Agreement of electrolyte models with activity coefficient data of sulfuric acid in water

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ABSTRACT

The calculation of thermodynamic properties of many strong electrolytes in solution, including aqueous sulfuric acid, has been performed over the past four decades using so-called thermodynamic models, such as the well-known Pitzer model. I have recently pointed out (Fraenkel, 2012) [15,16] that H_2SO_4 in water appears to follow the mean ionic activity pattern of a strong 1–3 electrolyte, and postulated that this H_3A acid may be H_4SO_5 fully ionizing to $3H^+$ ($3H_3O^+$) and HSO_5^{3-}. This contrasts with the traditional view of the aqueous acid – claimed to be supported by thermodynamic models – according to which H_2SO_4 retains its molecular structure in water and dissociates primarily to H^+ and HSO_4^-, and at <0.1 M, HSO_4^- dissociates further to H^+ and SO_4^{2-}. I now show that a good fit of Pitzer model with the activity coefficients reported by Hamer and Harned can be obtained for the "1–3 H_2SO_4" even by using the simple 3-parameter equation of the model; the best-fit Pitzer parameters are $\beta^{(0)} = 0.240$, $\beta^{(1)} = 4.30$ and $C_{MX} = -0.0134$, and the standard deviation, σ is 0.0152. With the corrected activity coefficients as proposed in the first reference above, the best-fit parameters are $\beta^{(0)} = 0.230$, $\beta^{(1)} = 3.60$ and $C_{MX} = -0.0120$, and $\sigma = 0.0081$. σ of the analysis of the "1–3 acid" is in both cases considerably lower than that of the "1–2 acid" ($\sigma = 0.049$) that provides a best-fit $\beta^{(1)}$ value of -3.000; a negative $\beta^{(1)}$ is inappropriate since it is parallel to a negative ion–ion distance of closest approach in Debye–Hückel-type expressions of the activity coefficient.

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1. Introduction

In spite of the tremendous role electrolyte solutions play in many fields of science and technology – biology and physiology [1–3], chemistry and physics [4–7], engineering and process design [8], catalytic reactions and their mechanisms [9], membrane processes [10], and more – a complete understanding of the thermodynamic behavior of such solutions is still lacking. Electrolyte solutions exhibit a "thermodynamic non-ideality" that results in "excess functions"; for example, osmotic coefficients and activity coefficients. Modeling electrolytes by fundamental electrostatic correlations [11] connecting between physical factors in solutions, e.g., permittivity and ion-size, and the excess functions, e.g., the *mean ionic activity coefficient*, $\gamma_\pm$ (molal), may further advance our comprehension of the physical factors influencing the thermodynamic properties of such systems. The present article focuses on one electrolyte system – sulfuric acid in water – and on the analysis of its thermodynamic nature *via* modeling.

Sulfuric acid, H_2SO_4, is world's most important industrial chemical [12], affecting our everyday life in many ways; it is used in lead

storage batteries, fertilizer production, catalytic processes, ore and mineral dissolution and processing, resin manufacture, etc. Aqueous H_2SO_4 has a strong impact on the environment, e.g., as acid rain, and on global climate, as aerosol in the troposphere and stratosphere [13,14]. We, therefore, should strive to improve our knowledge and understanding of the structure, chemical behavior and physical properties of the acid, especially in water solution. Previously, I revisited the analysis of the mean ionic activity [15] and the acidity and base neutralization [16] of aqueous sulfuric acid, in attempt to shed new light on the physicochemical nature of dissolved H_2SO_4. That study has called attention to the fact that aqueous sulfuric acid, in the approximate concentration range 0–5 M, behaves as a 1–3 strong electrolyte; a plausible explanation for this behavior is that the acid is, in fact, H_4SO_5 (*para*sulfuric acid) fully dissociating, practically in one step, to three protons (appearing as hydronium, i.e., H_3O^+ ions) and the trivalent anion HSO_5^{3-} (*para*bisulfate ion). I now revisit the examination of aqueous sulfuric acid by so-called thermodynamic models.

