Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 71 (2007) 2680–2698

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Application of the Pitzer ion interaction model to isopiestic data for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 298.15 and 323.15 K

Nicholas J. Tosca *, Alexander Smirnov, Scott M. McLennan

Department of Geosciences, State University of New York, Stony Brook, NY 11794-2100, USA

Received 15 August 2006; accepted in revised form 16 March 2007; available online 31 March 2007

Abstract

Recent isopiestic studies of the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 298.15 K are represented with an extended version of Pitzer's ion interaction model. The model represents osmotic coefficients for aqueous $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixtures from 0.45 to 3.0 m at 298.15 K and $0.0435 \leqslant y \leqslant 0.9370$. In addition, a slightly less accurate representation of a more extended molality range to 5.47 m extends over the same y values, translating to a maximum ionic strength of 45 m. Recent isopiestic data for the system at 323.15 K are represented with the extended Pitzer model over a limited range in molality and solute fraction. These datasets are also represented with the usual "3-parameter" version of Pitzer's model so that it may be incorporated in geochemical modeling software, but is a slightly less accurate representation of thermodynamic properties for this system. Comparisons made between our ion interaction model and available solubility data display partial agreement for rhomboclase and significant discrepancy for ferricopiapite. The comparisons highlight uncertainty remaining for solubility predictions in this system as well as the need for additional solubility measurements for Fe^{3+}-bearing sulfate minerals. The resulting Pitzer ion interaction models provide an important step toward an accurate and comprehensive representation of thermodynamic properties in this geochemically important system.

---

1. INTRODUCTION

Ferric iron-bearing acid sulfate solutions are important in many industrial and surficial environments on Earth, and it has recently been discovered that they were perhaps common in surficial environments on Mars. Describing the thermodynamic properties of Fe^{3+}-rich acid sulfate solutions is a critical step in understanding a variety of geologic problems that arise on both Earth and Mars. Environments on Earth affected by pyrite oxidation and associated acid mine drainage (AMD) continue to present a threat to biological activity as well as to water and soil quality in surrounding areas (Nordstrom and Alpers, 1999a,b). AMD processes often result in surface waters that are highly concentrated in Fe^{3+}, SO_4^{2-}, toxic metals such as As, Cd, Pb and Zn, and are extremely acidic. Indeed, some of the lowest pH values ever recorded on Earth have been recorded in AMD environments, with values approaching −3.6 (Nordstrom and Alpers, 1999b). More specifically, in the Richmond Mine at Iron Mountain, CA, Fe^{3+} has been found to occur at levels of approximately 147 g L^{-1}, or 1.7 mol kg^{-1} (when corrected for density) (Jamieson et al., 2005). Total sulfate concentrations in these systems have been reported to approach 5.3 mol kg^{-1}, which often equates to "excess" sulfuric acid as high as 2.5 mol kg^{-1} (Nordstrom and Alpers, 1999b; Jamieson et al., 2005).

In addition, Fe-rich acidic surficial environments on Mars have been recently discovered and their mineralogy and chemistry provide evidence that stable liquid water once existed on the surface of the red planet. Iron–sulfate minerals are viewed as an important component to martian secondary mineralogy and are thought to precipitate from

---

* Corresponding author. Fax: +631 632 8240.
E-mail address: ntosca@ic.sunysb.edu (N.J. Tosca).

0016-7037/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.gca.2007.03.020

evaporating acidic solutions that have weathered Fe- and Mg-rich basalt (Tosca et al., 2005; Tosca and McLennan, 2006). Accordingly, the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at high ionic strength is an important one and accurately describing the thermodynamics of solution compositions in this system at high ionic strength is a critical step in predicting the presence and stability of Fe and SO_4-containing minerals found in many terrestrial and planetary surficial environments.

The Pitzer ion interaction model has been used with much success in accurately representing the thermodynamic properties of mixed electrolyte solutions. The Pitzer model is a virial expansion that extends the Debye-Hückel expression for calculating, for example, ion activity coefficients and osmotic coefficients in solutions of high ionic strength (Pitzer, 1973; Pitzer and Kim, 1974; Pitzer, 1991). The equations contain relatively few adjustable parameters (often referred to as ''Pitzer'' parameters) that are defined for each system. Pitzer parameters may be calculated or optimized through statistical fits to a variety of thermodynamic measurements and allow many physical and chemical properties of the system of interest to be accurately described to high concentration and ionic strength. Since its development and application to a variety of electrolytes in the 1970's by K.S. Pitzer and colleagues, several variations to the Pitzer equations have been used to more accurately represent thermodynamic data for a variety of electrolyte systems. More specifically, Archer (1992) extended the Pitzer ion interaction model to include ionic strength-dependent third virial coefficients. Using this extended form of the Pitzer ion interaction model, Clegg et al. (1994) developed a highly accurate model describing thermodynamic properties of aqueous H_2SO_4 to 6.0 m, and several applications using this extended form have been made to a variety of electrolytes with much success (Rard and Wijesinghe, 2003).

The $Fe_2(SO_4)_3$–H_2SO_4–H_2O system, however, is complicated geochemically. The behavior of Fe^{3+}-containing electrolytes is complicated mainly by hydrolysis of the Fe^{3+} ion, which occurs at low pH (approx. 2.2) (Stumm and Morgan, 1996). Few experimental solubility data for this system exist and until very recently, few osmotic/activity coefficient data have existed in the literature to which the Pitzer model may be applied. Accordingly, the primary goal of this study is to calculate a set of Pitzer ion interaction parameters that provides a high-quality fit to the wide range of osmotic coefficient measurements obtained on $Fe_2(SO_4)_3$–H_2SO_4–H_2O mixtures by Velazquez-Rivera et al. (2006) and Rumyantsev et al. (2004). The resulting models can be used to describe chemical equilibria in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 298.15 K up to ionic strengths of approximately 45 m and total molalities of $[Fe_2(SO_4)_3$–$H_2SO_4]$ mixtures of up to 5.47 mol kg^{-1}. With an appropriate ion interaction model, the few solubility data that exist in the literature are evaluated and comparisons are made between thermodynamic measurements, solubility studies, and activity coefficient calculation in this system. In addition, as we discuss in further detail below, the use of the ion interaction model suggested in this study has numerous applications to terrestrial and planetary geochemical problems and provides an important step toward an accurate description of the thermodynamics of the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system.

2. ISOPIESTIC DATA FOR THE $FE_2(SO_4)_3$–H_2SO_4–H_2O SYSTEM

We consider three published isopiestic studies of the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system, reported by Majima and Awakura (1985), Rumyantsev et al. (2004), and Velazquez-Rivera et al. (2006). All studies were conducted at 298.15 K, with the Velazquez-Rivera et al. (2006) study reporting additional results at 323.15 K. Isopiestic data obtained by Majima and Awakura (1985) and Rumyantsev et al. (2004) employed H_2SO_4 as a standard, while Velazquez-Rivera et al. (2006) employed both NaCl and H_2SO_4 as standards when possible, as a cross-check on consistency and accuracy of experimental results. An initial evaluation of the three studies has been performed by Velazquez-Rivera et al. (2006) and we adopt the same procedure in determining a general level of agreement before data are chosen for analysis with the Pitzer model.

Because the Fe^{3+} ion exhibits extensive hydrolysis, thermodynamic properties of pure $Fe_2(SO_4)_3$ solutions can only be derived indirectly from present data. By assuming linearity between isopiestic molalities and the respective binary solutions in this system (i.e., $Fe_2(SO_4)_3$ and H_2SO_4) in accordance with the Zdanovskii rule (Zdanovskii, 1936; Velazquez-Rivera et al., 2006), molalities of the binary $Fe_2(SO_4)_3$ solutions may be estimated from published isopiestic results. Corresponding water activities of the isopleths are recalculated in terms of the stoichiometric osmotic coefficient (ϕ_{st}) through the following relation:

$$\phi_{st} = \frac{-1000 \ln a_w}{M_w(v_1 m_1 + v_2 m_2)}$$

where M_w is the molar mass of water (18.0152 g mol^{-1}), v_i is the number of individual species to which salt i dissolves (in this case, 5 for $Fe_2(SO_4)_3$ and 3 for H_2SO_4) and m_i is the molal concentration of salt i.

As discussed by Clegg and Seinfeld (2004) and Velazquez-Rivera et al. (2006), this relationship is not an accurate method for determining thermodynamic properties for mixtures of different charge types. However, this calculation does provide a method with which to compare present isopiestic data. Fig. 1 plots the stoichiometric osmotic coefficient for binary $Fe_2(SO_4)_3$ solution molalities extrapolated by first order polynomial equations. The extrapolated values for isopiestic results reported by Majima and Awakura (1985) display a significant discrepancy when compared to results reported by Rumyantsev et al. (2004) and Velazquez-Rivera et al. (2006). As noted by Rumyantsev et al. (2004) and Velazquez-Rivera et al. (2006), this discrepancy suggests that the isopiestic results reported by Majima and Awakura (1985) may be in error. Thus, for our analysis of isopiestic data in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system, we include no results from Majima and Awakura (1985) and proceed to a more detailed comparison of the Rumyantsev et al. (2004) and Velazquez-Rivera et al. (2006) studies.

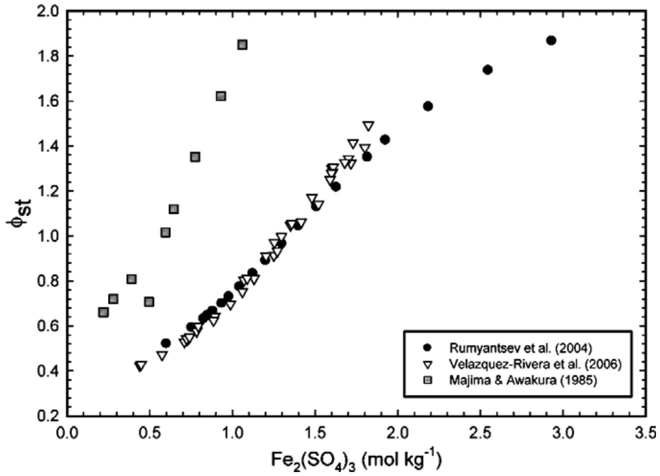

Fig. 1. Values of ϕ_{st} of $Fe_2(SO_4)_3$ binary solutions derived by first-order polynomial extrapolation of $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixtures to 0 m H_2SO_4 for three isopiestic studies of this system.

The solutions analyzed by Rumyantsev et al. (2004) can be described as $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixtures with y varying from 0.0435 to 0.9014 in 13 increments. The total molalities of the 246 solutions (equal to $[Fe_2(SO_4)_3] + [H_2SO_4]$) approach a maximum of 5.47 m as y approaches 1, and a minimum of 0.61 m as y approaches 0. In the Rumyantsev et al. (2004) study, H_2SO_4 was used as the only standard solution, with standard solutions run in triplicate and the average molality reported for each water activity value.

A recent isopiestic study conducted in this system was reported by Velazquez-Rivera et al. (2006), where 328 solutions were analyzed at 298.15 K with y values ranging from 0.749 to 0.937. The molality range for these data is between 0.45 m at low y and 3.64 m at high y. At 323.15 K, 168 solution compositions were studied, at the same range in y as the 298.15 K results over a range of 0.85–3.77 m. The properties of the solutions reported by Rumyantsev et al. (2004) and Velazquez-Rivera et al. (2006) at 298.15 and 323.15 K are listed in Table 1. In their study, Velazquez-Rivera et al. (2006) employed both NaCl and H_2SO_4 as isopiestic standards in some experiments and with either NaCl or H_2SO_4 used in others. Calculated water activities were derived in the Velazquez-Rivera et al. (2006) study using extended Pitzer ion interaction models of Archer (1992) for NaCl and Clegg et al. (1994) for H_2SO_4, and consisted of an average of either two or four standards. This calculation differs from the Rumyantsev et al. (2004) study, where water activity values were derived by using relations reported in Rard et al. (1976). To maintain consistency between isopiestic results analyzed in the present study, we have recalculated all of the results reported by Rumyantsev et al. (2004) with the extended Pitzer model of Clegg et al. (1994). This recalculation changed the reported stoichiometric osmotic coefficient values between +0.0043 and −0.0034. The resulting standard solution values are listed in Table 2.

Finally, for purposes of comparison to the isopiestic molalities evaluated in this study, recall that the maximum reported limits of Fe concentration in extreme acid mine waters equate to approximately 0.87 mol kg^{-1} $Fe_2(SO_4)_3$, with values approaching 2.7 mol kg^{-1} as excess SO_4 which may be taken as H_2SO_4 (e.g., Nordstrom and Alpers, 1999b; Jamieson et al., 2005). Indeed, in AMD and industrial chemical systems, Fe and H_2SO_4 concentrations are most often found at levels that correspond to the molality ranges of the isopiestic data discussed here. However, as the Rumyantsev et al. (2004) study reports values that extend to a maximum total molality of 5.47, we have applied the extended and 3-parameter Pitzer ion interaction models separately to limits of both 3.0 and 5.47 m, so as to gain accuracy over the pertinent molality ranges often found in natural and industrial systems and to provide models for evaluating systems at even higher molality at slightly lower accuracy.

