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Thermodynamics of Aqueous Sodium Sulfate from 273 to 373 K and Mixtures of Aqueous Sodium Sulfate and Sulfuric Acid at 298 K

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Thermodynamics of aqueous sodium sulfate from the temperatures 273 K to 373 K and mixtures of aqueous sodium sulfate and sulfuric acid at 298.15 K [a]

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[a] This paper is dedicated to Professor Loren Hepler in honor of his retirement.

Abstract-

New isopiestic vapor-pressure measurements on the aqueous system $\{(1-y)H_2SO_4+yNa_2SO_4\}$ along with earlier experimental investigations that span the range from $y = 0$ to $y = 1$ and infinitely dilute to supersaturated molalities have been analyzed in terms of the Pitzer ion-interaction model. Refined ion-interaction parameters for aqueous sodium sulfate valid over the temperature range 273 K to 373 K have been calculated and used for analysing results for mixtures containing sulfuric acid and sodium sulfate at 298.15 K. Analysis of experimental results for these aqueous mixtures required explicit consideration of the dissociation reaction of bisulfate ion. Previous treatments of aqueous sulfuric acid and subsequently the bisulfate dissociation equilibrium valid in the range 273 K to 343 K were employed as a first approximation in representing the mixed solutions. Two sets of Pitzer ion-interaction parameters are presented for (sodium sulfate + sulfuric acid). The validity of the first set is limited in ionic strength and molality to saturated solutions of pure aqueous sodium sulfate (4 mol·kg^{-1}). The second set of parameters corresponds to a slightly less precise representation but is valid over the entire range of experimental results considered. Both sets of parameters provide a more complete description of pure sulfuric acid solutions because of the removal of various redundancies of ion-interaction parameters. The specific ion-interaction terms used and the overall fitting procedure are described as well as selected examples of relevant thermodynamic calculations in the mixed system Na_2SO_4–H_2SO_4–H_2O.

1. Introduction

The aqueous binary systems composed of sulfuric acid or sodium sulfate or the ternary mixture formed from both are immensely important for a variety of chemical, geochemical, and industrial processes. The equilibrium properties of the binary systems have been extensively investigated especially at low molalities and near room temperature.[1] The importance of thermodynamic values leading to activities for these binary systems and in complex systems formed by combinations of all of these electrolytic species is paramount to understanding many equilibria of practical importance especially those involving dissolved species and vapor-liquid equilibria.[2]

Appropriate thermodynamic values leading to the variation of the Gibbs free energies with composition for the mixtures of sulfuric acid and sodium sulfate are limited. The current status on the amount and type of data available has been discussed by one of the authors.[3] Rard[3,4] has provided the most complete set of osmotic coefficients to date for the aqueous mixed system characterized by $\{(1-y)H_2SO_4 + yNa_2SO_4\}$ where y is the molality fraction of Na_2SO_4. His results cover the range $y = 0.12$ to $y = 0.85$ and extend to supersaturated molalities. Rard[3] has considered the mixture to consist in one case of two completely dissociated electrolytes. In the second case, the system is treated as a mixture of a 1:1 (sulfuric acid) and (2:1) (sodium sulfate) electrolyte.

The present analysis is intended to go further in that the speciation of the solutions determined by the bisulfate dissociation is explicitly considered. The equilibrium that accounts for deviations in treatments considering either total dissociation of sulfuric acid or treating sulfuric acid as a 1:1 electrolyte, is the bisulfate dissociation represented by:

$$HSO_4^-(aq) = H^+(aq) + SO_4^{2-}(aq). \tag{1}$$

There is good agreement among several investigators for the equilibrium constant for this reaction at 298.15 K[5,6] and the temperature dependence is well defined in the range 283.15 K to 328.15 K.[5,7] The stoichiometric activity coefficients and the ratio of appropriate ionic activity coeffcients required for calculation of amounts of species present at finite ionic strengths are

well known to 6 mol·kg^{-1} for H_2SO_4 (stoichiometric). Here we explicitly consider this equilibrium reaction in the representation of the experimental osmotic coefficients and subsequently the various activity coefficients required for use in such a treatment.