The literature view of aqueous sulfuric acid is that the dissolved acid is H_2SO_4 dissociating to a mixture of H^+, HSO_4^- and SO_4^{2-}, and it is a strong 1–1 electrolyte and a "moderately weak" [17] 1–2 electrolyte. This view appears to be at odds with the thermodynamic nature of aqueous H_2SO_4, as reflected by the change of the acid's

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$\gamma_\pm$ with concentration [15]; this contradiction prevails in spite of claims to the contrary made in the most authoritative literature on electrolyte solutions [17,18]. Analyses of aqueous sulfuric acid by thermodynamic models of ionic solutions, such as Pitzer model, have been published extensively [19–26]. Because such analyses have always been based on the traditional literature's view of aqueous H_2SO_4, in this report I examine Pitzer model to enquire whether (a) model fit with experiment, based on the literature's view, is indeed effective; (b) the fit indeed proves the electrolyte nature of the aqueous acid, asserting that the acid is a partially dissociated diprotic H_2SO_4; and (c) the model would, therefore, not fit with the acid as a fully dissociated ("strong") 1–3 electrolyte. I also provide a comparison between Pitzer model and the newly proposed DH–SiS model, an extended Debye–Hückel (DH) model, also known as the Smaller-ion Shell treatment [27]. To distinguish between the two types of models, I shall refer to the latter as "phenomenological model".

Pitzer *et al.* [19] applied the Pitzer equations [28,29] for the analysis of aqueous sulfuric acid, and by optimizing parameters to achieve best fit, they obtained fitted equations for the calculation of the excess functions of the acid in solution. Pitzer *et al.* tabulated the activity and osmotic coefficients of aqueous H_2SO_4 for various m values in the range 0.1–6. Clegg and coworkers [21–23] have later employed Pitzer model in modified forms for improving the analysis of sulfuric acid. They used an extended form of the Pitzer m-based model with an I-dependent third virial coefficient; the model parameters were fitted to data of excess functions, e.g., ionic activity, and the authors claimed [21] that the aim of their study was "*to provide an accurate and self-consistent description of aqueous solution activities and thermal properties of aqueous* H_2SO_4" with a broad range of temperatures (0–55 °C) and concentrations (up to 6m). In a recent report [22], "*Pitzer ion-interaction model*" has been used for calculating apparent molar volumes and solution densities for the ($H_2SO_4 + H_2O$) system; earlier [23], the same system was studied using a "*multicomponent mole-fraction-based thermodynamic model*", another version of Pitzer model. May *et al.* [24] have recently updated Pitzer treatment of ionic solutions for 183 different binary electrolytes and found six – H_2SO_4 among them – as "*completely intractable*" with Pitzer model. The authors pointed out that as many as eighteen free parameters, as specified by them (β's and C_{MX}'s), may have to be optimized for a complete characterization of the thermodynamic properties of a binary electrolyte at a given temperature and pressure; of those, 3-to-4 parameters are necessary for the activity coefficient (depending on ion charges). May *et al.* attributed the failure of Pitzer model to address the six intractable electrolytes to changes in chemical speciation occurring in those electrolytes at relatively low concentration, which require the explicit involvement of speciation equilibria. A very broad and detailed analysis of aqueous sulfuric acid has been recently reported by Que *et al.* [25] using a "*comprehensive thermodynamic model*" ("Chen model") based on a NRTL model for the activity coefficient, as developed previously [26]. A brief description and critique of Chen model and its use in the analysis of H_2SO_4 in water, is presented in Appendix A.

The goal of the present work is two-fold:

(1) A comparison of model fit, that is, theory with experiment, as $\gamma_\pm$ *vs.* concentration at 25 °C, for aqueous H_2SO_4; doing this using a thermodynamic model, represented here by the classical Pitzer model, for various choices of electrolyte valence families.