3. SOLUBILITY DATA FOR THE $FE_2(SO_4)_3$–H_2SO_4–H_2O SYSTEM

To date, there are only a handful of solubility studies that have been conducted in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system. These studies include investigations at 25 °C by Appleby and Wilkes (1922), Baskerville and Cameron (1935), Cameron and Robinson (1907), Posnjak and Merwin (1922) and Wirth and Bakke (1914). Unfortunately, there is a paucity of experimental solubility studies that have been conducted at 25 °C after the late 1930's. In addition, some of these studies discuss complications related to characterizing Fe(III)-bearing sulfate stability in this system, such as the sluggish rate at which most phases reach equilibrium (Posnjak and Merwin, 1922), the possible presence of poorly crystalline materials or colloidal suspensions (which could not likely be characterized with the analytical techniques employed at the time) (Baskerville and Cameron, 1935), reported occurrences of phase changes (Wirth and Bakke, 1914), as well as widely conflicting solid compositions and phase identification reported in the literature (Posnjak and Merwin, 1922; Baskerville and Cameron, 1935). For the above reasons (and because of a general lack of agreement between these studies regarding methods and data), we consider the available solubility data to be less reliable than recent isopiestic results for this system and

Table 1
Isopiestic data evaluated in this study for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 298.15 and 323.15 K (R 04, Rumyantsev et al., 2004; V-R 06, Velazquez-Rivera et al., 2006)

y	Measurements	Min m_T	Max m_T	T (K)	Ref.
0.9013	19	0.7318	5.4700	298.15	R 04
0.7925	19	0.7138	4.8976	298.15	R 04
0.7073	19	0.7007	4.5481	298.15	R 04
0.5917	19	0.6826	4.1670	298.15	R 04
0.5099	19	0.6707	3.9327	298.15	R 04
0.3896	19	0.6527	3.6547	298.15	R 04
0.3526	19	0.6481	3.5702	298.15	R 04
0.2871	19	0.6381	3.4447	298.15	R 04
0.2530	19	0.6346	3.3764	298.15	R 04
0.1923	18	0.6255	2.8430	298.15	R 04
0.1364	19	0.6185	3.1772	298.15	R 04
0.0752	19	0.6089	3.0862	298.15	R 04
0.0435	19	0.6050	3.0321	298.15	R 04
0.749–0.750	37	0.4530	3.0407	298.15	V-R 06
0.780–0.782	18	0.9993	3.1215	298.15	V-R 06
0.805	15	0.8396	3.0716	298.15	V-R 06
0.815–0.819	22	0.4538	3.2326	298.15	V-R 06
0.834	33	0.4536	3.2565	298.15	V-R 06
0.841	15	0.8473	3.1712	298.15	V-R 06
0.851–0.856	22	0.4548	3.3175	298.15	V-R 06
0.863–0.866	26	0.4539	3.3752	298.15	V-R 06
0.869–0.875	44	0.8543	3.3731	298.15	V-R 06
0.879–0.886	23	0.4550	3.2752	298.15	V-R 06
0.891–0.897	18	1.0326	3.4542	298.15	V-R 06
0.907–0.910	19	0.4558	3.3837	298.15	V-R 06
0.923–0.926	18	1.0500	3.5950	298.15	V-R 06
0.937	18	1.0522	3.6384	298.15	V-R 06
0.749–0.750	18	0.8474	3.2179	323.15	V-R 06
0.780	12	1.0527	3.2930	323.15	V-R 06
0.805–0.819	18	0.8559	3.3917	323.15	V-R 06
0.834–0.841	24	0.8579	3.4220	323.15	V-R 06
0.853	12	1.0683	3.4766	323.15	V-R 06
0.863–0.869	30	0.8638	3.5273	323.15	V-R 06
0.875–0.879	12	0.8656	3.1698	323.15	V-R 06
0.891	12	1.0832	3.6033	323.15	V-R 06
0.910	6	0.8728	3.2598	323.15	V-R 06
0.923	12	1.0997	3.7303	323.15	V-R 06
0.937	12	1.1034	3.7749	323.15	V-R 06

limit our analysis of the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system to the two isopiestic studies discussed above, Rumyantsev et al. (2004) and Velazquez-Rivera et al. (2006). However, for the purposes of comparison, we apply the final model to published solubility data to evaluate discrepancy among difference sources of thermodynamic data, as discussed below. Upon future evaluation, we expect that with new and additional thermodynamic measurements (especially at low molality), improvements will be made toward a more comprehensive and accurate representation of physical and chemical properties of this system.

4. REPRESENTATION OF ISOPIESTIC RESULTS WITH AN EXTENDED PITZER MODEL

4.1. Pitzer ion interaction equations

In aqueous solutions containing sulfuric acid, the first dissociation reaction of aqueous H_2SO_4 is essentially complete at concentrations less than about 40 mol kg^{-1} (Clegg et al., 1994; Clegg and Brimblecombe, 1995). However, the second dissociation reaction which governs the formation of the sulfate (SO_4^{2-}) and bisulfate (HSO_4^-) ions is not complete and is described with the following equilibrium expression

$$HSO_4^-(aq) \leftrightarrow SO_4^{2-}(aq) + H^+(aq) \qquad (1)$$

$$K_{HSO_4} = \frac{a_{H^+} a_{SO_4^{2-}}}{a_{HSO_4^-}} = \frac{(m_{H^+}\gamma_H)(m_{SO_4^{2-}}\gamma_{SO_4})}{(m_{HSO_4^-}\gamma_{HSO_4})} \qquad (2)$$

where K_{HSO_4} is the dissociation constant of HSO_4^-, m and a are the molality and activity, respectively, and γ_i is the activity coefficient of species i.

In applying the Pitzer formalism, if the association of two ions is significant, then it becomes necessary to include the complex and evaluate interaction parameters between

Table 2
H_2SO_4 standard concentrations and ϕ_{st} and a_w values recalculated with the Clegg et al. (1994) model used in the re-calculation of isopiestic data reported by Rumyantsev et al. (2004)

$m_{H_2SO_4}$	ϕ_{st}	a_w
0.7507	0.6943	0.972225
1.0298	0.7225	0.960586
1.1763	0.7391	0.954100
1.2283	0.7452	0.951733
1.2984	0.7537	0.948487
1.4191	0.7686	0.942753
1.5223	0.7818	0.937703
1.6771	0.8021	0.929876
1.8792	0.8295	0.919207
2.0783	0.8572	0.908207
2.3366	0.8940	0.893237
2.6070	0.9335	0.876750
2.9023	0.9776	0.857829
3.2190	1.0260	0.836527
3.7074	1.1024	0.801805
3.9891	1.1471	0.780898
4.6078	1.2448	0.733458
5.4056	1.3637	0.671385
6.2036	1.4692	0.611051

that complex and every other species in the system. Previous applications of the Pitzer model to systems containing H_2SO_4 have achieved success by explicitly considering HSO_4^- as a solution component and describing the system as a mixture containing H^+, HSO_4^-, SO_4^{2-} and H_2O. We adopt the same procedure by including Eq. (1) in this study and describe the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system as a mixture of Fe^{3+}, H^+, HSO_4^-, SO_4^{2-}, and H_2O.

Clegg et al. (1994) presented a generalized and highly accurate model for H_2SO_4 based on an extended form of the Pitzer equations. The Clegg et al. (1994) model is self-consistent and accurately represents osmotic coefficients, EMF measurements, degrees of dissociation of the HSO_4-ion (αSO_4), differential enthalpies of dilution and heat capacities for aqueous H_2SO_4 from 0 to 6.1 m, 273.15 to 328.15 K and at 1 atm pressure. The model has been applied to H_2SO_4 as an isopiestic standard and to isopiestic results for a variety of systems, including the $MgSO_4$–H_2SO_4–H_2O (Rard and Clegg, 1999) and Na_2SO_4–H_2SO_4–H_2O systems (Clegg and Whitfield, 1995). The equations used in this model are based on those derived by Archer (1992), and the only major departure from the usual Pitzer equations (referred to here as the "3-parameter" form) is the inclusion of ionic strength-dependent third virial coefficients. The advantage of the extended model is a more accurate representation of experimentally derived thermodynamic quantities over the usual "3-parameter" form of the Pitzer equations. Recent results have shown that this is especially true for strong electrolytes with a valence equal to or greater than 2 for the corresponding anion or cation (Rard and Wijesinghe, 2003).

In this study, we use the same extended form of the Pitzer ion interaction model to solve for Pitzer parameters representing Fe(III)–SO_4 and Fe(III)–HSO_4 interactions as well as pertinent ternary mixing parameters in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system. We do not list all of the equations used in our analysis here, but refer the reader to Appendix I of Clegg et al. (1994) where generalized equations for the extended Pitzer model are presented in detail. We follow the exact formulation listed in Appendix I of Clegg et al. (1994) for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system and provide the following short discussion of important details of our calculation methods in applying this formulation to the isopiestic results described above.

The parameters for H_2SO_4 used in this study are listed in Table 3 and are those used in the Clegg et al. (1994) model. Values for 323.15 K are also listed, with Debye-Hückel limiting slope values (A_ϕ, calculated with the polynomial expansion suggested by Archer and Wang (1990)) and dissociation constants for HSO_4^- ($K_{HSO_4^-}$) chosen for the analyses. These values must be used in conjunction with parameter values presented here in order to maintain consistency with the Clegg et al. (1994) model. In comparison to the "3-parameter" version of Pitzer's equations, the C_{ca} term (for each cation–anion pair) is made ionic strength dependent and is broken into two terms, $C_{ca}^{(0)}$ and $C_{ca}^{(1)}$, according to the following equation representing the quantity $C_{ca}^{T\phi}$, which appears in the calculation of the osmotic coefficient

$$C_{ca}^{T\Phi} = C_{ca}^{(0)} + C_{ca}^{(1)} \exp(-\omega_{ca}\sqrt{I}) \tag{3}$$

In Eq. (3), I is ionic strength, and ω_{ca} is an index that assumes a constant value. The values of ω_{ca} have varied according to the electrolyte under investigation and are set to 2.5 for H_2SO_4, but lower values of ~1.0 have been used for 2:2 electrolytes (Archer and Rard, 1998). In our discussion of statistical fits to isopiestic data below, we discuss our choice for the ω_{ca} term used in this study.

The second virial coefficient (B_{ca}^{ϕ}) in the calculation of the osmotic coefficient is represented by an analogous equation to Eq. (3), using the parameters $\beta_{ca}^{(0)}$ and $\beta_{ca}^{(1)}$ and α_{1ca} as

Table 3
Parameter values, Debye-Hückel limiting slopes and dissociation constants used for the Clegg et al. (1994) extended Pitzer model for H_2SO_4 at 298.15 and 323.15 K

Parameter	Value (298.15 K)	Value (323.15 K)
$\beta_{H\text{–}SO_4}^{(0)}$	−0.008386089	0.013830214
$\beta_{H\text{–}SO_4}^{(1)}$	0.314734575	−0.720540362
$C_{H\text{–}SO_4}^{(0)}$	0.010192247	0.008968599
$C_{H\text{–}SO_4}^{(1)}$	−0.323662604	−0.008254058
$\alpha_{1H\text{–}SO_4}$	2.0	2.478
$\omega_{H\text{–}SO_4}$	2.5	2.5
$\beta_{H\text{–}HSO_4}^{(0)}$	0.295903322	0.245209361
$\beta_{H\text{–}HSO_4}^{(1)}$	0.400482398	0.367293652
$C_{H\text{–}HSO_4}^{(0)}$	−0.005657867	−0.003758798
$C_{H\text{–}HSO_4}^{(1)}$	−0.409364247	−0.111136762
$\alpha_{1H\text{–}HSO_4}$	2.0	2.0
$\omega_{H\text{–}HSO_4}$	2.5	2.5
$\Theta_{SO_4\text{–}HSO_4}$	0	0
$\psi_{SO_4\text{–}HSO_4\text{–}H}$	0	0
A_ϕ	0.391475	0.410277
K_{HSO_4}	0.0105	0.0047

the index term (usually set to 2.0 for most electrolytes, and set to 1.4 for 2:2 electrolytes). However, for 2:2 and higher valence electrolytes, an additional term is added to the equation, requiring the $\beta^{(2)}_{\mathrm{ca}}$ parameter and the $\alpha_{2\mathrm{ca}}$ index. This latter term has been found only to affect the osmotic coefficient at molality values that are lower than the isopiestic method can reliably determine. Thus, we do not include the $\beta^{(2)}_{\mathrm{ca}}$ term in our formulation because of the lack of low-molality thermodynamic measurements.

The higher order electrostatic terms (${}^{E}\Theta_{\mathrm{cc'}}$ and ${}^{E}\Theta'_{\mathrm{cc'}}$) in the Pitzer equations become important where ions of likewise charge but different valence (i.e., Fe^{3+} and H^+) are mixed and therefore only appear in mixed electrolyte solutions. The terms are defined by the complex functions $J_0(x)$ and $J_1(x)$ and are computed in this study using two Chebyshev polynomial approximations (for regions where $x_{ij} \leqslant 1$ and $x_{ij} \geqslant 1$) as described by Harvie (1981) and Pitzer (1991). For the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system, the higher order electrostatic terms are critical, as unsymmetrical mixing effects between trivalent cations and H^+ are significant especially at low ionic strengths (Pitzer, 1975).