We have used the Pitzer ion-interaction model to treat the available osmotic coefficient results for this mixture at 298.15 K. The range of ionic strengths and molalities considered in the following treatment push the molality based ion-interaction model to near its limit. Previous precise formulations represent the thermodynamic properties of sulfuric acid[5,8,9] up to approximately 6 mol·kg^{-1}. Revised parameters for pure sodium sulfate presented later, extend to the limit of the available data (supersaturated). Many calculations involving the species of present interest are focussed on truly low ionic-strength regimes. We thus present results representative of the thermodynamic properties of the mixture useful in this dilute range of ionic strengths. There are of course other important uses of thermodynamic values for the mixed system at higher molalities for a variety of water activity calculations, vapor pressures, and solubility experiments. To this end, we present a complete set of parameters valid to 15 mol·kg^{-1} (stoichiometric) sulfuric acid and correspondingly high ionic strength values for the mixtures.

2. Speciation

The dissociation of bisulfate controls the distribution of species and thus the molalities of all species (except sodium ion) for solutions containing mixtures of sulfuric acid and sodium sulfate. Initial molalities of sodium sulfate and sulfuric acid in combination with the equilibrium constant expression and a suitable expression for the activity coefficients of the participating species can be solved for the molalities of ionic species present at equilibrium.

The equilibrium constant coresponding to the bisulfate equilibrium (equation (1)) is given by

$$K_{eq} = a_{\mathrm{H}} a_2 / a_1 = \{m_{\mathrm{H}} m_2 / (m^{\circ} m_1)\}(\gamma_{\mathrm{H}} \gamma_2 / \gamma_1) \tag{2}$$

where a, m, and γ represent activity, molality, and activity coefficient respectively and various abbreviations are defined as follows: $m^{\circ} = 1$ mol·kg^{-1}, and m_{H}, m_1, m_2, and m_{Na} denote

molalities of $H^+(aq)$, $HSO_4^-(aq)$, $SO_4^{2-}(aq)$, and $Na^+(aq)$ respectively, and $\gamma_{ratio} = (\gamma_H\gamma_2)/\gamma_1$.

The initial molalities of species are unambiguously defined for $\{(1-y)H_2SO_4 + yNa_2SO_4\}$ according to the total molality m_T and the mole ratio y. The various molalities of species written in terms of the equilibrium molality of hydrogen and the initial molalites of sodium sulfate ($m_{2,i}$) and sulfuric acid ($m_{1,i}$) are:

$$m_1 = 2m_{1,i} - m_H, \tag{3}$$
$$m_2 = m_{2,i} - m_{1,i} + m_H, \tag{4}$$

where

$$m_{1,i} = (1-y)m_T, \tag{5}$$
$$m_{2,i} = ym_T. \tag{6}$$

Here m_T represents the <u>total</u> molality and is equal to the sum of stoichiometric molalities of sodium sulfate and sulfuric acid.

The exact iterative procedure used to refine the speciation is discussed in detail in section 5. It suffices here to show the relation of intitial and equilibrium molalities.

3. Ion-interaction equations: sodium sulfate and sulfuric acid

Isopiestic results for the sodium sulfate and sulfuric acid mixtures were obtained over such a wide range of ionic strengths and molalities that a new higher precision fit was required for (sodium sulfate + water). Pabalan and Pitzer[10] have provided a detailed description of aqueous sodium sulfate in terms of the ion-interaction model. This treatment was intended for and covers a broad and higher temperature and pressure range and thus is not as precise at 298.15 K as a less broad representation could be. We have chosen representative values at 298.15 K and below from literature sources and the results of the Pabalan and Pitzer treatment from 303.15 K to 372.75 K to generate new parameters for sodium sulfate valid from 273.15 K to 372.75 K. The results of these calculations are presented following the presentation of appropriate equations.

Ion-interaction treatments of thermodynamic data for aqueous sulfuric acid from 278.15 K to 328.15 K have been presented by Pitzer <u>et al.</u>[5] and from 273.15 K to 343.15 K by Reardon

and Beckie.[8] These treatments are valid only up to an ionic strength set by 6 mol·kg^{-1} sulfuric acid. Reardon and Beckie[8] also included the higher order terms for unsymmetrical mixing that Pitzer et al.[5] had omitted. These terms are included in the present work. Results of fits employing both of these treatments are presented along with refined parameters derived from results for (sulfuric acid + sodium sulfate). Because several different applications of the ion-interaction equation are used, including refinement of parameters for the binary systems, we summarize all of the appropriate ion-interaction equations below.

