociation; Equilibrium Constant; pK_a ; COSMO-SAC.

1. Introduction

The acid dissociation constant, K_a , is essential for understanding the fundamental reactions in many physical and chemical processes.¹ The value of pK_a (logarithm of K_a) represents the quantitative strength of deprotonation of an acid in solution. It provides a convenient way to specify the dissociation constant for weakly acidic or basic groups, and is extremely informative.² For example, together with the octanol-water partition coefficient, pK_a allows for the estimation of the extent of a drug entering the blood streams.³ In an acid-base equilibrium reaction, the pK_a allows for the prediction of favored reaction direction as well as the concentrations of the individual species at a given pH. The knowledge of pH of a solution is indispensable in many facets of our life and environments. For geochemistry and environmental science, it is of decisive importance to determine accurate pH values of fresh waters.

In experiment, pK_a is usually determined at low solution concentrations and is constant only under limited range of concentrations. To describe the equilibrium properties of aqueous acid solutions over the whole concentration range, it is best to use the equilibrium constants K_{eq} of corresponding acid-base reactions. The equilibrium constant depends only on temperature and not composition and can be related to pK_a with the information of activity coefficient of all species in the solution. Bollas et al.⁴ applied the electrolyte-NRTL model to sulfuric acid aqueous solutions. They considered the two dissociation steps of sulfuric acid and obtained good agreement with experiment for the degree of dissociation, osmotic coefficient and mean ionic activity coefficient (MIAC). The binary interaction parameters were required to fit the experimental degree of dissociation data. Reschke et al.⁵ calculated the osmotic coefficient of electrolytes such as H_2SO_4 and H_3PO_4 with ePC-SAFT. In their work, the dissociation of weak acids was determined assuming a constant dissociation constant K_c (molality based equilibrium constant).

Despite its importance, the prediction of degree of dissociation of an acid and the solution pH over the whole range of concentration remains challenging. To achieve this, it is necessary to

be able to predict the equilibrium constant, K_{eq} , (or pK_a) and the concentration dependence of activity coefficients of all species in the solution. There are several empirical pK_a predictors such as ChemAxon, Epik, ACD pK_a DB but these methods often fail for molecules with completely novel chemical substructures.⁶ On the other hand, quantum mechanical (QM)-based⁷ or semiempirical QM⁸ methods can also be used for pK_a predictions. Despite of its sound theoretical basis, the state-of-the-art method results in a standard deviation in pK_a of about 1 log unit,^{6,9} or an error of a factor of 10. This can be significant in determining species concentrations. In this work, we propose to combine experimentally determined pK_a with a predictive activity coefficient model, COSMO-SAC,¹⁰ for the determination of K_{eq} . We show that this approach allows for more accurate prediction of the dissociation behavior and pH value of aqueous acid solutions over the whole concentration range. This approach thus provides a quantitative relation between the properties of the solution with the degree of deprotonation of acid.

2. Thermodynamics Background

The dissociation reactions of a monoprotic acid in aqueous solution can be expressed as:



where HA and A⁻ are the monoprotic acid and its conjugate base, respectively. H₃O⁺ represents the hydronium ions. The pK_a of HA is then defined as:

$$pK_a = -\log_{10} K_a \quad (1)$$

with

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \quad (2)$$

In the limit of very dilute acid concentration the dissociation constant can be expressed in terms of degree of dissociation, α , and the molar concentration of initially undissociated HA, C^o ,

$$K_a = \lim_{C^o \rightarrow 0} \frac{[A^-][H_3O^+]}{[HA]} \quad (3)$$

where α is the extent of dissociation of the acid and $C^o = [HA] + [A^-]$. On the other hand, the equilibrium constant K_{eq} of reaction R1 is expressed as

$$K_{eq} = a_{A^-} \frac{a_{H_3O^+}}{a_{AH} a_{H_2O}} = x_{A^-} \frac{x_{H_3O^+}}{x_{AH} x_{H_2O}} \gamma_{A^-} \frac{\gamma_{H_3O^+}}{\gamma_{AH} \gamma_{H_2O}} K_r \quad (4)$$

where K_x and K_r indicate the ratio of mole fractions and activity coefficients, respectively. When K_r is unity (i.e., $K_r = 1$), the aqueous acid solution is referred to as an ideal solution. To relate the molarity based K_a to mole fraction based K_{eq} , it is necessary to express mole fraction of each species (i.e., water (w), acid (HA), conjugated base (A^-), hydronium ion (H_3O^+)) in terms of the initial acid molar concentration C^o and degree of dissociation α , i.e.,

$$x_w = \frac{d - C^o M_{HA}}{d + C^o [(1 + \alpha) M_w - M_{HA}]} \quad (5)$$

$$x_{HA} = \frac{(1 - \alpha) C^o M_w}{d + C^o [(1 + \alpha) M_w - M_{HA}]} \quad (6)$$

$$x_{ion} = \frac{\alpha C^o M_w}{d + C^o [(1 + \alpha) M_w - M_{HA}]} \quad (7)$$

where *ion* can be either the anion or the cation (i.e., A⁻ or H₃O⁺). The *d* and *M_i* are density of solution [g/cm³] and molecular weight [g/mol] of species *i*, respectively. If the value of α is zero, x_{HA} becomes x_{HA}^o . Using eqns. 5 to 7 in eqn. 4, K_{eq} can be expressed as

$$K_{eq} = \frac{M_w}{[d + C^o((1+\alpha)M_w - M_{HA})]} \frac{\alpha^2 C^o}{(1-\alpha)a_{H_2O}} r_{A^-}^{-\frac{r_{H_3O^+}}{r_{HA}}} \quad (8)$$

For very dilute solutions, the density of solution approaches that of water and water activity becomes unity. Under this condition, the equilibrium constant can be simplified to

$$K_{eq} = \frac{M_w}{d_w} \frac{\alpha^2 C^o}{(1-\alpha)} r_{A^-}^{-\frac{r_{H_3O^+}}{r_{HA}}} = \frac{M_w}{d_w} K_a r_{A^-}^{-\frac{r_{H_3O^+}}{r_{HA}}} \quad (9)$$

Furthermore, choosing the reference state such that the infinite dilution activity coefficients of ions are unity, K_{eq} is further simplified to

$$K_{eq} = \frac{M_w}{d_w} K_a \frac{1}{r_{HA}^\infty} \quad (10)$$

Therefore, the equilibrium constant K_{eq} (which depends only on temperature and not solution composition) can be determined based on the knowledge of K_a (which is valid at infinite dilution limit) provided that the density and molecular weight of the solvent (in this case water, d_w) and the infinite dilution activity coefficient of the undissociated acid, r_{HA}^∞ , is known. In this work, we will use the COSMO-SAC model for calculating r_{HA}^∞ . For diprotic (e.g., H₂SO₄) and triprotic (e.g. H₃PO₄) acids, the expressions between K_{eq} and pK_a are provided in Supporting Information.