To describe experimentally derived osmotic coefficients for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system within the framework of the extended Pitzer ion interaction model, binary Pitzer parameters (e.g., $\beta^{(0)}_{\mathrm{ca}}$, $\beta^{(1)}_{\mathrm{ca}}$, $C^{(0)}_{\mathrm{ca}}$, and $C^{(1)}_{\mathrm{ca}}$) are needed to describe the interactions for the Fe(III)–SO_4, Fe(III)–HSO_4, H–SO_4 and H–HSO_4 ion pairs. Additionally, there are four possible ternary interaction parameters that are needed for this system: $\Psi_{\mathrm{H-Fe(III)-SO_4}}$, $\Psi_{\mathrm{H-Fe(III)-HSO_4}}$, $\Psi_{\mathrm{SO_4-HSO_4-Fe(III)}}$, $\Psi_{\mathrm{SO_4-HSO_4-H}}$. Lastly, for this system the terms $\Theta_{\mathrm{H-Fe(III)}}$ and $\Theta_{\mathrm{SO_4-HSO_4}}$ are needed to account for mixing between ions of the same sign. In using the Clegg et al. (1994) model to represent H–SO_4 and H–HSO_4 interactions, eight binary parameters are fixed, leaving four unknown binary parameters each for Fe(III)–SO_4 and Fe(III)–HSO_4 interactions. In addition, to maintain consistency with the Clegg et al. (1994) model for H_2SO_4, we set the $\Theta_{\mathrm{SO_4-HSO_4}}$ and $\Psi_{\mathrm{SO_4-HSO_4-H}}$ parameters equal to 0, leaving four mixing parameters unknown. In total, for the extended Pitzer ion interaction model, 12 unknown parameters are needed to represent ion interactions in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system.

4.2. Representation of the $Fe_2(SO_4)_3$–H_2O system

As mentioned above, deriving ion interaction parameters for the pure $Fe_2(SO_4)_3$–H_2O system is complicated by the hydrolysis of the Fe^{3+} ion according to the following reaction

$$Fe(H_2O)_6^{3+}(aq) \leftrightarrow Fe(H_2O)_5OH^{2+}(aq) + H^+(aq) \qquad (4)$$

The equilibrium constant for Eq. (4) is equal to $10^{-2.2}$, meaning that it is thermodynamically favored at pH levels above 2.2. When pH levels increase, further hydrolysis steps take place to form varieties of the hydroxo-aquacation produced in Eq. (4). It is the combination of these hydroxo-aquacation species that subsequently forms polynuclear complexes and leads to polymerization at increasing pH and/or increasing Fe concentration (Burgess, 1999). These reactions show that a pure Fe^{3+} and $SO_4{}^{2-}$-containing aqueous solution is impossible without the occurrence of appreciable H^+ concentration. Therefore, in the context of the Pitzer formalism, Fe(III)–SO_4 interaction parameters can only be attained indirectly.

In their analysis of reported isopiestic results, Rumyantsev et al. (2004) attempted to circumvent this complication in calculating binary parameters describing Fe(III)–SO_4 interactions. The parameters were calculated by extrapolating 19 isoactivity lines with 2nd order polynomials to 0 m H_2SO_4, resulting in 19 molalities of estimated binary $Fe_2(SO_4)_3$ solutions. The resulting hypothetical, non-hydrolyzed solution data were combined with artificial data points for the osmotic coefficient between 0 and 0.01 mol kg^{-1} $Fe_2(SO_4)_3$ that were generated with chemical speciation calculations. The α_1 and α_2 indices were allowed to vary during the calculations. However, in our evaluation of the isopiestic data in this system, we have chosen to re-evaluate the parameters for the $Fe_2(SO_4)_3$ system by including them in the global optimization calculations described below. The reason for not including these reported parameters is that the 19 compositions of $Fe_2(SO_4)_3$ are not direct thermodynamic measurements of the system and are derived by extrapolation only. Regressing directly measured isopiestic results and obtaining the pertinent parameters for this binary system indirectly is likely to result in a higher quality fit. As a result, the parameters derived in this study for the $Fe_2(SO_4)_3$ binary system must be applied cautiously to different systems, as the regression of Pitzer parameters from solution mixtures results in an interdependence of Pitzer parameters that requires them to be used collectively as a set. The most accurate approach would be to re-evaluate parameters for the $Fe_2(SO_4)_3$ system in different mixtures and compare the binary values to those derived in this study.

5. DATA ANALYSIS AND REGRESSION TECHNIQUES

The Pitzer equations for the osmotic coefficient can be written for each datum (e.g., each isopiestic measurement) and are linear with respect to the unknown Pitzer parameters provided the indices $\alpha_{1\mathrm{ca}}$ and ω_{ca} are held constant. Inserting known Pitzer parameters and collecting known and unknown terms, each Pitzer equation takes the form

$$\phi' = \sum_i AP_i + C \qquad (5)$$

where ϕ' is the non-stoichiometric osmotic coefficient used in the Pitzer equations, A is the constant coefficient belonging to the i-th Pitzer parameter, P_i, in Eq. (5) and C is a constant (Reardon and Beckie, 1987). Using a simple multiple linear regression model, a set of Pitzer parameters that provides the best fit to the experimental data can be calculated.

However, because $HSO_4{}^-$ is considered explicitly in this treatment of the Pitzer model, sulfate–bisulfate equilibria according to Eq. (1) presents a complication in the calculation of Pitzer parameters. At the outset of calculation and linear regression, equilibrium molalities of $SO_4{}^{2-}$, $HSO_4{}^-$ and H^+, and therefore the equilibrium ionic strength, are not known; yet they each appear in numerous instances in the terms that are collected to express the constant coefficient, A in Eq. (5). Accordingly, we have chosen an iterative method of parameter calculation, beginning with initial estimates for unknown molalities and ionic strength. Following Hovey et al. (1993) who employed a similar iterative regression technique, the initial molality values (m_i) used for the first calculation cycle were chosen by setting $m_{H+,i}$ and $m_{HSO_4-,i}$ equal to $m_{H_2SO_4,i}$ and $m_{SO_4,i}$ equal to $3m_{Fe_2(SO_4)_3}$. These initial molalities are used for the first linear regression, and a set of Pitzer parameters is derived. Then, equilibrium molalities are re-generated by calculating activity coefficients with the Pitzer parameter estimates and re-calculating the distribution of species in the system. Initial estimates for molality values were found to affect the derived Pitzer parameter values only slightly, however using the initial molality estimates above resulted in well-defined minima of the error function used for solving Pitzer parameters.

Throughout the regression calculations, equilibrium molalities are calculated by expressing the equilibrium dissociation reaction (Eq. (1)) solely in terms of H^+ molality and molalities of $Fe_2(SO_4)_3$ and H_2SO_4 components. The resulting quadratic relation may be solved for H^+ molality, which is used in turn to calculate the molalities of $HSO_4{}^-$, $SO_4{}^{2-}$ and ionic strength. The relation is as follows:

$$m_{H^+}^2 + m_{H^+}\left[\left(3m_{Fe_2(SO_4)_3} - m_{H_2SO_4}\right) + \frac{K_{HSO_4^-}}{A}\right] - \frac{K_{HSO_4^-}}{A}(2m_{H_2SO_4}) = 0 \quad (6)$$

$$a = 1 \quad (7)$$

$$b = \left(3m_{Fe_2(SO_4)_3} - m_{H_2SO_4}\right) + \frac{K_{HSO_4^-}}{A} \quad (8)$$

$$c = -\frac{K_{HSO_4^-}}{A}(2m_{H_2SO_4}) \quad (9)$$

$$A = \frac{(\gamma_{SO_4})(\gamma_H)}{(\gamma_{HSO_4})} \quad (10)$$

With the solution of H^+ molality, the molalities of the remaining species are calculated with the following expressions:

$$m_{HSO_4^-} = 2m_{H_2SO_4} - m_{H^+} \quad (11)$$

$$m_{SO_4^{2-}} = \left(3m_{Fe_2(SO_4)_3} + m_{H_2SO_4}\right) - m_{HSO_4^-} \quad (12)$$

$$m_{Fe^{3+}} = 2m_{Fe_2(SO_4)_3} \quad (13)$$

The process is iterated until convergence of molalities and ionic strength values is attained. New sets of ion interaction parameters are continuously re-estimated through linear regression and eventually, convergence is attained when speciation calculations from each iteration produce the same result. This iterative method described above for parameter estimation has been used in several previous ion interaction studies of H_2SO_4-containing systems (Reardon and Beckie, 1987; Reardon, 1989; Baes et al., 1993; Hovey et al., 1993).

Multiple linear regression calculations were done using MATLAB v6.5. The multiple linear regression algorithm in MATLAB solves the linear model

$$y = X\beta + \varepsilon \quad (14)$$

where y is an $n \times 1$ vector of observations (equal to $\phi' - C$ from Eq. (5)), X is $n \times p$ matrix of regressors (equal to A from Eq. (5)), β is a $p \times 1$ vector of parameters (equal to Pitzer parameters), and ε is an $n \times 1$ vector of random disturbances. A statistical analysis was performed for each iteration, including standard error, R-squared statistic, leverage matrices and coefficient covariance.

Upon parameter convergence and optimization, quantitative statistical analysis was performed on residual values, providing tests for a normal probability distribution as an indicator of the degree of randomness.

Preliminary fits using all isopiestic data reported by Rumyantsev et al. (2004) and Velazquez-Rivera et al. (2006) produced poor fits, especially at increasing m_T values. Accordingly, the disagreement between experimental studies in preliminary fits was evaluated quantitatively in order to discriminate among data points and weight/reject individual analyses. The discrimination procedure was performed by first optimizing Pitzer parameters to only Rumyantsev et al. (2004) data to a maximum of 3.6 m and re-calculating experimental values reported by Velazquez-Rivera et al. (2006). Re-calculation of the experimental Velazquez-Rivera et al. (2006) values resulted in good agreement of all points below 1 m with all errors less than 0.01 in ϕ_{st}. However, with increasing molality, the Velazquez-Rivera et al. (2006) values showed a systematic positive increase in error between +0.01 and +0.04 in ϕ_{st} as total molality increased from 1 to 3.6. Noting good agreement between both studies at values less than 1 m, we re-evaluated Pitzer parameters for the preliminary fit using data from Rumyantsev et al. (2004) to 3.6 m and data from Velazquez-Rivera et al. (2006) to 1 m. Thus, we rejected several values from the Velazquez-Rivera et al. (2006) study in our analysis of Pitzer parameters because the isopiestic data reported by Rumyantsev et al. (2004): (1) span a much larger and lower range in y (the only source of data for $y < 0.749$) which is critical in evaluating Pitzer parameters for the binary $Fe_2(SO_4)_3$ system, and (2) the Rumyantsev

Table 4
Experiment details of rejected values from the Velazquez-Rivera et al. (2006) study at 298.15 K

Experiment	Sample	Cup
3	6	9, 10
3	8	9–12
4	1	8, 9
4	2	8, 9, 10
4	3	8, 9, 10
4	4	2–5, 8–11
4	5	2–5, 8–12
4	7	All
4	8	All
6	1	8
6	2	8
6	3	8
6	4	8
6	5	8
6	6	8, 9
6	7	8, 9, 10
6	8	8, 9, 10
6	9	9, 10
6	10	9, 10
6	11	9, 10

et al. (2004) data appear to be much less scattered and hence, generally more precise than the Velazquez-Rivera et al. (2006) data. However, one apparently errant point from Rumyantsev et al. (2004) was rejected from the preliminary fit ($m\mathrm{Fe_2(SO_4)_3} = 2.5232$, $m\mathrm{H_2SO_4} = 0.11481$). More specifically, we rejected isopiestic values from the

Table 5
Extended Pitzer model parameter values, standard errors, standard deviation of fit (in ϕ_{st}) and total molality limits for Fe(III)–SO_4, Fe(III)–HSO_4, and mixing interactions for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 298.15 and 323.15 K

Parameter	Value	Standard error	Value	Standard error	Value	Standard error
$\beta^{(0)}_{\mathrm{Fe(III)–SO_4}}$	0.63321	0.03259	0.49164	0.03006	0.27002	0.03143
$\beta^{(1)}_{\mathrm{Fe(III)–SO_4}}$	11.96824	0.36712	13.29467	0.31754	11.00787	0.78588
$C^{(0)}_{\mathrm{Fe(III)–SO_4}}$	−0.00655	0.00036	−0.00511	0.00034	−0.01021	0.00312
$C^{(1)}_{\mathrm{Fe(III)–SO_4}}$	−0.02515	0.01542	0.04311	0.01412	0.19071	0.07749
$\alpha_{1\mathrm{Fe(III)–SO_4}}$	1.4	—	1.4	—	1.4	—
$\omega_{\mathrm{Fe(III)–SO_4}}$	0.5	—	0.5	—	0.5	—
$\beta^{(0)}_{\mathrm{Fe(III)–HSO_4}}$	0.60732	0.03959	0.41933	0.02140	1.05617	0.03443
$\beta^{(1)}_{\mathrm{Fe(III)–HSO_4}}$	7.51906	0.37011	8.29169	0.33558	8.30567	1.06528
$C^{(0)}_{\mathrm{Fe(III)–HSO_4}}$	−0.01300	0.00341	−0.01579	0.00131	−0.03862	0.01296
$C^{(1)}_{\mathrm{Fe(III)–HSO_4}}$	0.15243	0.01794	0.26704	0.01020	0.07297	0.07693
$\alpha_{1\mathrm{Fe(III)–HSO_4}}$	2.0	—	2.0	—	2.0	—
$\omega_{\mathrm{Fe(III)–HSO_4}}$	0.5	—	0.5	—	0.5	—
$\theta_{\mathrm{Fe(III)–H}}$	0.04927	0.02737	0.03429	0.01694	0	—
$\psi_{\mathrm{H–Fe(III)–HSO_4}}$	−0.00193	0.01136	−0.02380	0.00451	0.01553	0.01417
$\psi_{\mathrm{SO_4–HSO_4–Fe(III)}}$	−0.00658	0.01258	0.00815	0.00508	0	—
$\psi_{\mathrm{H–Fe(III)–SO_4}}$	0.02825	0.00575	0.00976	0.00392	0	—
T (K)	298.15		298.15		323.15	
σ	0.0034	—	0.0041	—	0.0027	—
m_T	3.00	—	5.47	—	3.77	—