The fundamental ion-interaction equation can be written for the excess Gibbs energy of a pure electrolyte:

$$G^{\mathrm{E}}/(w_w RT) = f(I) + 2\nu_{\mathrm{M}}\nu_{\mathrm{X}}(m/m^{\circ})^2[B_{\mathrm{MX}} + \nu_{\mathrm{M}} z_{\mathrm{M}}(m/m^{\circ})C_{\mathrm{MX}}] \tag{7}$$

where appropriate quantities are defined by

$$f(I) = -\left[4(I/m^{\circ})A_{\phi}\ln\{1 + b(I/m^{\circ})^{1/2}\}\right]/b \tag{8}$$

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}} g\{\alpha_1(I/m^{\circ})^{1/2}\} + \beta^{(2)}_{\mathrm{MX}} g\{\alpha_2(I/m^{\circ})^{1/2}\} \tag{9}$$

$$g\{\alpha(I/m^{\circ})^{1/2}\} = 2\left[1 - \{1 + \alpha(I/m^{\circ})^{1/2}\}\exp\{-\alpha(I/m^{\circ})^{1/2}\}\right]/\{\alpha^2(I/m^{\circ})\} \tag{10}$$

Also A_{ϕ} is the Debye-Hückel slope for the osmotic coefficient, w_w is the mass of water present in kg, and β and C terms are interaction parameters functions of the solute, temperature and pressure, and describe binary and ternary ion-interactions. All Debye-Hückel slopes were derived from Archer and Wang.[11] The maximum difference in A_{ϕ} from the earlier values of Bradley and Pitzer[12] is 0.0003 in the range 273 K to 373 K. The α terms represent the ionic strength dependence of the various B terms as given by equation (9). The optimum values of α_1 have been found to range from 1.4 to 2.0 for various electrolytes depending on the ions present. Usually, 1:1 and 2:1 electrolytes are best treated when α_1 has the value 2.0. There is theoretical evidence that α_2 is proportional to A_{ϕ}.[13] The significance of the α_2 and thus the $\beta^{(2)}$ term is thoroughly discussed by Pitzer.[13] The term in $\beta^{(2)}$ was omitted except for one final calculation discussed in section 5.

The osmotic coefficient of aqueous sodium sulfate is given in terms of the ion-interaction model by:

$$\phi - 1 = -\left(\partial G^{\mathrm{E}}/\partial w_w\right)_{n_i} / (RT \sum_i m_i) \tag{11}$$

$$= 2f^{\phi} + (4/3)(m/m^{\circ})B^{\phi}_{\mathrm{Na2}} + (4\sqrt{2}/3)(m/m^{\circ})^2 C^{\phi}_{\mathrm{Na2}} \tag{12}$$

The stoichiometric mean ionic activity coefficient is represented by

$$\ln \gamma_{\pm} = (\nu_{\mathrm{M}} \ln \gamma_{\mathrm{M}} + \nu_{\mathrm{X}} \ln \gamma_{\mathrm{X}})/\nu \tag{13}$$

$$= \left\{\nu_{\mathrm{M}} \left[\partial\{G^{\mathrm{E}}/(w_w RT)\}/\partial m_{\mathrm{M}}\right]_{n_w} + \nu_{\mathrm{X}} \left[\partial\{G^{\mathrm{E}}/(w_w RT)\}/\partial m_{\mathrm{X}}\right]_{n_w}\right\} / \nu. \tag{14}$$

For Na_2SO_4, $\nu_{\mathrm{M}} = 1$, $\nu_{\mathrm{X}} = 2$, and $\nu = 3$ whereupon

$$\ln \gamma_{\pm} = 2f^{\gamma} + (4/3)(m/m^{\circ})B^{\gamma}_{\mathrm{Na2}} + (4\sqrt{2}/3)(m/m^{\circ})^2 C^{\gamma}_{\mathrm{Na2}} \tag{15}$$

and the various terms are defined by·

$$f^{\phi} = -A_{\phi}(I/m^{\circ})^{1/2}/\{1 + b(I/m^{\circ})^{1/2}\} \tag{16}$$

$$B^{\phi}_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}} \exp\{-\alpha_1(I/m^{\circ})^{1/2}\} + \beta^{(2)}_{\mathrm{MX}} \exp\{-\alpha_2(I/m^{\circ})^{1/2}\} \tag{17}$$

$$f^{\gamma} = -A_{\phi}\left[(I/m^{\circ})^{1/2}/\{1 + b(I/m^{\circ})^{1/2}\} + (2/b)\ln\{1 + b(I/m^{\circ})^{1/2}\}\right] \tag{18}$$

$$B^{\gamma} = B_{\mathrm{MX}} + B^{\phi}_{\mathrm{MX}} \tag{19}$$

$$C^{\phi} = 2 \mid z_{\mathrm{M}} z_{\mathrm{X}} \mid^{1/2} C_{\mathrm{MX}} = (2/3)C^{\gamma}_{\mathrm{MX}} \tag{20}$$

Here and elsewhere b is a universal parameter equal to 1.2.