One of the properties of central interest in aqueous solutions of acids and bases is the pH. When an acid dissociates in aqueous solution, the proton (H⁺) immediately combines with water

to form the hydronium (H_3O^+) ion. The value of pH in this work is calculated based on the molar concentration of H_3O^+ (moles per liter, M).

$$\text{pH} = -\log_{10} \hat{a} \quad (11)$$

3. The Activity Coefficient Model

The COSMO-SAC activity coefficient model¹⁰ is combined with the Pitzer-Debye-Hückel model¹¹ to describe the activity coefficient due to short-range, surface-contact and long-range, charge-charge interactions.

$$\ln \gamma_i = \ln \gamma_i^{\hat{a} \text{PDH}} + \ln \gamma_i^{\text{COSMO-SAC}} \quad (12)$$

where $\gamma_i^{\text{COSMO-SAC}}$ and γ_i^{PDH} represent contributions from COSMO-SAC and PDH models, respectively. The asterisks in above equation indicate the use of unsymmetric reference states for the activity coefficient: pure liquid for neutral species (i.e., water and acids), and infinite dilution for charged species (i.e., hydronium ion, dissociated ions)¹²⁻¹⁴. Reference state is where activity coefficient becomes unity. The short-range interactions include surface segment interactions from electrostatic (non-hydrogen bonding), hydrogen bonding, ionic, and ionic group, and size and shape effects

$$\ln \gamma_i^{\text{COSMO-SAC}} = n_i \sum_t^{nhb, OH, OT} \sum_{\sigma_m} p_i^t(\sigma_m) [\ln \Gamma_s^t(\sigma_m) - \ln \Gamma_i^t(\sigma_m)] + \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (13)$$

where $n_i = A_i/a_{eff}$ is the number of surface segments of species i , A_i is the surface area, and a_{eff} is

the effective segment area, the coordination number z is taken to be 10, and $\varphi_i = x_i r_i / \sum_j x_j r_j$

and $\theta_i = x_i q_i / \sum_j x_j q_j$ are the volume and surface area fractions (r_i and q_i are the normalized volume and surface area, respectively).

The σ -profile $p_i^s(\sigma_m)$ is the probability of finding a segment of screening charge density σ_m of species i . The superscript s indicates one of the three kinds of surfaces: none hydrogen bonding (nhb) and the hydroxyl group (OH), and other hydrogen bonding groups(OT). $\Gamma_j(\sigma_m)$ is the activity coefficient of a single segment m with a charge density σ_m , and is determined from

$$\ln \Gamma_j^t(\sigma_m^t) = -\ln \left\{ \sum_s^{nhb, OH, OT} \sum_{\sigma_n} p_j^s(\sigma_n^s) \Gamma_j^s(\sigma_n^s) \exp \left[-\Delta W(\sigma_m^t, \sigma_n^s) / kT \right] \right\} \quad (14)$$

where subscript j may be solution S or a pure species i . $\Delta W(\sigma_m, \sigma_n)$ is the segment exchange energy representing the interaction between two segments of charge density σ_m and σ_n . The complete description of $\Delta W(\sigma_m, \sigma_n)$ between different types of segments can be found in Hsieh and Lin¹⁵.

On the other hand, the Pitzer-Debye-Hückel model¹¹ is employed to account for the long-range interactions.

$$\ln \gamma_i^{\text{PDH}} = -\sqrt{\frac{1000}{M_s}} A_\phi \zeta_i \quad (15)$$

where M_s is the molecular weight of solvent and ρ is the closest approach parameter ($\rho = 2.5a(2e^2N_a d_s / (M_s \epsilon_s kT))^{0.5}$, which a is the sum of the radii of each ion ($a_+ + a_-$). I_x is the ionic strength ($I_x = 1/2 \sum_i x_i z_i^2$, where z_i is the electrovalence of species i) and A_ϕ is the Debye-Hückel constant ($A_\phi = 1/3(2\pi N_a d_s / 1000)^{1/2} (Q_e^2 / \epsilon_s kT)^{3/2}$, with d_s being the density of solvent, N_a the Avogadro's number, Q_e the charge of an electron, ϵ_s the average dielectric of solvent, and k the Boltzmann constant). The ion-pair is considered as a co-solvent in the previous work.¹³ The solvent properties are averaged from neutral components,^{13,16} i.e., $M_s = \sum_j x_j / (\sum_k x_k) M_j$, $\epsilon_s = \sum_j M_j x_j / (\sum_k x_k M_k) \epsilon_j$ and $1/d_s = \sum_j x_j / (\sum_k x_k) / d_j$. The PDH+COSMOSAC has been shown to provide a very accurate description of the properties of ionic liquid solutions.^{12,13,17-20}

4. Computational Details

The needed σ -profiles for the COSMO-SAC model are generated using the quantum chemistry package DMol³ implemented in Cerius2.²¹ The molecular geometry is optimized in the ideal gas phase, and is obtained from energy minimization using density functional theory with nonlocal VWN-BP functional with the DNP v4.0 basis set.^{22,23} The COSMO calculation²⁴ is then performed to obtain the screening charges.

For an acid with known K_a , the equilibrium constant K_{eq} can be calculated from eq. 10 with the IDAC of acid in water determined using the PDH+COSMO-SAC model. Once K_{eq} is available, the equilibrium degree of dissociation for a given initial acid concentration, x_{HA}^0 , can then be determined from eq. 4. The equilibrium concentration of each species (i.e., HA, H₂O, A⁻, H₃O⁺, etc.) is then calculated from eqns. 5 to 7. The pH value of the solution is calculated from eq. 11.

The total pressure of an aqueous acid solution is obtained from the summation of the partial pressure of each undissociated components (i.e., HA and water).

$$P = \sum_{HA, H_2O} x_i \gamma_i P_i^{sat} \quad (16)$$

The pK_a , r_{HA}^∞ and K_{eq} used in this work are summarized in Table 1. In order to analyze the effect of species non-ideality, the properties are determined using two different methods: consideration of acid dissociation reaction (e.g., eq. 4, denoted as AD) and consideration of acid dissociation but assuming ideal solution, (i.e., eq. 4 with $K_r=1$, denoted as AD-ideal).