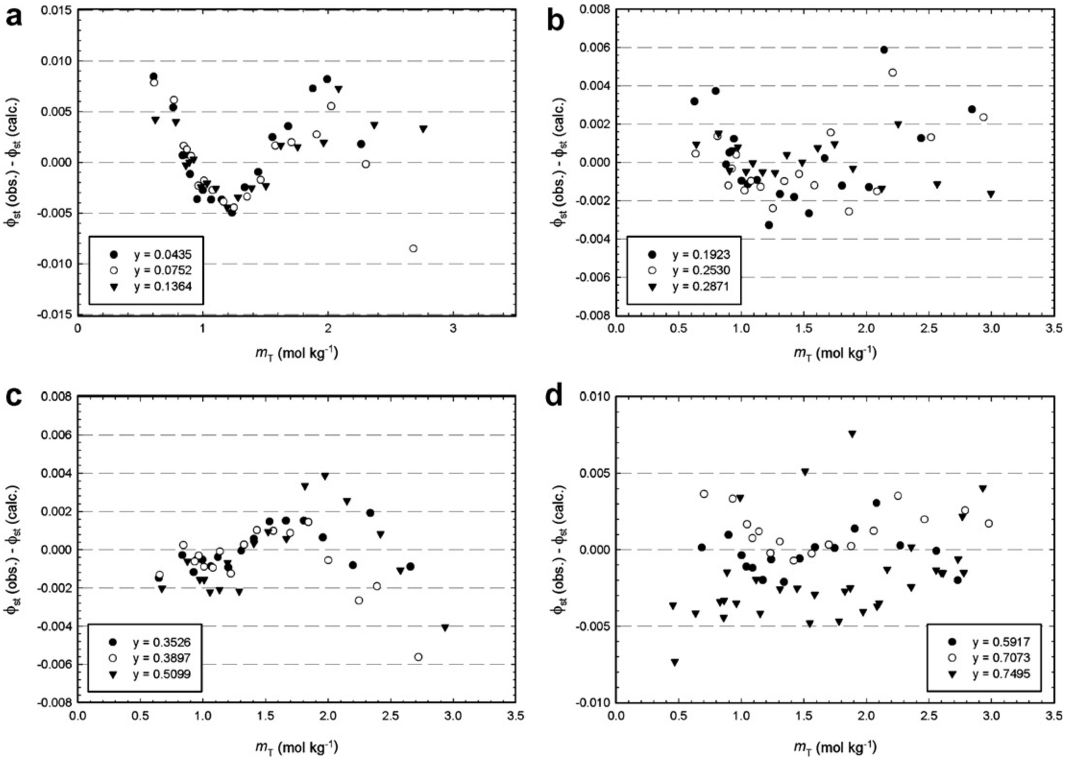

Fig. 2. Residuals between experimentally derived osmotic coefficient values and model calculated values for $\{(1 - y)\mathrm{Fe_2(SO_4)_3} + y\mathrm{H_2SO_4}\}$ mixtures at increasing y values from 0.0435 to 0.7495 at 298.15 K to 3.0 m. (a) $y = 0.0435$, 0.0752, 0.1364; (b) $y = 0.1923$, 0.2530, 0.2871; (c) $y = 0.3526$, 0.3897, 0.5099 and (d) $y = 0.5917$, 0.7073, 0.7495. The model calculated values for ϕ_{st} were generated with the extended Pitzer ion interaction parameters listed in Tables 3 and 5.

Velazquez-Rivera et al. (2006) study that were in an error of more than three times the standard deviation of the preliminary fit (0.0109). It is worth noting that while the Rumyantsev et al. (2004) data were used to establish a preliminary fit only extend to $y = 0.9013$ at a maximum, most of the rejected values were at y values slightly lower than 0.9013, with only four data points showing large enough error at y values greater than 0.9013 to still be rejected. The disadvantage to this approach is that there are only two reliable isopiestic studies used in this analysis and a more critical evaluation of all of the data could be facilitated with additional isopiestic data spanning an equal range in y comparable to the Rumyantsev et al. (2004) study. The rejected values from Velazquez-Rivera et al. (2006) are listed in Table 4. Detailed reporting of isopiestic methods by Velazquez-Rivera et al. (2006) allows the experiment number, sample interval number and cup position to be tabulated with the rejected values in this study. Interestingly, several of the most discrepant values correspond to one or two cup positions throughout different sampling intervals (i.e., cup #8, experiment #6, samples 1–8). In addition, Fig. 1 shows an increasing discrepancy in the estimation of binary

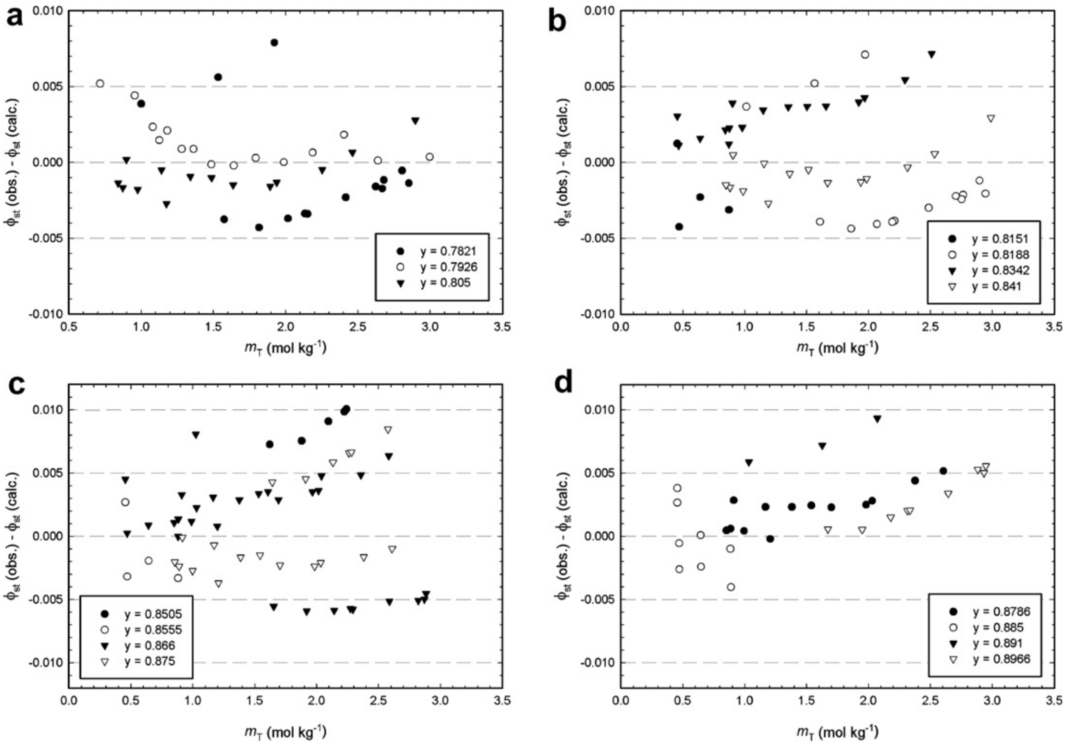

Fig. 3. Residuals between experimentally derived osmotic coefficient values and model calculated values for $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixtures at increasing y values from 0.7821 to 0.8966 at 298.15 K to 3.0 m. (a) $y = 0.7821, 0.7926, 0.805$; (b) $y = 0.8151, 0.8188, 0.8342, 0.841$; (c) $y = 0.8505, 0.8555, 0.866, 0.875$ and (d) $y = 0.8786, 0.885, 0.891, 0.8966$. The model calculated values for ϕ_{st} were generated with the extended Pitzer ion interaction parameters listed in Tables 3 and 5.

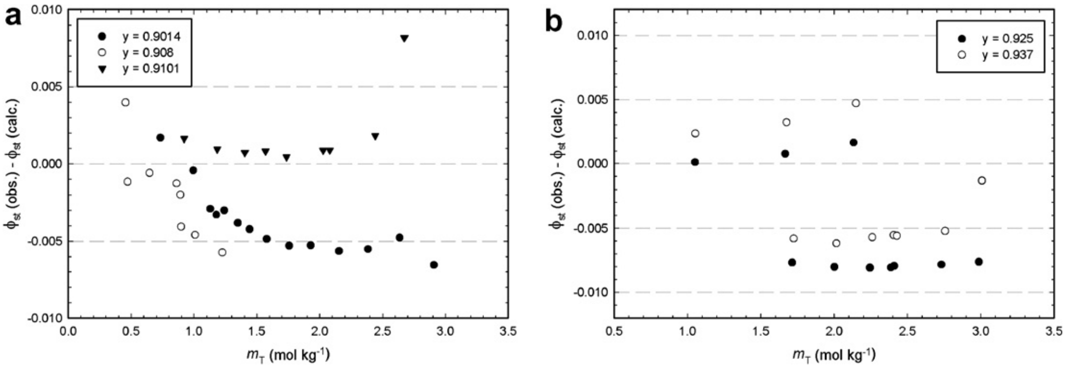

Fig. 4. Residuals between experimentally derived osmotic coefficient values and model calculated values for $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixtures at increasing y values from 0.9014 to 0.937 at 298.15 K to 3.0 m. (a) $y = 0.9014, 0.908, 0.9101$ and (b) $y = 0.925, 0.937$. The model calculated values for ϕ_{st} were generated with the extended Pitzer ion interaction parameters listed in Tables 3 and 5.

solution properties from isopiestic results at higher molality. However, while we cannot definitively label these results in error until a wider range of isopiestic data become available, the methods described above provide a quantitative means of preserving as much data from both isopiestic studies as possible.

6. RESULTS

Final statistical fits to discriminated isopiestic data were performed to 3.0 and 5.47 m for results at 298.15 K. An additional fit was performed with reported data from Velazquez-Rivera et al. (2006) at 323.15 K, which cover a limited range in m_T and y.

For all calculations, we found that setting $\alpha_{1\mathrm{Fe-SO_4}} = 1.4$ (as opposed to 2.0) and $\alpha_{1\mathrm{Fe-HSO_4}} = 2.0$ produced higher quality fits and adopt these values throughout the study. Additionally, for the $\omega_{\mathrm{Fe-SO_4}}$ and $\omega_{\mathrm{Fe-HSO_4}}$ values, we used values of 0.5, 1.0 and 2.5 in our regression analyses and found that setting both values equal to 0.5 produced marginally higher quality fits than using 1.0, both of which produced significantly higher quality fits than a value of 2.5.

The resulting optimized parameter values for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system to 3.0 m at 298.15 K are listed in Table 5. The resulting standard deviation of the fit is 0.0034, with a total of 457 analyses included in the regression. Figs. 2–5 display the residuals in the stoichiometric osmotic coefficient as a function of m_T for each y value. At the two lowest y values of 0.0435 and 0.0752 only (Fig. 2a), "cycling" patterns of the residuals are apparent. This may be a result of a lack of binary $Fe_2(SO_4)_3$ data with which to better constrain the $Fe_2(SO_4)_3$ parameters at these y values. However, these errors fall within an acceptable range and are the only values that display discernable patters across the system. Collectively, however, the residuals are all essentially random and form an approximate normal distribution with 70% of all analyses falling within 1σ, 94%

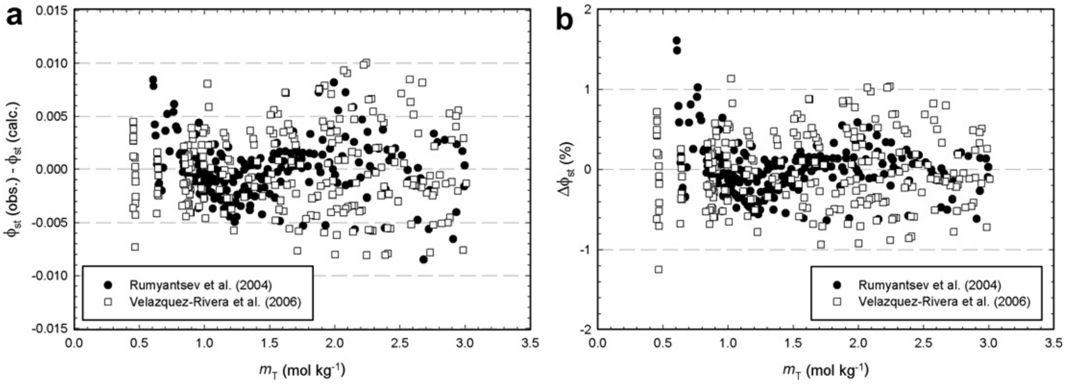

Fig. 5. Residuals between experimentally derived osmotic coefficient values and model-calculated values for $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixture data reported by Rumyantsev et al. (2004) and Velazquez-Rivera et al. (2006) at 298.15 K to 3.0 m (a) and with residuals expressed as relative percent of the osmotic coefficient value for all data (b).