Aqueous solutions containing sulfuric acid are not completely dissociated at any range of molalities of practical interest. As such, this electrolyte must be treated as a mixture of species, amounts of which are defined according to the dissociation equilibrium for bisulfate ion represented by equation (1).

The excess Gibbs energy for a solution containing any number of cations and anions (excluding neutral solutes) is given by[13]

$$G^{E}/(w_w RT) = f(I) + 2\sum_c\sum_a m_c m_a\{B_{ca} + (\sum_c m_c z_c)C_{ca}\} + \sum_c\sum_{c'} m_c m_{c'}\,(2\Phi_{cc'} + \sum_a m_a \psi_{cc'a}\Big) + \sum_a\sum_{a'} m_a m_{a'}\left(2\Phi_{aa'} + \sum_c m_c \psi_{aa'c}\right) + \ldots \quad (21)$$

The Φ and ψ terms represent the contributions from mixing dissimilar electrolytes and are present only for systems containing different cations and/or anions. The exact form of these terms is discussed later in reference to sulfuric acid. Equation (21) is appropriate for systems containing any number of ionic species and is easily modified to handle mixtures of ionic species with neutral molecules. Equation (21) reduces to equation (7) for the special case of a single electrolyte.

The bisulfate dissociation constant value is well defined at 298.15 K by results of fits to osmotic coefficients and electromotive force measurements by Pitzer et al.[5] This result combined with the corresponding enthalpy and heat capacity change for dissociation of bisulfate ion leads to the equation for the equilibrium constant presented by Hovey and Hepler,[7] that is valid over a wider temperature range. Potentiometric measurements leading to values for the dissociation constant at still higher temperatures[14] are consistent with these more precise low-temperature results.

Previous applications of the ion-interaction model to sulfuric acid solutions have not utilized all possible ion-interaction terms because of various near-redundancies among parameters. The dissociation of bisulfate ion restricts the molality ratios of the species present to slowly varying values that hinder reliable regression of some parameters especially the mixing terms. A detailed treatment of sulfuric acid solutions in terms of the ion-interaction model and the various parameter redundancies is given by Pitzer et al.[5] The new isopiestic measurements for mixtures of sodium sulfate and sulfuric acid cover such a wide range of ionic strengths and molalities that all available interaction parameters become significant, some in the sense that they are of a small enough magnitude to have a zero value.

The ion-interaction equations for the osmotic coefficients of aqueous sulfuric acid on a

mixed basis are given by:

$$\phi_{\text{mix}} - 1 = \{2/(m_{\text{H}} + m_1 + m_2)\} \left[f^{\phi} I + (m_{\text{H}} m_1/m^{\circ})(B^{\phi}_{\text{H1}} + ZC_{\text{H1}}) + (m_{\text{H}} m_2/m^{\circ})(B^{\phi}_{\text{H2}} + ZC_{\text{H2}}) + (m_1 m_2/m^{\circ})\{\Phi^{\phi}_{12} + (m_{\text{H}}/m^{\circ})\psi_{12H}\} \right] \quad (22)$$

where

$$Z = \sum_i (m_i/m^{\circ}) \mid z_i \mid \quad (23)$$

and m_1 and m_2 are equilibrium molalities of HSO_4^-(aq) and SO_4^{2-}(aq), respectively.

This expression is easily derived from equation (21) and its appropriate derivative represented by equation (11). The activity coefficient ratio for the bisulfate dissociation reaction in pure sulfuric acid solutions is given by:

$$\ln(\gamma_{\text{H}}\gamma_2/\gamma_1) = 4F + \{(m_1 - m_{\text{H}})/m^{\circ}\}(2B_{\text{H1}} + ZC_{\text{H1}}) + \{(m_2 + m_{\text{H}})/m^{\circ}\}(2B_{\text{H2}} + ZC_{\text{H2}}) + 2\{m_{\text{H}} m_1/(m^{\circ})^2\}C_{\text{H1}} + 2\{m_{\text{H}} m_2/(m^{\circ})^2\}C_{\text{H2}} + 2\{(m_1 - m_2)/m^{\circ}\}\Phi_{12} + \{(m_1 m_2 + m_1 m_{\text{H}} - m_2 m_{\text{H}})/(m^{\circ})^2\}\psi_{12H} \quad (24)$$