5. Results and Discussions

5.1 The degree of dissociation over full concentration range

Figure 1 shows the degree of dissociation, α , for several weak acids calculated from K_{eq} given in Table 1. The proposed method in this work successfully reproduces the experimentally determined degree of dissociation. The predicted α shows a considerable difference with or without consideration of solution non-ideality (i.e., AD vs. AD-ideal). The methods with considering activity coefficient of species in the solution (i.e., AD) shows a higher accuracy than those without considering non-ideality (i.e., AD-ideal). As can be seen in Figure 2, the solution non-ideality (K_r) varies significantly with acid concentration, resulting in a strong concentration dependency in K_r . Therefore, assuming ideal solution (commonly seen in the literature) fails to correctly reproduce the degree of dissociation of acetic acid over the whole concentration range.

The situation is more complicated for strong acids due to the formation of hydration complex, i.e., $\text{HA}(\text{H}_2\text{O})_n$,^{25,26} particularly in the dilute state. For this reason, the experimental pK_a values^{25,27} for nitric acid are reported in broad range from -1.3 to -3.78 and for sulfuric acid from -3.59 to -8.3, respectively (see Table 1). More detailed analysis show that the difference is a result of different hydration complexes being considered. E. Högfeldt²⁵ reported that the pK_a for nitric acid takes the value of -1.44, -2.09 and -3.78 for $\text{HNO}_3(\text{H}_2\text{O})_3$, $\text{HNO}_3(\text{H}_2\text{O})$ and HNO_3 , respectively. For sulfuric acid, the pK_{a1} values are -4.93 and -8.3 for $\text{H}_2\text{SO}_4(\text{H}_2\text{O})$ and H_2SO_4 , respectively.

The different pK_a values result in the equilibrium constants K_{eq} (see Table 1) which lead to different degrees of dissociation. Figure 3 shows the effect of different pK_a values on the degree of dissociation α for nitric acid in aqueous solutions. The difference in α based on different pK_a values (i.e., -1.3, -2.09, -3.78) is clear and the predicted α from using a small pK_a value (-3.78) is in better agreement with the experimental data. This implies that the pK_a value for non-hydrated HNO_3 is more suitable for the calculation of K_{eq} in our method. The predicted α without considering non-ideality (i.e., AD-ideal) is overestimated. This again shows the importance of inclusion of the activity coefficient in the calculation of equilibrium species concentrations in acidic aqueous solutions.

The sulfuric acid has two protons. The experimental value of pK_{a1} of the first deprotonation (R2 in Supporting Information) also shows large variations (i.e., -3.59, -4.93, -8.3).²⁵ Figure 4 depicts the predicted degree of dissociation α_1 and α_2 for sulfuric acid according to the extreme pK_{a1} values (i.e., -3.59 and -8.3). The predicted α_1 with $pK_{a1}=-8.3$ is much closer to experimental α_1 than that with $pK_{a1}=-3.59$. The experimental dissociation degree α_1 (symbols in Figure 4: +, ×,

-) remains as unity up to 0.4 mole fraction of sulfuric acid (i.e., $x_{\text{sulfuric acid}}^o \approx 0.4$), while the predicted value decreases after the mole fraction reached 0.1 and 0.2 for $pK_{a1} = -3.58$ and -8.3 , respectively. However, none of these pK_{a1} values reproduces the non-monotonic concentration dependence of α_2 , which is known as the redissociation phenomenon. This phenomenon is found by the competition between the dilution of undissociated specie and the molecular interactions.¹² The discrepancy between the predicted and experimental data might be caused by more complicated hydration effect of water. Robertson and Dunford²⁶ investigated the hydration effect of water on reactions R2 and R3 (see Supporting Information) and suggested that H_2SO_4 and HSO_4^- may react with different number of water molecules. Accordingly, the reaction between bisulfate and water is formed favorably in dilute sulfuric acid solution (i.e., $< 40 \text{ m C}_{\text{H}_2\text{SO}_4^o}$) with $\text{HSO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^{+n} + \text{SO}_4^{2-n}$ ($n \in 0, 1, 2, 3$). In concentrated sulfuric acid solution (i.e., $> 40 \text{ m C}_{\text{H}_2\text{SO}_4^o}$) the reaction between sulfate and water is favored; $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^{+n} + \text{HSO}_4^{1-n}$. In both reactions, as the number of n is increased, the association constant $\log K_a$ is larger; that is, the R2 and R3 dissociation process with more water molecule are favored. In our prediction, however, the hydrated forms with different number of water molecule are not considered.

On the other hand, the first deprotonation reaction (R2) is determined to be 100% in many experiment due to the fact that there is essentially no molecular sulfuric acid (H_2SO_4) in 40 molal acid (ca. 80 wt%) based on infrared spectra experiment.²⁸ Therefore, R2 is often ignored (i.e., $\alpha_1=1$) and only the degree of dissociation (α_2) for second deprotonation step (R3) are reported.²⁹⁻
³⁶ Figure 5 shows the predicted result with the assumption of $\alpha_1=1$. It is interesting to note that when the first deprotonation is assumed to be 100%, our model correctly predicts the

redissociation phenomenon in second dissociation process (R3), albeit with a higher value of α_2 compared to experimental (symbols in Figure 5: o, \square , Δ , \diamond).

Figure 6 illustrates the predicted degree of dissociation of phosphoric acid (α_1 , α_2 and α_3) for each dissociation step. The first dissociation step is more favored than the other two steps. Second dissociation (α_2) slightly decreases as the concentration of phosphoric acid is increased. Third dissociation (α_3) is almost negligible. The first degree of dissociation is under-predicted compared to experimental data. The main discrepancy might be coming from the consideration of the anionic dimer $H_5P_2O_8^{-4}$ by the additional dissociation reaction (i.e., $H_3PO_4 + H_2PO_4^{-2} \leftrightarrow H_5P_2O_8^{-4}$) in the experiment analysis procedure.³⁷⁻³⁹ The dissociation constant K_a (=1.263) of this reaction is much larger than the value of 0.007107 for first dissociation step (i.e., $H_3PO_4 + H_2O \leftrightarrow H_3O^{+1} + H_2PO_4^{-2}$). Therefore, the consideration of an additional reaction leads to favorable first dissociation step. In other words, anionic dimer contributes a high degree of dissociation α_1 . Cherif et al.³⁹ also reported a similar result with Raman spectroscopy that the higher degree of dissociation α_1 at high phosphoric acid concentration range is found when anionic dimer $H_5P_2O_8^{-4}$ is taken into account. Figure 7 supports such a fact. The consideration of anionic dimer $H_5P_2O_8^{-4}$ shows a better agreement to the experimental degree of dissociation^{37,39-41} α_1 as well redissociation of phosphoric acid.