(2) A comparison of model fit for aqueous H_2SO_4 between Pitzer model and DH–SiS; from this, a conclusion can be drawn on the ability of Pitzer model to distinguish between different cases of sulfuric acid speciation in water, and the quality

of the Pitzer model fit as compared to that of a "non-thermodynamic" model (DH–SiS) that optimizes with experiment by adjusting ion-size parameters (ISPs) instead of virial coefficients.

Following Section 2, in which the models and computation methods of the current work are presented briefly, Section 3 (Results) provides first a "calibration" of the Pitzer equation used in the current analysis, *vs.* electrolytes of valence families pertaining to the analysis of sulfuric acid; it then presents fits of Pitzer equation with the original activity data of the acid, as reported by Hamer and Harned, see [18]; finally, Section 3 presents similar fits, including that of DH–SiS, with the corrected data of Hamer and Harned, as reported recently [15]. Section 4 (Discussion) interprets the results in view of the models used and their strengths and limitations, and Section 5 (Conclusion) summarizes the main results of the present model comparison.

2. Models and computation methods

2.1. Pitzer equation

In the present study, I have used the 3-parameter Pitzer equation for $\gamma_\pm$ as a function of ionic strength and concentration, i.e., the equation with $\beta^{(0)}$, $\beta^{(1)}$ and C_{MX} as the only adjustable parameters [28,29]. Cast in a straightforward and an easy-to-use form, this equation is

$$\log \gamma_\pm = -\frac{1}{3}\mathcal{A}\,|z_M z_X| \left[\left(\frac{I^{1/2}}{1+bI^{1/2}}+\frac{2}{b}\ln(1+bI^{1/2})\right)+\left(\frac{2v_M v_X}{v}\right)\left(\right.\right.$$
$$\left.\times\left\{2\beta^{(0)}+\frac{2\beta^{(1)}}{\alpha^2 I}\left[1-\left(1+\alpha I^{1/2}-\frac{1}{2}\alpha^2 I\right)\exp(-\alpha I^{1/2})\right]\right\}m\right.$$
$$\left.\left.+C_{MX}\,\frac{2(v_M v_X)^{3/2}}{v}\right)m^2\right].$$

(1)

In equation (1), I is ionic strength, m is molality, z_M and z_X are the corresponding valences (or ionic charges) of the cation and anion, v_M and v_X are the number of cations and the number of anions, respectively, in the molecular formula of the electrolyte, and $v = v_M + v_X$. In water at 25 °C, the value of the α and b parameters are arbitrarily chosen as 2 and 1.2, respectively [28,29]. $\mathcal{A}$ is the well-known constant of the DH limiting law (DHLL); in water at 25 °C, its value in molal scale is 0.51006 (kg-solvent/mol-solute)$^{1/2}$ [30].

Using a simple Microsoft Excel computation program, I have optimized the fit of equation (1) with experimental data ($\gamma_\pm$ *vs.* concentration) through adjusting $\beta^{(0)}$, $\beta^{(1)}$ and C_{MX}. All electrolytes examined here are in water at 25 °C. The fit in all cases was done, as in the literature [28,29], by adjusting the three Pitzer parameters simultaneously until reaching the lowest standard deviation, σ. σ has been calculated using Excel's STDEV function run over all consecutive data points (of $\gamma_\pm$) as reported in the literature, at a chosen m range. The range of concentration of the computation is referred to as "fit range". The results of the above fits are discussed below and summarized in table 1.

2.2. DH–SiS expression

In order to present Pitzer model in a broader perspective in terms of its ability to analyze aqueous sulfuric acid, the model is compared here with the DH–SiS model [15,27]. Unlike Pitzer model, DH–SiS is not a semiempirical thermodynamic model but an *ab initio* (phenomenological) model, somewhat simplified, that