where F for sulfuric acid is given by:

$$F = f^{\gamma} + \{m_{\text{H}} m_1/(m^{\circ})^2\}B'_{\text{H1}} + \{m_{\text{H}} m_2/(m^{\circ})^2\}B'_{\text{H2}} + \{m_1 m_2/(m^{\circ})^2\}\Phi'_{12} \quad (25)$$

and f^{γ} was defined by equation (18), and the B' terms that represent the ionic strength derivatives of the various B terms are given by:

$$B'_{\text{MX}} = \left[\beta^{(1)}_{\text{MX}}\, g'\{\alpha_1(I/m^{\circ})^{1/2}\} + \beta^{(2)}_{\text{MX}}\, g'\{\alpha_2(I/m^{\circ})^{1/2}\}\right] / (I/m^{\circ}) \quad (26)$$

where

$$g'\{\alpha(I/m^{\circ})^{1/2}\} = -2\left[1 - \left\{1 + \alpha(I/m^{\circ})^{1/2} + \alpha^2(I/m^{\circ})/2\right\}\exp\{-\alpha(I/m^{\circ})^{1/2}\}\right] / \{\alpha^2(I/m^{\circ})\} \quad (27)$$

The binary mixing parameter Φ_{12} in equation (24) is related to the parameter Φ^{ϕ}_{12} appearing in equation (22) and others by:

$$\Phi^{\phi}_{12} = \Phi_{12} + I\Phi'_{12}, \quad (28)$$

where Φ'_{12} is the ionic strength derivative of Φ_{12}. Theoretical investigations by Pitzer[15] and Friedman[16] have led to rigorous expressions for Φ'_{12} for the case of unsymmetrical mixing. Here unsymmetrical mixing refers to the mixing of ions of the same sign but with different valency. Appropriate expressions for this binary term are thus

$$\Phi'_{12} = {}^{E}\theta'_{12}(I), \tag{29}$$

where Φ_{12} is defined to have the ionic strength dependence

$$\Phi_{12} = \theta_{12} + {}^{E}\theta_{12}(I). \tag{30}$$

Combining these expressions with equation (28) leads to

$$\Phi^{\phi}_{12} = \theta_{12} + I^{E}\theta'_{12}(I) + {}^{E}\theta_{12}(I). \tag{31}$$

The terms ${}^{E}\theta'_{12}(I)$ and ${}^{E}\theta_{12}(I)$ can be determined from theory. Convenient polynomial expressions for calculation of these terms were derived by Harvie[17] and are summarized by Pitzer.[13] These expressions were used here to calculate all theoretical unsymmetrical mixing terms. The term θ_{12} is determined by regression of experimental results.

The stoichiometric osmotic coefficient for sulfuric acid (ϕ) refers to the completely dissociated standard state and is related to the osmotic coefficient on a mixed basis by:

$$\phi = \{(m_1 + m_2 + m_{\mathrm{H}})/(3m)\}\phi_{\mathrm{mix}} \tag{32}$$

where m is the stoichiometric molality of sulfuric acid and the various m_i values are equilibrium molalities of the various species present.

4. Ion-interaction equations: mixtures of sodium sulfate and sulfuric acid

The main purpose of the present work is to represent satisfactorily the thermodynamic properties and hence the osmotic coefficients for $\{(1-y)\mathrm{H_2SO_4} + y\mathrm{Na_2SO_4}\}(\mathrm{aq})$ over the range from pure sulfuric acid to pure sodium sulfate. Because of the molality range of the experimental investigations, the ion-interaction model must be applied to extremely concentrated solutions and hence to very severely non-ideal conditions. The extensive array of osmotic coefficients

for this system is extremely valuable in that it may be used to generate expressions useful for thermodynamic properties anywhere in the three-component system up to the molality limit investigated.

Rard[3,4] has precisely fitted his isopiestic values for the mixtures for the molality fractions investigated. These fits, however, do not permit calculations of thermodynamic properties outside of these exact fractions. We attempt maximum utility and a complete representation by the present calculations.