5.2 The pH value over full range

The pH measurement is mainly carried out at very dilute concentration range because of the structural vulnerability of pH electrode.^{42,43} Thus, the measurement of pH is very limited at high

concentration ranges, where the non-ideality for ions is very strong and the pH value shows a significant difference with and without considering activity coefficients of ions.⁴⁴ On the other hand, the prediction with COSMO-SAC model allows for the calculation over the whole concentration range with considering interactions among molecules such as water, undissociated acid and ions (cations and anions). The concentration for each species depends on the degree of dissociation of the undissociated acid. Calculation of the pH of weak acids is a bit more complicated than determining the pH of a strong acid because weak acids do not completely dissociate in water. Therefore, the degree of dissociation of acid should be included in the prediction of pH. The proposed method can be applied directly to calculate the pH of acids in aqueous solution.

Figure 8 shows the comparison of experimental and predicted pH of several acidic aqueous solutions over whole concentration range. The predicted pH with the consideration of the dissociation of acetic acid captures the tendency of experimental pH, $\text{pH}(\text{exp.})$ which is estimated from experimental degree of dissociation with acetic acid's concentration (i.e., $\text{pH}(\text{exp.}) = -\log_{10}[\alpha \cdot C_{\text{HA}}^0]$). The pH value for all acids drops rapidly by adding more acid into the solution at low concentrations. The pH value eventually approaches 7 as the solution becomes very concentrated and most of the acid molecules are in the undissociated state. As can be seen in Figure 8b, the slopes for pH vs acid's concentration at dilute concentration range show different values. Such results are attributed to the consideration of non-ideality ($\gamma_A \neq 1$) of the activity coefficient of conjugated base A^- . A stronger acid shows a more rapid decrease in the pH value with increasing concentration, since strong acid is easily dissociated in comparison to weak acids.

Figure 9 illustrates the predicted and experimental pH values for sulfuric acid. The experimental pH (i.e., pH(exp.)) values are obtained from experimental measurement.^{45,46} The predicted pH values are estimated based on the concentration of hydronium ions H_3O^+ (i.e., $\text{pH} = -\log_{10}[(\alpha_1 + \alpha_2) \cdot C_{\text{H}_2\text{A}^\circ}]$). The predicted pH values with the assumption of $\alpha_1 = 1$ (i.e., $\alpha_1 = 1$, $\text{p}K_{a2} = 1.99$) and those with the two protonation steps (i.e., $\text{p}K_{a1} = -8.3$, $\text{p}K_{a2} = 1.99$) are similar even though the predicted degree of dissociation of sulfuric acid shows a considerably difference (see Figure 4 and 5). At high concentration range, the difference between the two assumptions increases. However, there is no experimental data at such high concentrations to discern which model is more appropriate.

5.3 The vapor pressure of acidic aqueous solution

Here we investigate the effect of acid's dissociation on its macroscopic property, vapor pressure of the solution. For weak acids the effects are minor because the vapor pressure is dominated by that of water at low acid concentrations (where α is large). The total pressure becomes dominated by the undissociated acid at high acid concentrations (where α is small). The vapor pressure of formic acid and acetic acid are illustrated in Figure S1 (in Supporting Information).

On the other hand, the dissociation of strong acids has a great influence on the solution vapor pressure. Figure 10 shows the predicted results of the vapor pressure as a function of nitric acid (Figure 10a) and sulfuric acid (Figure 10b) concentration in aqueous solutions. For nitric acid, both the partial pressure of water and nitric acid, and the vapor pressure of the mixture from

the proposed method are in good agreement with experiment. If nitric acid and sulfuric acid aqueous solutions are considered as an ideal solution, the partial and total pressures are both overestimated because their activity coefficients are a unity while in real solution are less than unity. Therefore, proper consideration of deprotonation and solution non-ideality is very important for accurate prediction of their vapor pressures of aqueous solutions containing strong acids.

6. Conclusions

In this work, we derive the formula to obtain the equilibrium constant K_{eq} from experimental pK_a . The so determined equilibrium constant is then used to predict the degree of dissociation for weak/strong acids, its pH and vapor pressure in aqueous solutions. Our analysis show that the activity coefficients (and their ratios, K_r) are critical for accurate determination of the degree of deprotonation of acid over a wide concentration range. The combined use of PDH and COSMO-SAC model provides satisfactory prediction of the needed species activity coefficients. Both the predicted pH values and vapor pressure are found to be in good agreement with experiments. The use of K_{eq} thus extends one's capability to describe the properties of acidic aqueous solutions beyond where pK_a is applicable.

It is worthwhile to address the assumptions and limitations of the proposed approach. In this work, we consider only the most important dissociation reactions (R1 or monoprotic acids, R2+R3 for diprotic acids, and R4+R5+R6 for triprotic acids). The possible formation of various hydrated acidic ions is completely ignored. This may be overly simplified. However, we also find that, with a proper choice of pK_a value for the unhydrated acids, the predicted properties can

be in very good agreement with the experiment. While for the formation of hydrated ions should deserve more study, the proposed model should find its use in many practical applications where the thermodynamic properties of acidic solutions are needed over a wide range of concentrations.