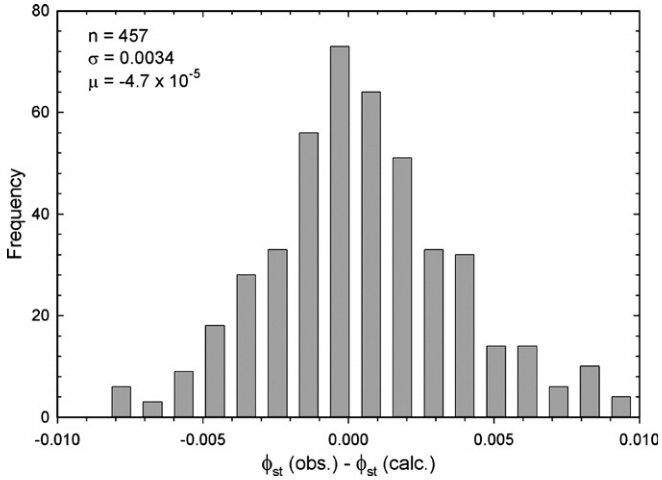

Fig. 6. Histogram plot of residuals between experimentally derived osmotic coefficient values and model-calculated values for $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixture data (457 values) to 3.0 m at 298.15 K. The standard deviation in ϕ_{st} of the fit (s) is 0.0034, with a mean value (m) of -4.7×10^{-5}. The distribution of all residual values included in the analysis is approximately a normal, random distribution.

falling within 2σ, and 99.8% falling within 3σ (Fig. 6). In a perfect normal distribution, where all residuals would be random, 68%, 95%, and 99.7% of all data points would fall within 1σ, 2σ, and 3σ, respectively. Alternatively, the quality of the fits to experimental data can be expressed by the standard error of estimate (SE) (Marion, 2002), which is defined by

$$\mathrm{SE}\ (\%) = \left\{ \sum \left[\left(\frac{M_i - E_i}{E_i} \right) \times 100 \right]^2 \Big/ n \right\}^{0.5} \tag{15}$$

where M_i is the model estimate of the osmotic coefficient and E_i is the corresponding experimental measurement of the osmotic coefficient and n is the number of observations. The resulting model results in a fit to osmotic coefficient data to 3.0 m of 0.40%. In general, the Velazquez-Rivera et al. (2006) data are more scattered, displaying a standard deviation of 0.0039, compared to the Rumyantsev et al. (2004) data only, which display a standard deviation of 0.0028. Additional isopiestic studies will allow more rigorous discrimination of data from each study, resulting in an even more accurate fit to larger ranges in total molality and solute molality fraction (y). Using this model, calculated values of osmotic and activity coefficients for the system at rounded molality values to 3.0 m are listed in Table 6.

The optimized parameter values for all of the discriminated isopiestic data to 5.47 m at 298.15 K are listed in Table 5. The overall standard deviation of the fit is 0.0041 in ϕ_{st}, translating to a standard error of estimate equal to 0.46%, with a total of 503 analyses included in the regression. The residuals are shown in Figs. 7–10 as a function of m_T for each y value. With the exception of the two lowest y values, which also display come "cycling patterns" (discussed above) the residuals are essentially random and, similar to the analysis to 3.0 m, form a distribution that is close to that of a normal distribution, with 66%, 95% and 99.8% of all analyses falling within 1σ, 2σ, and 3σ, respectively (Fig. 11). This higher molality fit is less accurate than the 3.0 m fit, and is a consequence of extending the Pitzer for-

Table 6

Model-calculated values of the dissociated fraction of total sulfate ($\alpha(SO_4^{2-})$), the stoichiometric osmotic coefficient (ϕ_{st}), and single ion activity coefficients as a function of solute molality fraction (y) at rounded values of total molality (m_T) for $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ solutions at 298.15 K

m_T (mol kg^{-1})	y	$\alpha(SO_4)$	ϕ_{st}	γ (H^+)	ln γ (Fe^{3+})	γ (HSO_4^-)	γ (SO_4^{2-})
0.6	0.0	1.0000	0.5123	0.1453	−7.0352	2.7572	0.1861
1	0.0	1.0000	0.7426	0.1416	−7.2655	6.7769	0.2284
1.5	0.0	1.0000	1.0942	0.1990	−7.0661	19.3910	0.3371
2	0.0	1.0000	1.4251	0.3880	−6.6848	46.6912	0.5130
2.5	0.0	1.0000	1.6985	1.0147	−6.2759	91.2425	0.7593
3	0.0	1.0000	1.8989	3.5063	−5.9121	142.8676	1.0617
0.6	0.2	0.9005	0.5312	0.1734	−6.6580	2.2508	0.1778
1	0.2	0.9080	0.7073	0.1598	−6.9367	4.7951	0.1984
1.5	0.2	0.9101	1.0027	0.1918	−6.7995	12.2132	0.2649
2	0.2	0.9022	1.3012	0.2906	−6.4469	27.9920	0.3764
2.5	0.2	0.8873	1.5505	0.5267	−6.0429	55.5291	0.5254
3	0.2	0.8711	1.7234	1.0992	−5.6791	94.8723	0.6891
0.6	0.4	0.7605	0.5572	0.2182	−6.1783	1.8530	0.1713
1	0.4	0.7731	0.6874	0.1972	−6.4805	3.3645	0.1746
1.5	0.4	0.7838	0.9153	0.2130	−6.4063	7.3564	0.2055
2	0.4	0.7806	1.1668	0.2709	−6.0972	15.4580	0.2653
2.5	0.4	0.7643	1.4037	0.3898	−5.6894	29.8251	0.3521
3	0.4	0.7407	1.5981	0.6107	−5.2679	52.1635	0.4558
0.6	0.6	0.5721	0.5848	0.2923	−5.5469	1.5425	0.1608
1	0.6	0.5771	0.6816	0.2715	−5.8343	2.3790	0.1536
1.5	0.6	0.5904	0.8460	0.2827	−5.7950	4.2866	0.1592
2	0.6	0.5977	1.0333	0.3239	−5.5356	7.8143	0.1791
2.5	0.6	0.5926	1.2260	0.4014	−5.1564	13.8630	0.2137
3	0.6	0.5757	1.4092	0.5290	−4.7151	23.3991	0.2615
0.6	0.8	0.3661	0.6210	0.4198	−4.6228	1.2572	0.1274
1	0.8	0.3578	0.6889	0.4107	−4.8468	1.6941	0.1109
1.5	0.8	0.3587	0.7991	0.4383	−4.8075	2.5180	0.1024
2	0.8	0.3631	0.9244	0.4931	−4.5759	3.8143	0.1006
2.5	0.8	0.3655	1.0568	0.5746	−4.2330	5.8127	0.1037
3	0.8	0.3618	1.1911	0.6904	−3.8193	8.7887	0.1112
0.6	1.0	0.2096	0.6815	0.7205	−2.9322	0.8222	0.0623
1	1.0	0.2240	0.7193	0.7471	−2.7142	0.9376	0.0373
1.5	1.0	0.2470	0.7789	0.8055	−2.3267	1.1591	0.0246
2	1.0	0.2709	0.8462	0.8834	−1.8973	1.4838	0.0187
2.5	1.0	0.2939	0.9178	0.9784	−1.4542	1.9433	0.0155
3	1.0	0.3136	0.9925	1.0941	−1.0014	2.5774	0.0137

mulation to higher molality, which generally sacrifices accuracy at lower molalities (Pitzer, 1991). The higher molality values indeed decrease the accuracy, as is often the case with application of the Pitzer model. However, it is important to note that Rumyantsev et al. (2004) reported an average H_2SO_4 standard solution concentration of 6.2036 m for the highest molality experiment. The reported molality is above the 6.1 m H_2SO_4 limit of the Clegg et al. (1994) model that we have used to calculate the water activity for the sample cups analyzed during the experiment. Rumyantsev et al. (2004) chose to calculate the water activity from H_2SO_4 from an equation suggested by Rard et al. (1976) in a critical evaluation of the osmotic coefficients of aqueous H_2SO_4. The difference between the Rumyantsev et al. (2004) calculated value and the reported value decreases the reported ϕ_{st} values by 0.0029 to 0.0034, and decreases the ϕ_{st} value of the standard by 0.0027. We have chosen to use the value calculated with the Clegg et al. (1994) model to maintain internal consistency and note that the difference between the two models of 0.0027 is within the standard deviation of the Rard et al. (1976) model (0.0033) and sufficiently close to the standard deviation of the Clegg et al. (1994) model at 298.15 K (0.0024).

In this study, we have also applied the Pitzer formulation to isopiestic data reported by Velazquez-Rivera et al. (2006) at 323.15 K. Initial fits used data that were not discriminated, and a fit of insufficient quality was derived, producing an overall standard deviation of 0.0052, which is significantly more scattered than the reported errors in the experiments indicate. However, the resulting fits showed trends among some of the residuals. Fig. 12 illustrates the error in residuals as a function of sample episode for the two isopiestic experiments conducted at 323.15 K using the preliminary fit. Fig. 12 indicates that the two experiments appear discrepant with each other, however it cannot be determined reliably at this time which data points are in error. Both experiments cover a broad range in y (with experiment 4 covering the largest range), and we suggest that the discrepancy is unlikely to be a result of the Pitzer formulation used. Instead, to further evaluate the quality of the isopiestic data and the Pitzer formulation at 323.15 K, we provide a statistical fit for experiment 4 only, as the results appear to display good internal agreement and appear generally accurate and precise, but offset only by the inclusion of experiment 3 in the regression. The standard deviation of the resulting fit is 0.0027 with 120 values included in the regression analysis (Figs. 13 and 14). The corresponding parameters for the extended Pitzer model applied to these data are listed in Table 5. Although the data for experiment 4 collectively are the most precise and appear to be the most accurate, it should be noted that these discrepancies must be resolved with additional data for this system at 323.15 K. Some uncertainty still remains as to the accuracy of the data, because several values were rejected from the same experiments conducted at 298.15 K.

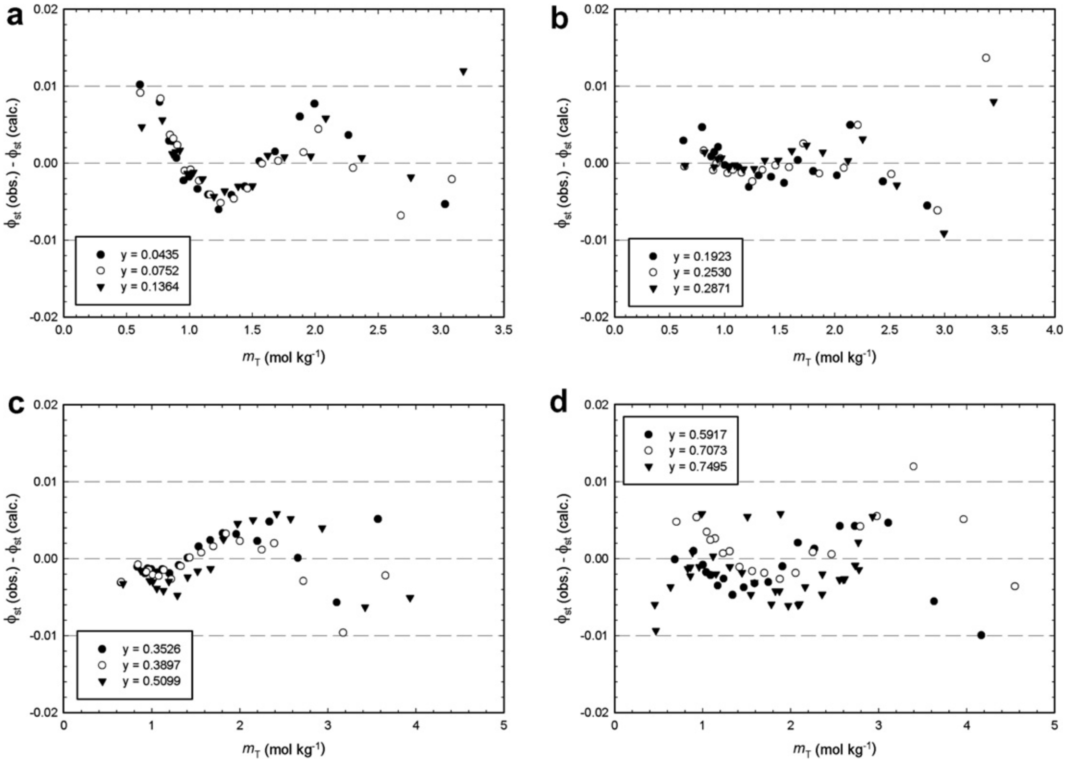

Fig. 7. Residuals between experimentally derived osmotic coefficient values and model calculated values for $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixtures at increasing y values from 0.0435 to 0.7495 at 298.15 K to 5.47 m. (a) $y = 0.0435, 0.0752, 0.1364$; (b) $y = 0.1923, 0.2530, 0.2871$; (c) $y = 0.3526, 0.3897, 0.5099$ and (d) $y = 0.5917, 0.7073, 0.7495$. The model calculated values for ϕ_{st} were generated with the extended Pitzer ion interaction parameters listed in Tables 3 and 5.