The appropriate equation required for fits of osmotic coefficients pertaining to solutions containing sodium sulfate and sulfuric acid is given by:

$$\begin{aligned}\phi_{\mathrm{mix}} - 1 \;=\; & 2\Big[f^{\phi} I + (m_{\mathrm{H}} m_1/m^{\circ})\left(B^{\phi}_{\mathrm{H1}} + ZC_{\mathrm{H1}}\right) + (m_{\mathrm{H}} m_2/m^{\circ})\left(B^{\phi}_{\mathrm{H2}} + ZC_{\mathrm{H2}}\right) + \\ & (m_{\mathrm{Na}} m_1/m^{\circ})\left(B^{\phi}_{\mathrm{Na1}} + ZC_{\mathrm{Na1}}\right) + (m_{\mathrm{Na}} m_2/m^{\circ})\left(B^{\phi}_{\mathrm{Na2}} + ZC_{\mathrm{Na2}}\right) + \\ & (m_{\mathrm{H}} m_{\mathrm{Na}}/m^{\circ})\left\{\Phi^{\phi}_{\mathrm{HNa}} + (m_1/m^{\circ})\psi_{\mathrm{HNa1}} + (m_2/m^{\circ})\psi_{\mathrm{HNa2}}\right\} + \\ & (m_1 m_2/m^{\circ})\left\{\Phi^{\phi}_{12} + (m_{\mathrm{H}}/m^{\circ})\psi_{12H} + (m_{\mathrm{Na}}/m^{\circ})\psi_{12Na}\right\}\Big]/(m_{\mathrm{H}} + m_{\mathrm{Na}} + m_1 + m_2)\end{aligned} \tag{33}$$

All amounts of species (except $Na^+(aq)$) are controlled by the dissociation equilibrium involving bisulfate ion. The activity coefficient ratio for this dissociation equilibrium is given by:

$$\begin{aligned}\ln(\gamma_{\mathrm{H}}\gamma_2/\gamma_1) \;=\; & 4F + \{(m_1 - m_{\mathrm{H}})/m^{\circ}\}(2B_{\mathrm{H1}} + ZC_{\mathrm{H1}}) + \{(m_2 + m_{\mathrm{H}})/m^{\circ}\}(2B_{\mathrm{H2}} + ZC_{\mathrm{H2}}) \\ & -(m_{\mathrm{Na}}/m^{\circ})(2B_{\mathrm{Na1}} + ZC_{\mathrm{Na1}}) + (m_{\mathrm{Na}}/m^{\circ})(2B_{\mathrm{Na2}} + ZC_{\mathrm{Na2}}) + \\ & 2\{m_{\mathrm{H}} m_1/(m^{\circ})^2\}C_{\mathrm{H1}} + 2\{m_{\mathrm{H}} m_2/(m^{\circ})^2\}C_{\mathrm{H2}} + 2\{m_{\mathrm{Na}} m_1/(m^{\circ})^2\}C_{\mathrm{Na1}} + \\ & 2\{m_{\mathrm{Na}} m_2/(m^{\circ})^2\}C_{\mathrm{Na2}} + 2\{(m_1 - m_2)/m^{\circ}\}\Phi_{12} + 2(m_{\mathrm{Na}}/m^{\circ})\Phi_{\mathrm{HNa}} + \\ & \{(m_1 m_2 + m_1 m_{\mathrm{H}} - m_2 m_{\mathrm{H}})/m^{\circ}\}\psi_{12H} + \{m_{\mathrm{Na}}(m_1 - m_2)/(m^{\circ})^2\}\psi_{12Na} + \\ & \{m_{\mathrm{Na}}(m_1 - m_{\mathrm{H}})/(m^{\circ})^2\}\psi_{HNa1} + \{m_{\mathrm{Na}}(m_{\mathrm{H}} + m_2)/(m^{\circ})^2\}\psi_{HNa2}\end{aligned} \tag{34}$$

where F is defined for mixtures of sodium sulfate and sulfuric acid by:

$$\begin{aligned}F \;=\; & f^{\gamma} + \{m_{\mathrm{H}} m_1/(m^{\circ})^2\}B'_{\mathrm{H1}} + \{m_{\mathrm{H}} m_2/(m^{\circ})^2\}B'_{\mathrm{H2}} + \{m_{\mathrm{Na}} m_1/(m^{\circ})^2\}B'_{\mathrm{Na1}} + \\ & \{m_{\mathrm{Na}} m_2/(m^{\circ})^2\}B'_{\mathrm{Na2}} + \{m_1 m_2/(m^{\circ})^2\}\Phi'_{12} + \{m_{\mathrm{H}} m_{\mathrm{Na}}/(m^{\circ})^2\}\Phi'_{\mathrm{NaH}}\end{aligned} \tag{35}$$

and f^{γ} and the form of the B' terms were defined previously.