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Table

Table 1. The experimental values of pK_a and predicted equilibrium constants K_{eq} for acids in aqueous solutions

Acids and water	pK_a (experiment)	r_{HA}^{∞} (predicted)	K_{eq} (eq. 10)
formic acid	$pK_a=3.75^{26}$	1.33	2.42×10^{-6}
acetic acid	$pK_a=4.76^{26}$	3.66	8.58×10^{-8}
butyric acid	$pK_a=4.83^{26}$	46.26	5.78×10^{-9}
nitric acid	$pK_a=-1.3^{26}$	0.57	6.32×10^{-1}
	$pK_a=-2.09^{26}$		3.90
	$pK_a=-3.78^{25}$		1.91×10^2
sulfuric acid	$pK_{a1}=-3^{26}$	0.000551463	$K_{eq(1)}=3.28 \times 10^4$
	$pK_{a1}=-4.93^{25}$		$K_{eq(1)}=2.79 \times 10^6$
	$pK_{a1}=-8.3^{25}$		$K_{eq(1)}=6.54 \times 10^9$
	$pK_{a2}=1.99^{26}$		$K_{eq(2)}=1.85 \times 10^{-4}$
phosphoric acid	$pK_{a1}=2.148^{26}$	0.00765171	$K_{eq(1)}=1.68 \times 10^{-2}$
	$pK_{a2}=7.198^{26}$		$K_{eq(2)}=1.15 \times 10^{-9}$
	$pK_{a3}=12.35^{26}$		$K_{eq(3)}=8.07 \times 10^{-15}$

Figure Captions

Figure 1. The predicted degree of dissociation for formic acid (a), acetic acid (b) and butyric acid (c). The experimental data are obtained from reference (formic acid⁴⁷⁻⁴⁹, acetic acid^{50,51}, butyric acid⁴⁷ and nitric acid⁵²⁻⁵⁵).

Figure 2. The contributions of K_x and K_r for acetic acid aqueous solution.

Figure 3. The degree of dissociation of nitric acid in aqueous solution based on different pK_a values. The experimental data are obtained from reference⁵²⁻⁵⁵.

Figure 4. The degree of dissociation of sulfuric acid in aqueous solution based on different pK_{a1} values (i.e., -8.3 and -3.59) with the mole fraction of sulfuric acid, $x_{H_2A}^o$ in log scale (a) and in linear scale (b). The experimental data are obtained from references: (+, o) Robertson and Dunford²⁶; (x) Leuchs and Zundel³⁰; (●) Margarella et al.³¹; (□) Kerker³²; (■) Wu and Feng³³; (Δ) Knopf et al.³⁴; (▲) Chen and Irish³⁵; (-,◇) Hood and Reilly⁵⁶; (◆) Young et al.³⁶

Figure 5. The degree of dissociation of sulfuric acid in aqueous solution based on $\alpha_1=1$ and $pK_{a2}=1.99$ with the mole fraction of sulfuric acid, $x_{H_2A}^o$ in log scale (a) and in linear scale (b). All symbols are same as those in Figure 4.

Figure 6. The degree of dissociation of phosphoric acid with the mole fraction of phosphoric acid, $x_{H_3A}^o$ in log scale (a) and in linear scale (b). The experimental data are obtained from reference^{37,39-41}.

Figure 7. The degree of dissociation of phosphoric acid with the mole fraction of phosphoric acid, $x_{H_3A}^o$ with considering anionic dimer $H_5P_2O_8^{-6}$.

Figure 8. The experimental and predicted pH (molality base) of acid aqueous solutions over whole concentration range.

Figure 9. The experimental and predicted pH (molality base) of sulfuric acid aqueous solution over whole concentration range. The experimental data are obtained from reference^{39, 40}.

Figure 10. The experimental^{57,58} and predicted vapor pressure for (a) nitric acid ($pK_a=-3.78$) aqueous solution and (b) sulfuric acid ($pK_a=-8.3$) aqueous solution.

Figure

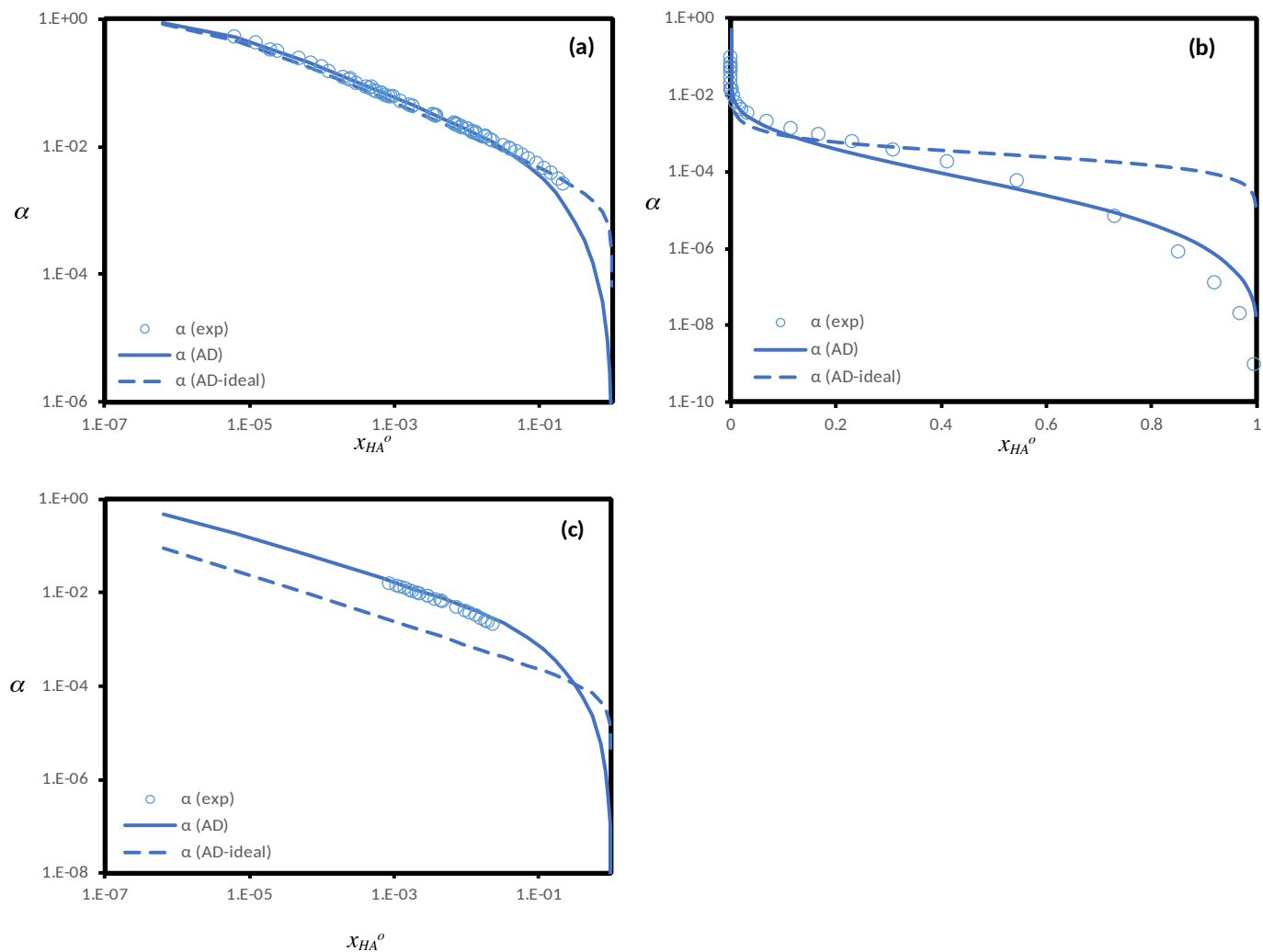


Figure 1. The predicted degree of dissociation for formic acid (a), acetic acid (b) and butyric acid (c). The experimental data are obtained from reference (formic acid⁴⁷⁻⁴⁹, acetic acid^{50,51}, and butyric acid⁴⁷).