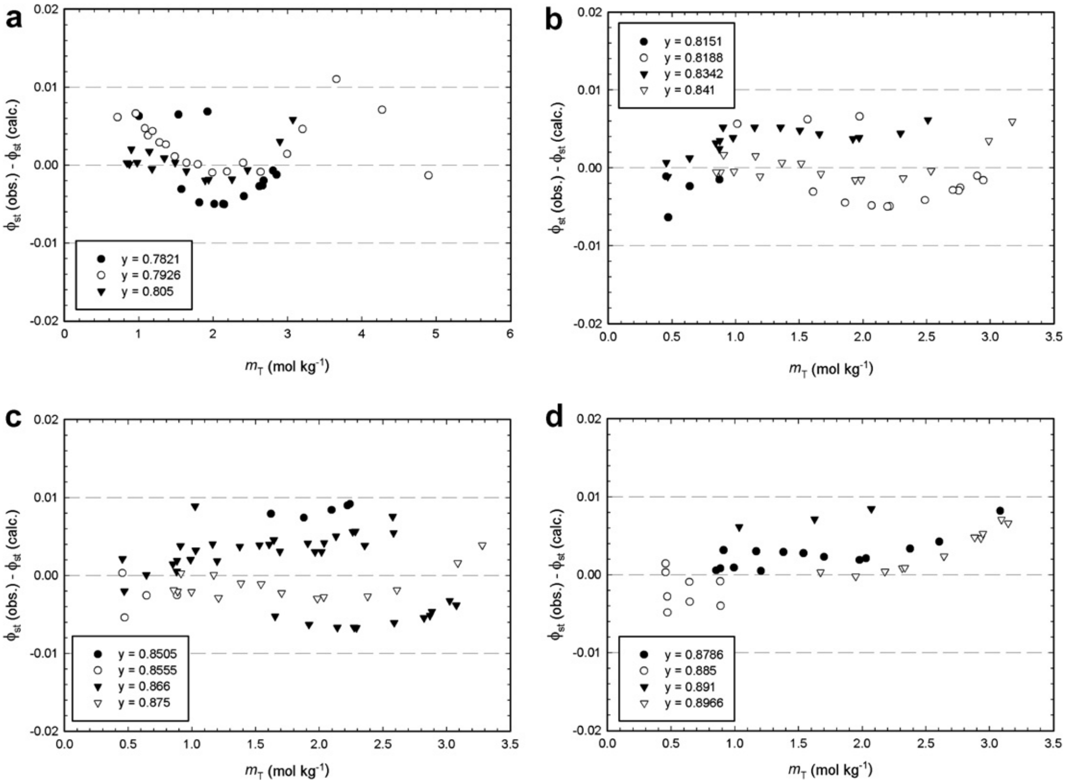

Fig. 8. Residuals between experimentally derived osmotic coefficient values and model calculated values for $\{(1-y)\mathrm{Fe_2(SO_4)_3} + y\mathrm{H_2SO_4}\}$ mixtures at increasing y values from 0.7821 to 0.8966 at 298.15 K to 5.47 m. (a) $y = 0.7821$, 0.7926, 0.805; (b) $y = 0.8151$, 0.8188, 0.8342, 0.841; (c) $y = 0.8505$, 0.8555, 0.856, 0.875 and (d) $y = 0.8786$, 0.885, 0.891, 0.8966. The model calculated values for ϕ_{st} were generated with the extended Pitzer ion interaction parameters listed in Tables 3 and 5.

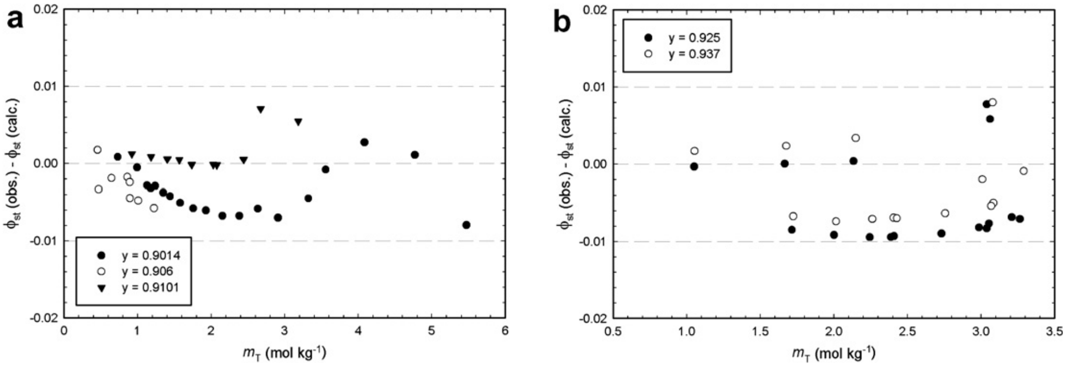

Fig. 9. Residuals between experimentally derived osmotic coefficient values and model calculated values for $\{(1-y)\mathrm{Fe_2(SO_4)_3} + y\mathrm{H_2SO_4}\}$ mixtures at increasing y values from 0.9014 to 0.937 at 298.15 K to 5.47 m. (a) $y = 0.9014$, 0.906, 0.9101 and (b) $y = 0.925$, 0.937. The model calculated values for ϕ_{st} were generated with the extended Pitzer ion interaction parameters listed in Tables 3 and 5.

For each of the fits described above, the datasets were fitted to the "3-parameter" version of Pitzer's model, with parameter values, standard errors, standard deviations and molality ranges listed in Table 7. The normal 3-parameter version of Pitzer's model is currently used by a variety of chemical modeling software, including PHRQPITZ and Geochemist's Workbench. However, as noted by Rard and Wijesinghe (2003), these programs include no provision for using extended variants of the Pitzer formulation. Accordingly, we have used the 3-parameter variation of Pitzer's model for H_2SO_4 using parameters suggested by Reardon and Beckie (1987) at 298.15 and 323.15 K. The parameters were derived using the polynomials provided in their study. The standard deviation for the fits at 298.15 K for a total molality of 3.0 and 5.47 are 0.0048 and 0.0059, respectively. The larger standard deviations most likely result from a combination of using a less accurate model to represent the H_2SO_4

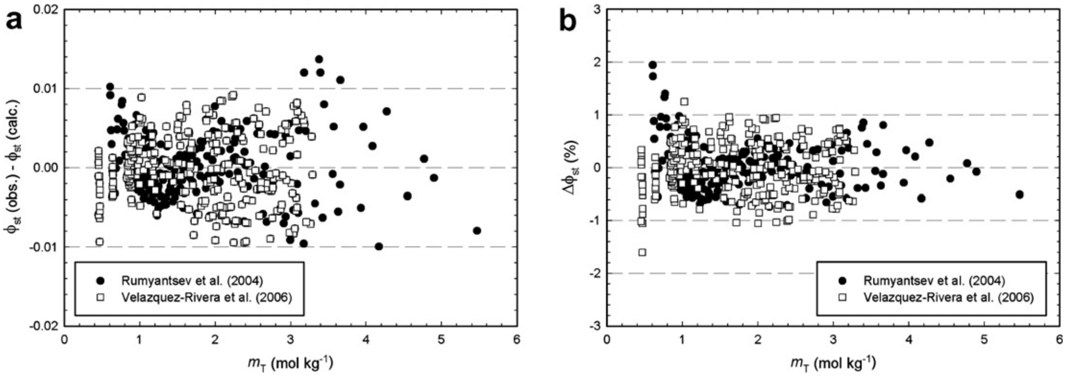

Fig. 10. Residuals between experimentally derived osmotic coefficient values and model-calculated values for $\{(1-y)\mathrm{Fe_2(SO_4)_3} + y\mathrm{H_2SO_4}\}$ mixture data reported by Rumyantsev et al. (2004) and Velazquez-Rivera et al. (2006) at 298.15 K to 5.47 m (a) and with residuals expressed as relative percent of the osmotic coefficient value for all data (b).

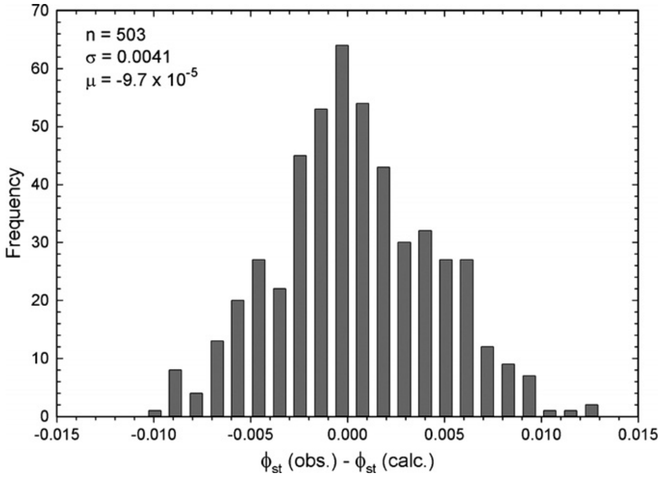

Fig. 11. Histogram plot of residuals between experimentally derived osmotic coefficient values and model-calculated values for $\{(1-y)\mathrm{Fe_2(SO_4)_3} + y\mathrm{H_2SO_4}\}$ mixture data (503 values) to 5.47 m at 298.15 K. The standard deviation in ϕ_{st} of the fit (s) is 0.0041, with a mean value (m) of -9.7×10^{-5}. The distribution of all residual values included in the analysis is approximately a normal, random distribution.

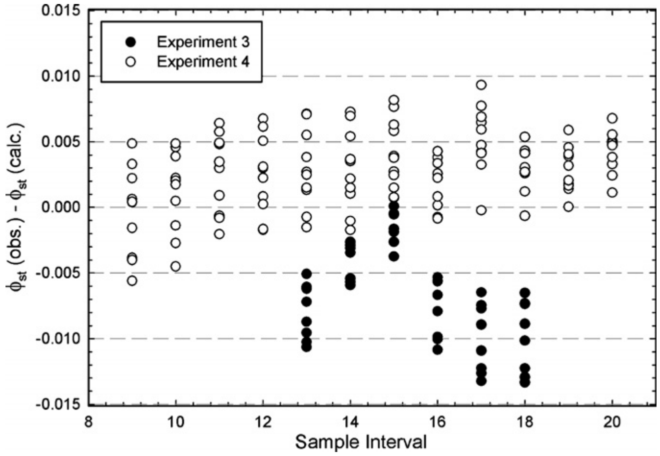

Fig. 12. Residuals between experimentally derived osmotic coefficient values and model calculated values using a preliminary fit for all data reported by Velazquez-Rivera et al. (2006) at 323.15 K for the two isopiestic experiments conducted for this system.

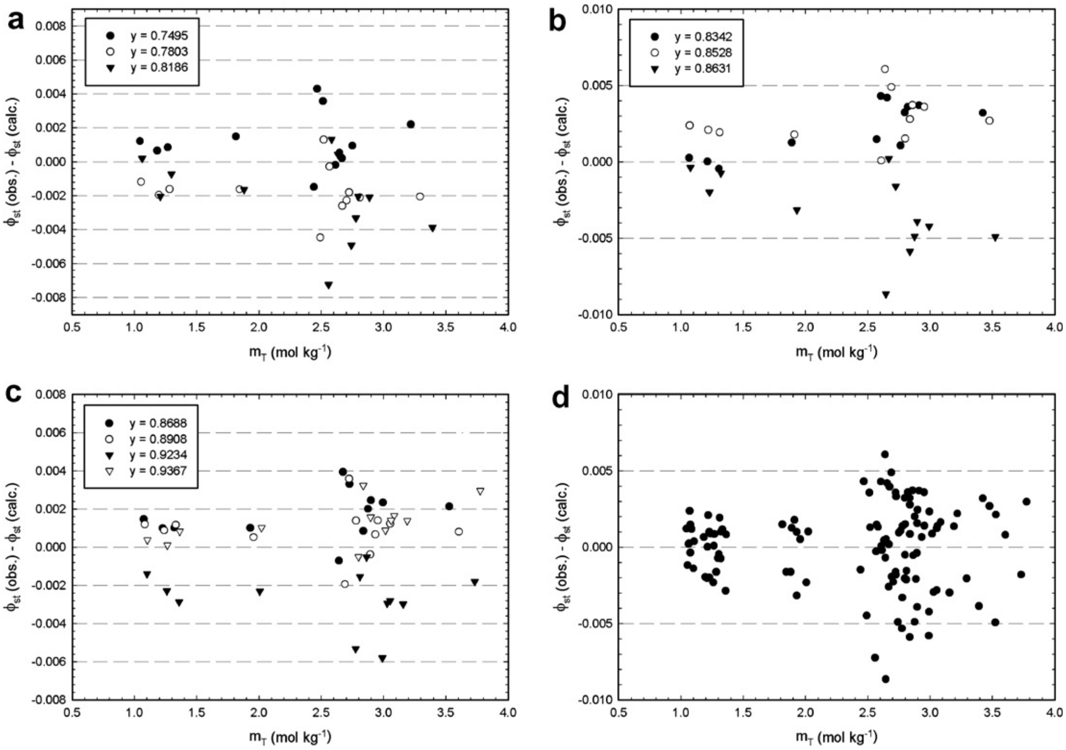

Fig. 13. Residuals between experimentally derived osmotic coefficient values and model calculated values for $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixtures at increasing y values from 0.7495 to 0.9367 at 323.15 K to 3.77 m (experiment 4 only). (a) $y = 0.7495$, 0.7803, 0.8166; (b) $y = 0.8342$, 0.8528, 0.8631; (c) $y = 0.8688$, 0.8908, 0.9234, 0.9367 and (d) all data. The model calculated values for ϕ_{st} were generated with the extended Pitzer ion interaction parameters listed in Tables 3 and 5.