Now that the ion-interaction equations have been outlined, the actual fitting procedure and relevant discussion can be approached. The power of the ion-interaction model is the logical framework on which it is based. This can be most easily seen by examination of equation (21) for the excess Gibbs energy of a mixture of species. Although the final equations may look cumbersome, their simplicity can be realized by the manner in which they are extended to more complex mixtures.

5. Results of calculations

The thermodynamic properties of aqueous solutions containing sodium sulfate have been extensively investigated over wide ranges of temperature and pressure.[10,18] However, there are no precise representations that cover the range from the freezing temperature to the normal boiling temperature of pure water. We are specifically interested in this temperature range for future analyses of properties for pure and mixed electrolytes. Because of these requirements, we have reevaluated the ion-interaction parameters for sodium sulfate from 273 K to 373 K.

Experimental results that lead to the osmotic coefficient of aqueous sodium sulfate solutions from isopiestic, direct vapor pressure, and freezing point depression measurements were selected for the regression. Rard and Miller[19] have reviewed most appropriate results for sodium sulfate and have indicated which are of sufficient precision to include in meaningful fits. At 298.15 K, the vapor pressure measurements from Gibson and Adams[20] were used after conversion from 300.65 K to 298.15 K using enthalpies of dilution at 298.15 K from Thompson et al.[21] and appropriate heat capacities from Desnoyers et al.[22] Methods for converting osmotic coefficients at various temperatures to another reference temperature are outlined in standard texts.[23,24] Freezing temperatures of solutions containing sodium sulfate determined by Randall and Scott[25] and Indelli[26] were converted to 273.15 K and to 298.15 K (the latter for comparison with fitted results by Rard and Miller[19]) using the same procedure and auxiliary values. Isopiestic measurements leading to osmotic coefficients at 298.15 K were taken from Rard and Miller,[19] Downes and Pitzer,[27] and Platford.[28] Other isopiestic measurements valid at 273.15 K were taken from Platford,[29] and at 288.15 K from Childs

and Platford.[30] For temperatures between 298.15 K and 372.75 K, osmotic coefficients were calculated from the equations presented by Pabalan and Pitzer.[10] These equations are based on a wide array of thermodynamic results leading to osmotic coefficients as well as the various temperature derivatives of the Gibbs energies. Since the Pabalan and Pitzer treatment is intended for representation to high temperatures, the fitting procedure defined above generates thermodynamic values for sodium sulfate consistent with this treatment at the higher temperatures.

The parameters represented by equation (12) were initially fitted to the experimental results at 298.15 K using $\alpha_1 = 2.0$ to obtain values for the parameters $\beta^{(0)}_{\mathrm{Na2}}$, $\beta^{(1)}_{\mathrm{Na2}}$, and C^{ϕ}_{Na2}. Systematic deviations from the experimental results were found both for this and for a value of $\alpha_1 = 1.4$ used by Pabalan and Pitzer.[10] The value $\alpha_1 = 1.7$ resulted in removing essentially all systematic deviations between fitted and experimental results and led to the lowest overall standard deviation of fit. The $\beta^{(2)}$ term did not significantly improve the fits and was thus omitted. The quality of fit at 298.15 K can be seen in figure 1 where differences between fitted and experimental osmotic coefficients are plotted as a function of $m^{1/2}$.

Results from experimental measurements at temperatures other than 298.15 K were fitted using the value of 1.7 for α_1 whilst constraining the temperature dependence of the interaction parameters to be of the form:

$$p(T) = p(T_{\mathrm{ref}}) + b\,(1/T - 1/T_{\mathrm{ref}}) + c\ln\,(T/T_{\mathrm{ref}}) \tag{36}$$

where T_{ref} is defined to be 298.15 K. Slightly higher overall standard deviations were found using quadratic or other three-parameter equations. The temperature dependences of $\beta^{(0)}_{\mathrm{Na2}}$, $\beta^{(1)}_{\mathrm{Na2}}$, and C^{ϕ}_{Na2} are described by coefficients for use in equation (36), and are given in table 1 along with values for the parameters at 298.15 K.

The results of fits with the same weighting for the various sets as used by Rard and Miller,[19] led to an overall standard deviation of 0.0014 compared with the standard deviation of 0.0013 for their 6-parameter fit. With a weighting involving a lowered contribution of the freezing temperature and vapor pressures, the final weighted standard deviation for the set at 298.15

K was found to be 0.0010 for osmotic coefficients. The overall standard deviation for the global regression to results in the range 273.15 K to 372.75 K was found to be 0.0019 using temperature-dependent equations for the interaction parameters represented by equation (36). Deviations between calculated and experimental values from 273.15 K to 372.75 K are shown in figure 2. Smoothed values of the osmotic coefficient and activity coefficient at various temperatures are shown in figure 3 and are listed in table 2.