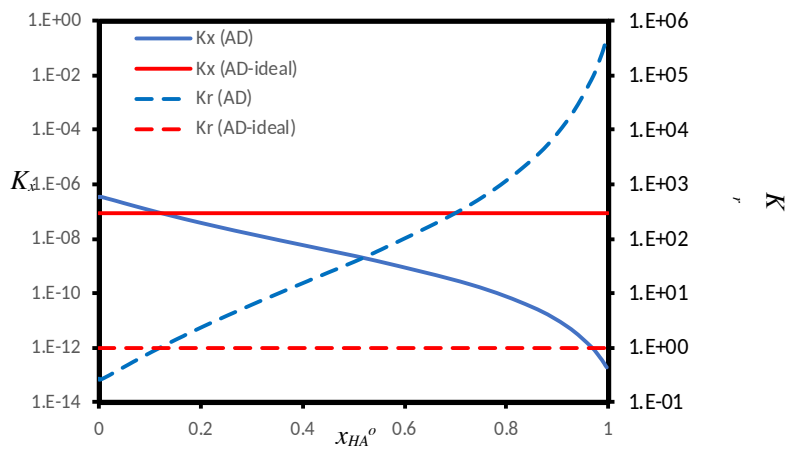


Figure 2. The contributions of K_x and K_r for acetic acid aqueous solution.

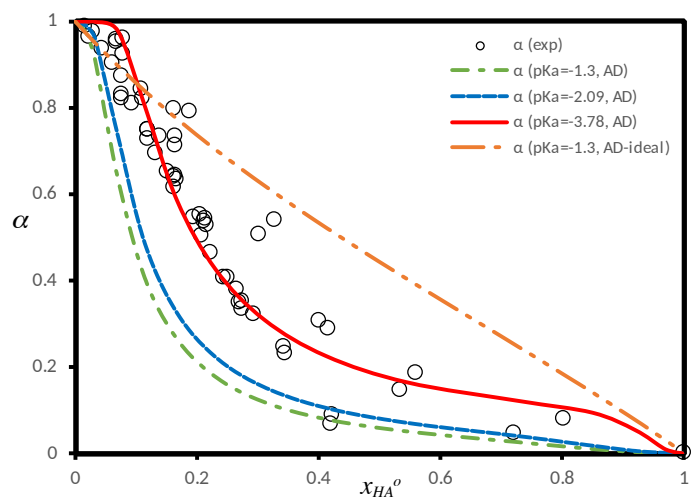


Figure 3. The degree of dissociation of nitric acid in aqueous solution based on different pK_a values. The experimental data are obtained from reference ⁵²⁻⁵⁵.

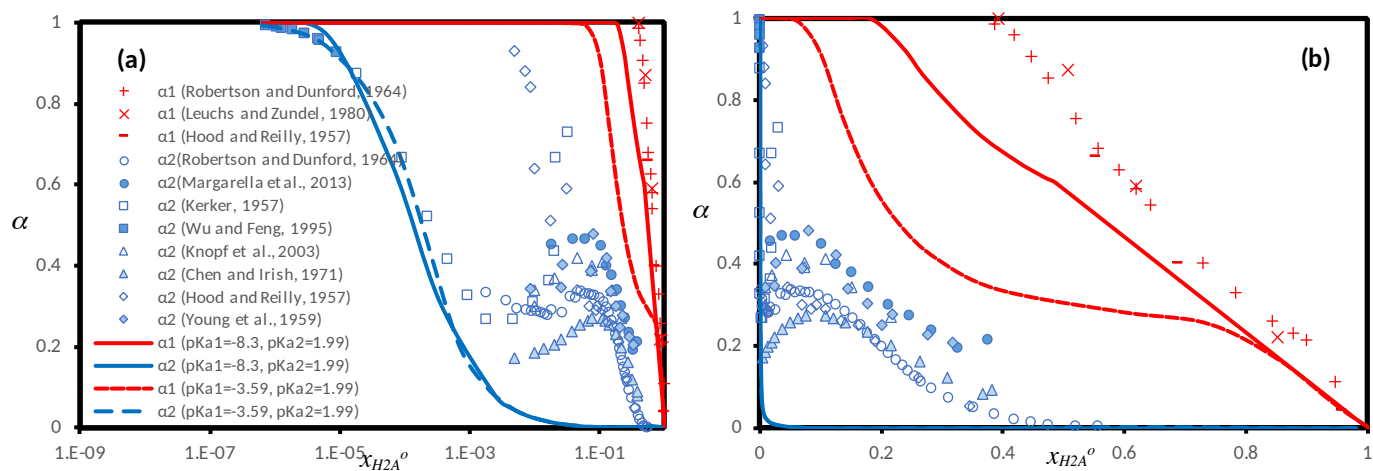


Figure 4. The degree of dissociation of sulfuric acid in aqueous solution based on different pK_{a1} values (i.e., -8.3 and -3.59) with the mole fraction of sulfuric acid, x_{H2A}^o in log scale (a) and in linear scale (b). The experimental data are obtained from references: (+, o) Robertson and Dunford²⁶; (x) Leuchs and Zundel³⁰; (●) Margarella et al.³¹; (□) Kerker³²; (■) Wu and Feng³³; (Δ) Knopf et al.³⁴; (▲) Chen and Irish³⁵; (-,◇) Hood and Reilly⁵⁶; (♦) Young et al.³⁶.