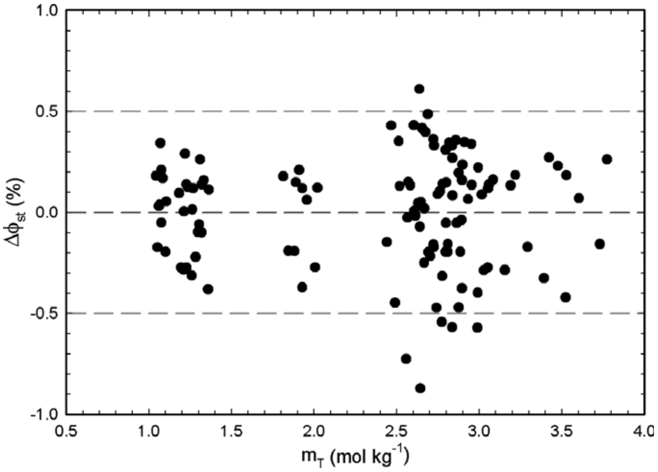

Fig. 14. Residuals between experimentally derived osmotic coefficient values and model-calculated values for $\{(1-y)Fe_2(SO_4)_3 + yH_2SO_4\}$ mixture data (experiment 4 only) reported by Velazquez-Rivera et al. (2006) at 323.15 K to 3.77 m with residuals expressed as relative percent of the osmotic coefficient value for all data.

system, as well as a different formulation using a constant third virial coefficient. It should be noted that the Clegg et al. (1994) model for the H_2SO_4 system is a factor of two more accurate than the Reardon and Beckie (1987) model. The same procedure was adapted to the data for 323.15 K, with a standard deviation of 0.0034 in ϕ_{st}. Although less accurate, we have included the Pitzer parameters for the normal 3-parameter formulation so that they may be used in conjunction with geochemical modeling programs such as PHRQPITZ and Geochemist's Workbench. However, as extended variations of the Pitzer formulation are now in common use, it would be ideal for such programs to include flexibility in the Pitzer formulations. Lastly, as we discuss below, the understanding of solubility relations for this system remain incomplete.

Table 7
Three-parameter Pitzer model parameter values, standard errors, standard deviation of fit (in ϕ_{st}) and total molality limits for Fe(III)–SO_4, Fe(III)–HSO_4, and mixing interactions for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 298.15 and 323.15 K

Parameter	Value	Standard error	Value	Standard error	Value	Standard error
$\beta^{(0)}_{\mathrm{Fe(III)-SO_4}}$	0.58784	0.00196	0.58864	0.00235	0.40983	0.06810
$\beta^{(1)}_{\mathrm{Fe(III)-SO_4}}$	11.65136	0.14563	11.16851	0.17480	12.47581	0.94465
$C_{\mathrm{Fe(III)-SO_4}}$	−0.00626	0.00007	−0.00631	0.00007	0.00112	0.00620
$C^{\phi}_{\mathrm{Fe(III)-SO_4}}$	−0.03067		−0.03092		0.00548	
$\alpha_{1\mathrm{Fe(III)-SO_4}}$	1.4	—	1.4	—	1.4	—
$\beta^{(0)}_{\mathrm{Fe(III)-HSO_4}}$	0.76349	0.01195	0.81413	0.01138	1.17043	0.04468
$\beta^{(1)}_{\mathrm{Fe(III)-HSO_4}}$	6.31030	0.26835	6.30150	0.36451	8.49723	1.21977
$C_{\mathrm{Fe(III)-HSO_4}}$	−0.00059	0.00165	−0.00918	0.00094	−0.04604	0.00517
$C^{\phi}_{\mathrm{Fe(III)-HSO_4}}$	−0.00204		−0.03179		−0.15950	
$\alpha_{1\mathrm{Fe(III)-HSO_4}}$	2.0	—	2.0	—	2.0	—
$\theta_{\mathrm{Fe(III)-H}}$	0.22875	0.02350	0.20010	0.02008	0	
$\psi_{\mathrm{H-Fe(III)-HSO_4}}$	0.02621	0.00728	0.02812	0.00374	0.03790	0.01326
$\psi_{\mathrm{SO_4-HSO_4-Fe(III)}}$	−0.03717	0.00629	−0.01195	0.00324	0	
$\psi_{\mathrm{H-Fe(III)-SO_4}}$	−0.02390	0.01013	−0.02504	0.00751	0	
T (K)	298.15		298.15		323.15	
σ	0.0048	—	0.0059	—	0.0034	—
m_T	3.0	—	5.47	—	3.77	—

7. SOLUBILITY RELATIONS IN THE $FE_2(SO_4)_3$–H_2SO_4–H_2O SYSTEM AT 25 °C: COMPARISON TO AVAILABLE DATA

As mentioned above, for Fe(III)–sulfate mineral phases there is a paucity of recent reliable solubility data. As a result, many aspects of Fe(III)–sulfate compounds are not fully understood, especially their stability relations in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 25 °C. However, recent studies by J. Majzlan and colleagues (Majzlan et al., 2004a,b, 2005, 2006) continue to report measured thermodynamic quantities needed to describe phase stability in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system. For example, Majzlan et al. (2006) recently derived $\Delta G_f{}^o$ values for ferricopiapite, rhomboclase, natural Al-bearing coquimbite, and $Fe_2(SO_4)_3(H_2O)_5$. The ΔG^o_f values are used to calculate ΔG^o_r and values for the equilibrium constant for can be calculated independently of ion interaction models, using the relationship

$$\Delta G^o_r = -RT\ln K \qquad (16)$$

Using the two different methods for deriving equilibrium constants for solid phases, comparisons can be made between the ion interaction model presented in this study, equilibrium constants calculated with recent thermodynamic data by Majzlan et al. (2006), and previous solubility studies conducted in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 25 °C.

To facilitate this comparison, we have focused on two minerals that exert control on Fe(III) and SO_4 concentrations in acidic solutions—rhomboclase and ferricopiapite. Using measured thermodynamic values for these phases reported by Majzlan et al. (2006), (listed in Table 8), we calculate solubility curves for rhomboclase and ferricopiapite using the extended Pitzer model described above to 5.47 m. Using selected data from solubility studies in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system, differences in solubility between literature-reported values and those calculated with our ion interaction model could more readily be identified. The selected solubility data for rhomboclase are those values for which authors have reported equilibrium with respect to an "acid Fe–sulfate mineral". This mineral phase

Table 8
Literature-reported ΔG^o_f values for aqueous species, rhomboclase, ferricopiapite, and calculated ΔG^o_r values for their solubility reactions

Species/phase	ΔG^o_f (kJ mol^{-1})	ΔG^o_r (kJ mol^{-1})	Ref.
H_2O (l)	−237.14	—	CO 89
Fe^{3+} (aq)	−16.28	—	P& K 95
$SO_4{}^{2-}$ (aq)	−744.0	—	CO 89
Rhomboclase	−2688	—	
$(H_3O)_{1.34}Fe(SO_4)_{2.17}(H_2O)_{3.06}$ (Rhomboclase) = Fe^{3+}(aq) + $2.17SO_4{}^{2-}$ + $4.4H_2O$ + $1.34H^+$	—	13.8	
Ferricopiapite	−10089.8	—	M 06
$Fe_{4.78}(SO_4)_6(OH)_{2.34}(H_2O)_{20.71}$ (Ferricopiapite) + $2.34H^+$ = $4.78Fe^{3+}$(aq) + $6SO_4{}^{2-}$ + $23.05H_2O$	—	81.9	M 06

CO 89, Cox et al. (1989); P & K 95, Parker and Khodakovskii (1995); M 06, Majzlan et al. (2006).

is usually reported empirically as $Fe_2O_3{\cdot}4SO_3{\cdot}9H_2O$, and was later suggested by (Posnjak and Merwin, 1922) to be the mineral rhomboclase. For ferricopiapite, we have chosen two datasets—one from (Baskerville and Cameron, 1935), who reported the equilibrium phase as $Fe_2O_3{\cdot}2.5SO_3{\cdot}7H_2O$, and one from (Wirth and Bakke, 1914), who referred to the phase as "copiapite" and/or "β-copiapite".

The results of the solubility calculations are listed in Table 9 and are shown graphically in Fig. 15. For rhomboclase solubility, there is a general discrepancy that decreases with increasing $m\mathrm{H_2SO_4}$. In general, the differences in rhomboclase solubility are minor above 4 m H_2SO_4. Below this value however, the solubility data reported by (Wirth and Bakke, 1914) display an essentially constant discrepancy between the predicted values of approximately 1 m H_2SO_4. For ferricopiapite, the solubility data are in poor agreement with the ion interaction model using reported ΔG^{o}_{f} values. In Table 9, these differences are listed alternatively in the difference in ΔG^{o}_{r} values between those calculated by our model and those derived from reported literature data. The differences in ΔG^{o}_{r} range from 2.4 to 6.0 kJ mol^{-1} and average 4.5 kJ mol^{-1} for rhomboclase. Given the reported error for the ΔG^{o}_{f} value for rhomboclase (±2.7 kJ mol^{-1}), and its somewhat varying composition (Majzlan et al., 2006), the agreement is encouraging and points toward partial agreement between independent activity coefficient calculation, measurement of thermodynamic properties, and solubility determinations for this

Table 9

Selected solubility data reported with respect to rhomboclase and ferricopiapite, solute molality and molality fraction and ΔG^{o}_{r} values relative to literature values for their solubility reactions calculated with the ion interaction model presented in this study

$Fe_2(SO_4)_3$ (mol kg^{-1})	H_2SO_4 (mol kg^{-1})	y	$\Delta G^{o}_{r(\mathrm{calc})}$ (kJ mol^{-1})	Reaction	Ref.
0.47	4.94	0.91	11.4	Rh	B & C (1935)
0.71	4.42	0.86	10.2	Rh	B & C (1935)
0.83	4.13	0.83	9.8	Rh	B & C (1935)
0.85	4.10	0.83	9.7	Rh	B & C (1935)
1.18	3.24	0.73	8.9	Rh	C & R (1907)
0.39	5.43	0.93	10.7	Rh	A & W (1922)
0.68	4.52	0.87	10.3	Rh	W & B (1914)
1.00	3.68	0.79	9.4	Rh	W & B (1914)
1.33	2.97	0.69	8.4	Rh	W & B (1914)
1.51	2.70	0.64	7.8	Rh	W & B (1914)
1.57	2.57	0.62	7.9	Rh	W & B (1914)
1.68	2.23	0.57	8.3	Rh	W & B (1914)
1.88	1.97	0.51	7.8	Rh	W & B (1914)
1.67	1.86	0.53	54.6	Fc	B & C (1935)
1.70	1.44	0.46	59.0	Fc	B & C (1935)
1.81	1.11	0.38	61.0	Fc	B & C (1935)
1.89	0.65	0.26	66.3	Fc	B & C (1935)
1.96	0.32	0.14	71.9	Fc	B & C (1935)
1.80	0.86	0.32	64.8	Fc	W & B (1914)
1.84	0.81	0.31	64.8	Fc	W & B (1914)
1.95	0.26	0.12	74.0	Fc	W & B (1914)

B & C (1935), Baskerville and Cameron (1935); C & R (1907), Cameron and Robinson (1907); A & W (1922), Appleby and Wilkes (1922); W & B (1914), Wirth and Bakke (1914); (Rh), rhomboclase; (Fc), ferricopiapite.

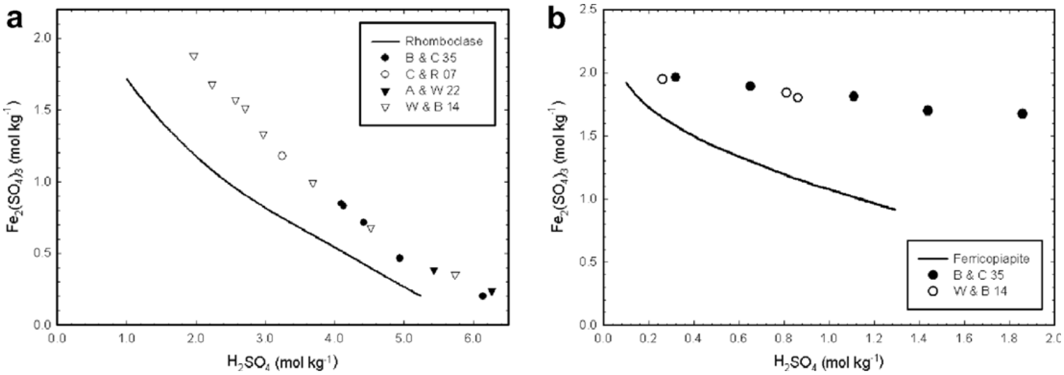

Fig. 15. Predicted and measured solubilities of rhomboclase (a) and ferricopiapite (b). Calculated solubilities use ΔG^{o}_{r} values derived from literature-reported values for $\Delta G_{f}{}^{o}$ for aqueous species and rhomboclase and ferricopiapite (Table 8) (B & C, Baskerville and Cameron (1935); C & R, Cameron and Robinson (1907); A & W, Appleby and Wilkes (1922); W & B, Wirth and Bakke (1914)).

phase. Differences for ferricopiapite, however, are much larger and range from 7.9 to 27.3 kJ mol^{-1} with an average difference of -17.3 kJ mol^{-1}. The reported error for ΔG_f^o ferricopiapite is ± 9.3 kJ mol^{-1}. There may be several reasons for these discrepancies. For example, Majzlan et al. (2006) have shown that rhomboclase and ferricopiapite display variable and non-stoichiometric occupancy which means that the composition of these phases may vary. In calculating ΔG_r^o, such differences may affect the equilibrium constant and in turn, calculated solubility. In addition, because of the difficulty in separating solid and liquid phases in this system (Appleby and Wilkes, 1922), several of the solubility studies available for ferricopiapite and rhomboclase determined the composition of solid phases indirectly by graphical methods. In addition, (Baskerville and Cameron, 1935) report the presence of colloidal dispersions in solution, increasing the likelihood that excess Fe and SO_4 may have contributed to solution analyses. This would be consistent with the relative positions of calculated and reported solubilities of rhomboclase and ferricopiapite in Fig. 15. Another possibility is that some solubility data are not at equilibrium. Disequilibrium may be possible for the (Wirth and Bakke, 1914) study, which reports an ongoing physical change with the "basic iron sulfate salt", which they describe as "copiapite". Accordingly, (Posnjak and Merwin, 1922) suggested that the method of adding ferric oxide to ferric sulfate solutions used by (Wirth and Bakke, 1914) to reach equilibrium may have proceeded at an exceedingly slow rate. Rhomboclase may not have suffered from such complications owing to its ready precipitation from highly concentrated solutions, as reported by Majzlan et al. (2006) and Tosca et al. (2004). One final possibility that cannot be ruled out until this discrepancy is resolved with further data is that the isopiestic data are in error. However, the general agreement between both studies used to derive Pitzer parameters for this system and the incorporation of the Clegg et al. (1994) model for sulfuric acid results in a model that accurately represents a much larger set of reported solution properties.