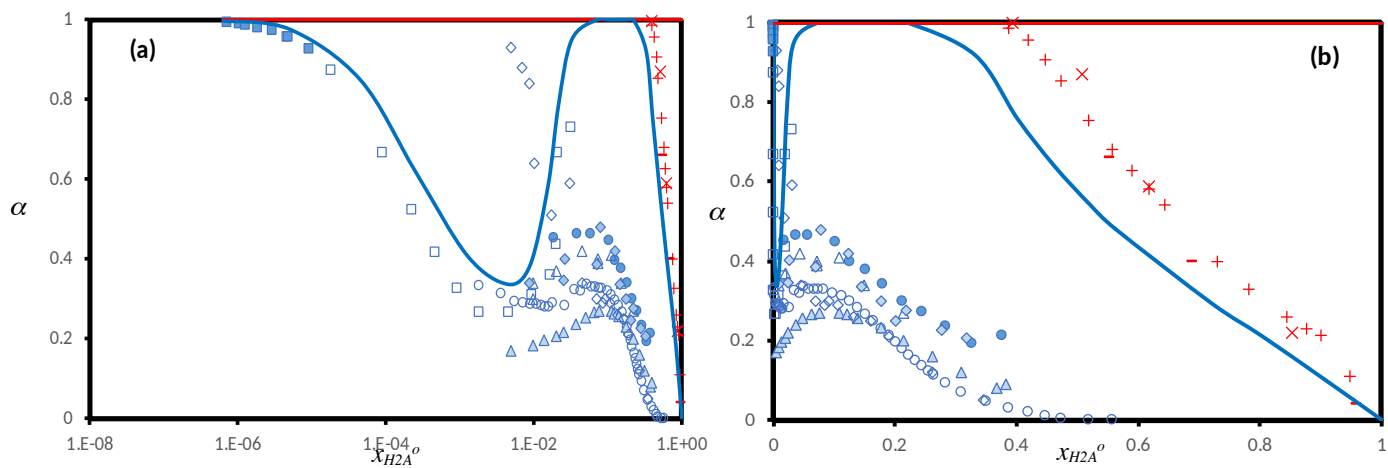


Figure 5. The degree of dissociation of sulfuric acid in aqueous solution based on $\alpha_1=1$ and $pK_{a2}=1.99$ with the mole fraction of sulfuric acid, x_{H2A^0} in log scale (a) and in linear scale (b). All symbols are same as those in Figure 4.

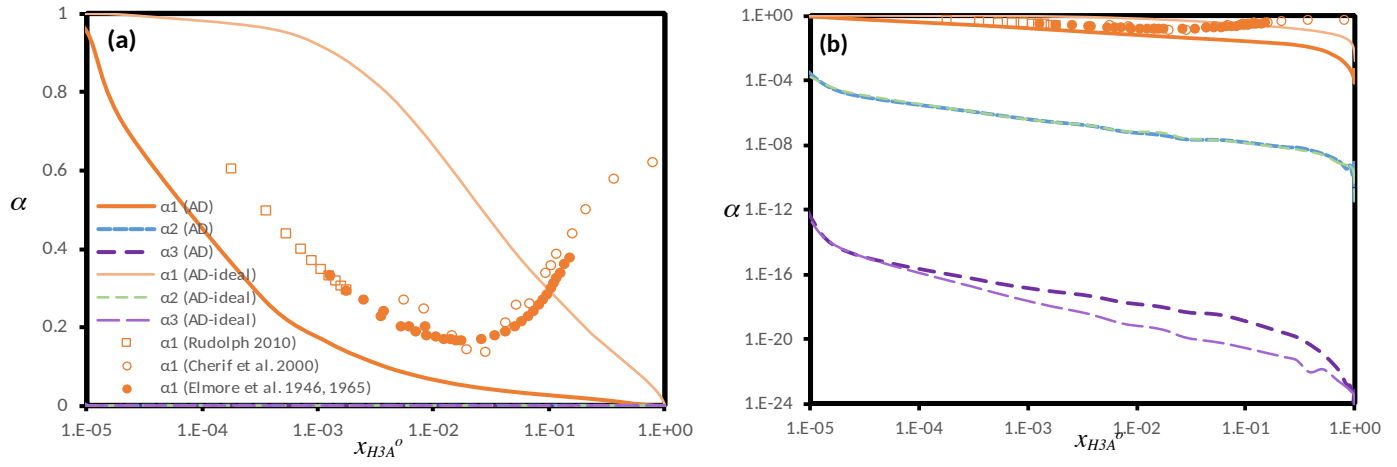


Figure 6. The degree of dissociation of phosphoric acid (in linear scale (a) and in log scale (b)) with the mole fraction of phosphoric acid, x_{H3A}^o in log scale. The experimental data are obtained from reference^{37,39-41}.

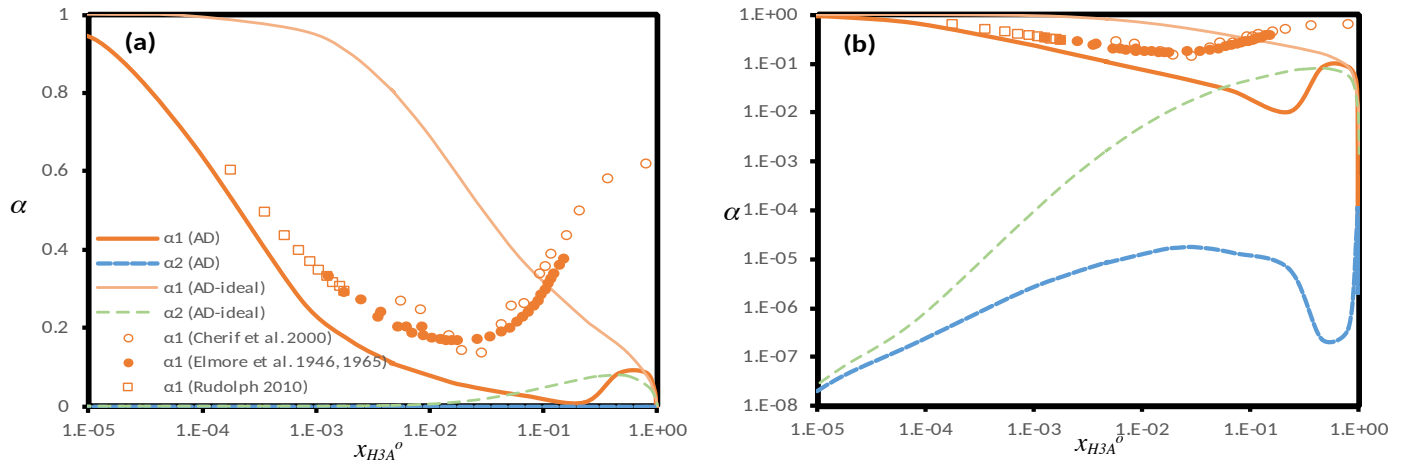


Figure 7. The degree of dissociation of phosphoric acid (in linear scale (a) and in log scale (b)) with the mole fraction of phosphoric acid, x_{H3A}^o with considering anionic dimer $H_5P_2O_8^{--}$.

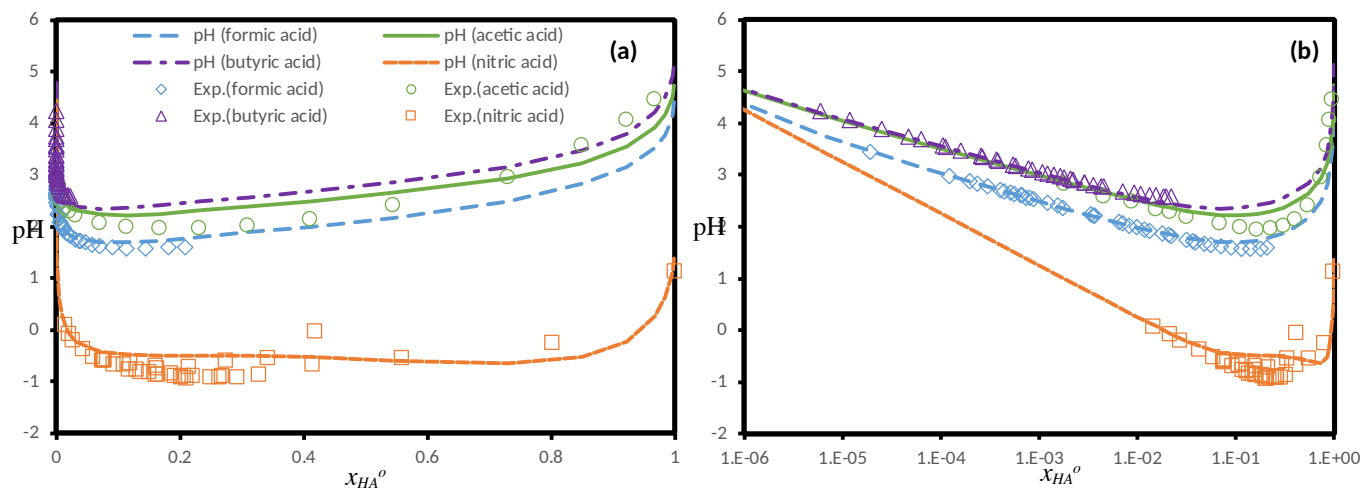


Figure 8. The experimental and predicted pH (molality base) of acid aqueous solutions over whole concentration range in linear scale (a) and in log scale (b).

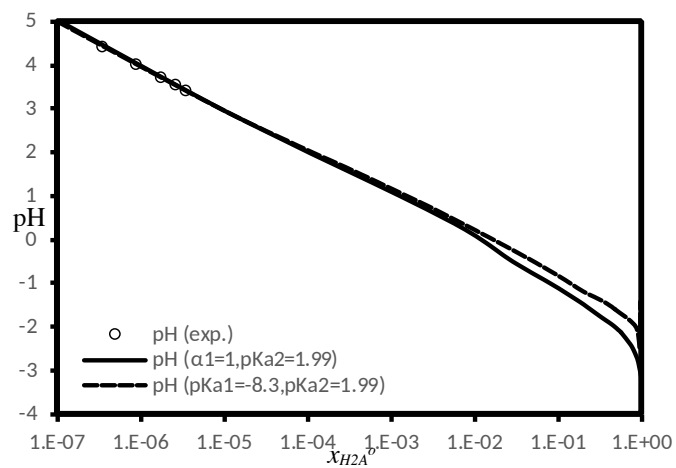


Figure 9. The experimental and predicted pH (molality base) of sulfuric acid aqueous solution over whole concentration range. The experimental data are obtained from reference.^{39, 40}

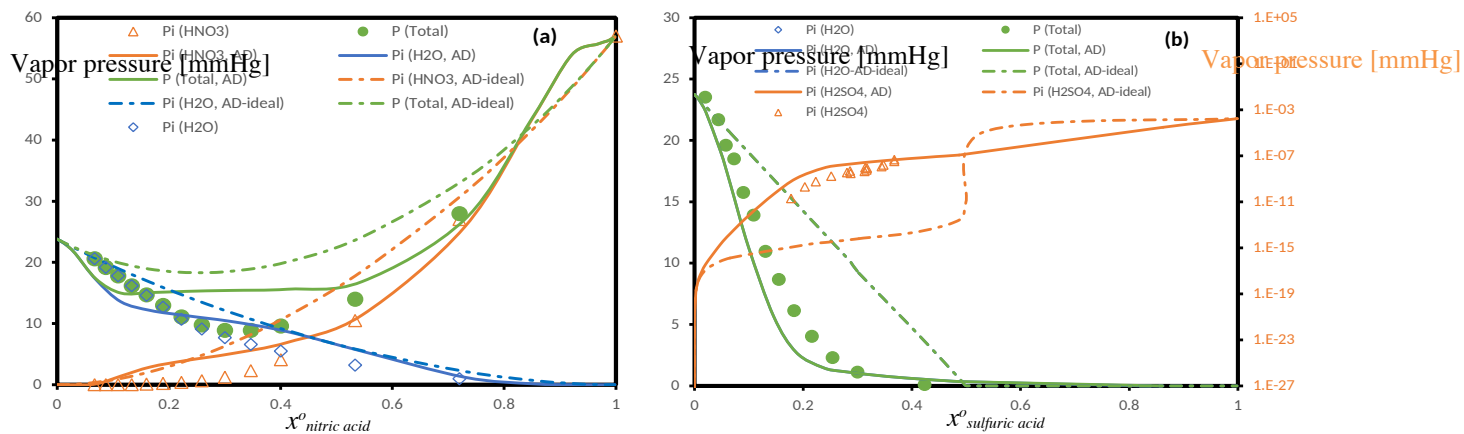


Figure 10. The experimental⁵⁷⁻⁵⁹ and predicted vapor pressure for (a) nitric acid ($pK_a=-3.78$) aqueous solution and (b) sulfuric acid ($pK_{a1}=-8.3$) aqueous solution.