The most important conclusion to be drawn from these comparisons is that there is only partial agreement between predicted and measured rhomboclase solubility at high H_2SO_4 regions (i.e., Baskerville and Cameron, 1935) values and some values from (Wirth and Bakke, 1914), but agreement between reported and predicted values of ferricopiapite solubility is poor. The complications mentioned above for measuring solubility in this system are well known from other field and laboratory-based studies. Indeed, additional solubility data for Fe^{3+}–sulfate phases in this system are needed to resolve the discrepancies noted above, as well as additional thermodynamic measurements to represent regions of low molality for this system.

8. CONCLUSIONS

In conclusion, the results described above show that isopiestic data of solutions in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system can be accurately described within the framework of the Pitzer ion interaction model over the essentially complete region of solute molality fraction at 298.15 K to 3.0, and 5.47 m. The incorporation of the Clegg et al. (1994) model for H_2SO_4 in this system increases the applicability of the model to other systems containing aqueous sulfuric acid and ferric iron. Indeed, multiple sources of data are needed to further validate the model. The comparison between measured thermodynamic properties and those derived from solubility studies shows that mineral-solution equilibrium under certain conditions in the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system is complicated by several factors. More solubility data are needed to attain agreement between various methods of determining phase stability in this system and the above complications should continue to be addressed in future solubility determinations. However, integration of activity coefficient calculation, thermodynamic, and solubility measurements shows partial agreement and the results are encouraging. The ultimate goal for the system remains a comprehensive and accurate description of solution and solid phase thermodynamic properties and future work will only continue to improve the accuracy and reliability of thermodynamic calculations for this system. Perhaps the most important applications of such research, however, involves the improved understanding of Fe and sulfate-rich environments on Earth (such as industrial waste and acid mine drainage sites and their remediation) as well as unique environments on Mars that provide detailed chemical windows into ancient surficial conditions on that planet.

ACKNOWLEDGMENTS

The authors thank Brian Hahn for many helpful discussions regarding statistics and regression techniques. In addition, the authors thank three anonymous reviewers and the Associate Editor, Dr. Robert Byrne, for suggestions that greatly improved the quality of the manuscript, specifically with regard to evaluation of the $Fe_2(SO_4)_3$ system and discussion of solubility data. This research was supported by NASA Mars Fundamental Research Program Grant NNX06AB67G to SMM.

REFERENCES

Appleby M. P., and Wilkes S. H. (1922) The system ferric oxide–sulphuric acid–water. *J. Chem. Soc.* **121**, 337–348.

Archer D. G. (1992) Thermodynamic properties of the NaCl + H_2O system. 2. Thermodynamic properties of NaCl (aq), NaCl·2H_2O (cr), and phase-equilibria. *J. Phys. Chem. Ref. Data* **21**, 793–829.

Archer D. G., and Rard J. A. (1998) Isopiestic investigation of the osmotic and activity coefficients of aqueous $MgSO_4$ and the solubility of $MgSO_4 \cdot 7H_2O$(cr) at 298.15 K: thermodynamic properties of the $MgSO_4 + H_2O$ system to 440 K. *J. Chem. Eng. Data* **43**, 791–806.

Archer D. G., and Wang P. M. (1990) The dielectric-constant of water and Debye-Huckel limiting law slopes. *J. Phys. Chem. Ref. Data* **19**, 371–411.

Baes, Jr., C. F., Reardon E. J., and Moyer B. A. (1993) Ion interaction model applied to the $CuSO_4$–H_2SO_4–H_2O system at 25 °C. *J. Phys. Chem.* **97**, 12343–12348.

Baskerville W. H., and Cameron F. K. (1935) Ferric oxide and aqueous sulfuric acid at 25 °C. *J. Phys. Chem.* **39**, 769–779.

Burgess J. (1999) Ions in solution: basic principles of chemical interactions. Horwood.

Cameron F. K., and Robinson C. (1907) Ferric sulphates. *J. Phys. Chem.* **11**, 641–650.

Clegg S. L., and Brimblecombe P. (1995) Application of a multicomponent thermodynamic model to activities and thermal properties of 0–40 mol kg^{-1} aqueous sulfuric acid from <200 to 328 K. *J. Chem. Eng. Data* **40**, 43–64.

Clegg S. L., and Seinfeld J. H. (2004) Improvement of the Zdanovskii-Stokes-Robinson model for mixtures containing solutes of different charge types. *J. Phys. Chem. A* **108**, 1008–1017.

Clegg S. L., Rard J. A., and Pitzer K. S. (1994) Thermodynamic properties of 0–6 mol/kg aqueous sulfuric acid from 273.15 to 328.15 K. *J. Chem. Soc., Faraday Trans.* **90**, 1875–1894.

Clegg S. L., and Whitfield M. (1995) A chemical model of seawater including dissolved ammonia and the stoichiometric dissociation-constant of ammonia in estuarine water and seawater from 2 °C to 40 °C. *Geochim. Cosmochim. Acta* **59**, 2403–2421.

Cox J. D., Wagman D. D., and Medvedev V. A. (1989) *CODATA Key Values for Thermodynamics*. Hemisphere Publishing Corp., New York.

Harvie, C. E. (1981) Theoretical investigations in geochemistry and atom surface scattering. Ph.D. Dissertation, U.C. San Diego.

Hovey J. K., Pitzer K. S., and Rard J. A. (1993) Thermodynamics of Na_2SO_4(aq) at temperatures T from 273 to 373 K and of $\{(1-y)H_2SO_4 + yNa_2SO_4\}$(aq) at $T = 298.15$ K. *J. Chem. Thermodyn.* **25**, 173–192.

Jamieson H. E., Robinson C., Alpers C. N., McCleskey R. B., Nordstrom D. K., and Peterson R. C. (2005) Major and trace element composition of copiapite-group minerals and coexisting water from the Richmond Mine, Iron Mountain, California. *Chem. Geol.* **215**, 387–405.

Majima H., and Awakura Y. (1985) Water and solute activities of H_2SO_4–$Fe_2(SO_4)_3$–H_2O and HCl–$FeCl_3$–H_2O solution systems: Part I. Activities of water. *Metallurgical Trans. B* **16B**, 433–439.

Majzlan J., Navrotsky A., McCleskey R. B., and Alpers C. N. (2006) Thermodynamic properties and crystal structure refinement of ferricopiapite, coquimbite, rhomboclase, and $Fe_2(SO_4)_3(H_2O)_5$. *Eur. J. Mineralogy* **18**, 175–186.

Majzlan J., Navrotsky A., and Schwertmann U. (2004a) Thermodynamics of iron oxides: Part III. Enthalpies of formation and stability of ferrihydrite ($\sim Fe(OH)_3$), schwertmannite ($\sim FeO(OH)_{3/4}(SO_4)_{1/8}$), and ε-$Fe_2O_3$. *Geochim. Cosmochim. Acta* **68**, 1049–1059.

Majzlan J., Navrotsky A., Stevens R., Donaldson M., Woodfield B. F., and Boerio-Goates J. (2005) Thermodynamics of $Fe_2(SO_4)_3$. *J. Chem. Thermodyn.* **37**, 802–809.

Majzlan J., Stevens R., Boerio-Goates J., Woodfield B. F., Navrotsky A., Burns P. C., Crawford M. K., and Amos T. G. (2004b) Thermodynamic properties, low-temperature heat-capacity anomalies, and single crystal X-ray refinement of hydronium jarosite, $(H_3O)Fe_3(SO_4)_2(OH)_6$. *Phys. Chem. Miner.* **31**, 518–531.

Marion G. M. (2002) A molal-based model for strong acid chemistry at low temperatures (<200 to 298 K). *Geochim. Cosmochim. Acta* **66**, 2499–2516.

Nordstrom, D. K., and Alpers, C. N. (1999a) Geochemistry of acid mine waters. In *The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques, and Health Issues* (eds. G. S. Plumlee and M. J. Logsdon). Society of Economic Geologists, Inc., Littleton.

Nordstrom, D. K., and Alpers, C. N. (1999b) Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. In *Proceedings of the National Academy of Sciences*, vol. 96, 3455–3462.

Parker V. B., and Khodakovskii I. L. (1995) Thermodynamic properties of the aqueous ions (2+ and 3+) of Iron and the key compounds of iron. *J. Phys. Chem. Ref. Data* **24**(5), 1699–1745.

Pitzer K. S. (1973) Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **77**, 268–277.

Pitzer K. S. (1975) Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms. *J. Solut. Chem.* **4**, 249.

Pitzer, K. S. (1991) Ion interaction approach: theory and data correlation. In *Activity Coefficients in Electrolyte Solutions* (ed. K. S. Pitzer). CRC Press, Boca Raton.

Pitzer K. S., and Kim J.-J. (1974) Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes. *J. Am. Chem. Soc.* **96**, 5701.

Posnjak E., and Merwin H. E. (1922) The system, Fe_2O_3–SO_3–H_2O. *J. Am. Chem. Soc.* **44**, 1965–1994.

Rard J. A., and Clegg S. L. (1999) Isopiestic determination of the osmotic coefficient and activity coefficients of $\{zH_2SO_4 + (1-z)MgSO_4\}$ at $T = 298.15$ K. II. Results for $z = (0.43040, 0.28758, \text{and } 0.14399)$ and analysis with Pitzer's model. *J. Chem. Thermodyn.* **31**, 399–429.

Rard J. A., Habenschuss A., and Spedding F. H. (1976) Review of osmotic coefficients of aqueous H_2SO_4 at 25 °C. *J. Chem. Eng. Data* **21**, 374–379.

Rard J. A., and Wijesinghe A. M. (2003) Conversion of parameters between different variants of Pitzer's ion-interaction model, both with and without ionic strength dependent higher-order terms. *J. Chem. Thermodyn.* **35**, 439–473.

Reardon E. J. (1989) Ion interaction model applied to equilibria in the $NiSO_4$–H_2SO_4–H_2O system. *J. Phys. Chem.* **93**, 4630–4636.

Reardon E. J., and Beckie R. D. (1987) Modelling chemical equilibria of acid mine drainage: the $FeSO_4$–H_2SO_4–H_2O system. *Geochim. Cosmochim. Acta* **51**, 2355–2368.

Rumyantsev A. V., Hagemann S., and Moog H. C. (2004) Isopiestic investigation of the systems $Fe_2(SO_4)_3$–H_2SO_4–H_2O, $FeCl_3$–H_2O, and Fe(III)–(Na, K, Mg, Ca)Cl_n–H_2O at 298.15 K. *Zeitschrift fur Physikalische Chemie* **218**, 1089–1127.

Stumm W., and Morgan J. J. (1996). *Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters*. John Wiley & Sons, New York.

Tosca N. J., McLennan S. M., Lindsley D. H., and Schoonen M. A. A. (2004) Acid-sulfate weathering of synthetic Martian basalt: the acid fog model revisited. *J. Geophys. Res.—Planets* **109**. doi:10.1029/2003JE00221.

Tosca N. J., McLennan S. M., Clark B. C., Grotzinger J. P., Hurowitz J. A., Knoll A. H., Schroeder C., and Squyres S. W. (2005) Geochemical modeling of evaporation processes on Mars: insight from the sedimentary record at Meridiani Planum. *Earth Planetary Sci. Lett.* **240**, 122–148.

Tosca N. J., and McLennan S. M. (2006) Chemical divides and evaporite assemblages on Mars. *Earth Planetary Sci. Lett.* **241**, 21–31.

Velazquez-Rivera M., Palmer D. A., and Kettler R. M. (2006) Isopiestic measurement of the osmotic coefficients of aqueous $\{xH_2SO_4 + (1-x)Fe_2(SO_4)_3\}$ solutions at 298.15 and 323.15 K. *J. Solut. Chem.* **35**, 1699–1730.

Wirth F., and Bakke B. (1914) Untersuchung über Ferrisulfate. Darstellung und Eigenschaften der verschiedenen normalen, basischen und sauren Ferrisulfate. Löslichkeits- und Stabilitätsverhältnisse in Wasser und Schwefelsäure. Kristallisationsgang. *Zeitschrift für anorganische Chemie* **87**, 13–46.

Zdanovskii A. B. (1936) Trudy Solyanoi Laboratorii. *Akad. Nauk. SSSR* **6**, 70.

Associate editor: Robert H. Byrne