As can be seen in figure 1 and by the relative standard deviations cited above, the results for sodium sulfate are represented within experimental uncertainty at 298.15 K and just outside of experimental uncertainty at other temperatures as illustrated by figure 2. The activity coefficients and osmotic coefficients of sodium sulfate resulting from this treatment are very similar to the results from Pabalan and Pitzer.[10] Smoothed values for these quantities are presented in figure 3. The effect of temperature, as can be seen in the figure, is not large on the scale presented but of course does account for the temperature derivative properties $H_m - H_m^o$ and $C_{p,m} - C_{p,m}^o$.

The treatments of aqueous sulfuric acid have been discussed in a preceding section. The most useful treatments are from Pitzer et al.[5] and Reardon and Beckie.[8] The latter investigation covers a wider temperature range and includes the higher-order mixing terms although some details of the analysis are unclear.

Though Pitzer et al.[5] did not include the theoretical unsymmetrical mixing terms, their regression does represent the thermodynamic values within experimental uncertainty and thus is entirely satisfactory for replication of stoichiometric osmotic coefficients. We have tested both treatments in our calculations for the mixed system. Both sets of parameters are based on fits that omitted certain empirical mixing parameters because of redundancy. It is possible that these redundancies will be removed for the mixed system and thus a more complete set of parameters may be obtained.

Rard [3,4] has summarized experimental results for mixtures of sulfuric acid and sodium sulfate at 298.15 K and associated uncertainties for each set. The only other set of osmotic

coefficient data used for the regression were the results of Stokes[32] for the molality fraction of 0.5 (ie. pure sodium bisulfate). The iterative procedure for regression of the mixed system is outlined below.

We have used an iterative procedure using m_{H} as the variable to solve the dissociation equilibrium and hence amounts of all species. Various molalities of species are related to the equilibrium molality of hydrogen and initial molalites as described by equations (3) through (6). The molality of hydrogen ion is conveniently defined by the quadratic solution to the equilibrium constant expression written solely in terms of initial molalities and hydrogen ion molality.

$$a = \gamma_{ratio}, \tag{37}$$

$$b = \gamma_{ratio}(m_{2,i} - m_{1,i}) + K_{eq}, \tag{38}$$

$$c = -2m_{1,i}K_{eq}, \tag{39}$$

$$m_{\mathrm{H}} = \{-b \pm (b^2 - 4ac)^{1/2}/(2a)\}. \tag{40}$$

The iterative solution is attained by initially setting m_1 and m_{H} equal to $m_{1,i}$(stoichiometric sulfuric acid), m_2 equal to $m_{2,i}$(stoichiometric sodium sulfate) and the activity coefficient ratio γ_{ratio} calculated as described by equation (24). This activity coefficient ratio is then used to modify all molalities of species, and the calculation is repeated until convergence of m_{H} is observed.

The non-linear regression optimizes the ion-interaction parameters based iteratively on converged speciation solutions for each composition studied. The sequentially optimized interaction parameters then lead to new activity coefficient ratios and a whole new set of equilibrium molalities of species. Eventually, convergence is obtained for the ion-interaction parameters when speciation calculations from successive iterations produce the same result. This calculation was sensitive to the initial guesses of the ion-interaction parameters, although well-defined minima were found for each type of regression.

The only variable ion-interaction parameters generated when fitting the results for mixtures using previous formulations for the ion-interaction parameters of pure sodium sulfate and

sulfuric acid, are the binary and ternary interactions not present in either of the two binary systems. As can be seen by examination of equations (33) through (35) the only variable parameters are the binary terms: $\beta^{(0)}_{\mathrm{Na1}}$, $\beta^{(1)}_{\mathrm{Na1}}$, C^{ϕ}_{Na1}, θ_{NaH}, and the ternary parameters ψ_{12Na}, ψ_{HNa1}, and ψ_{HNa2}. Rard[3,4] has used a total of 46 empirical parameters for representation of osmotic coefficients for the mixture along the 7 fixed molality fractions studied. The results of these regressions by Rard are extremely precise, and in most cases within estimates of experimental uncertainty.

The experimental osmotic coefficients reported by Rard[3,4] and by Stokes[32] must be modified slightly for conversion to mixed-basis quantities since both sets refer to completely dissociated standard states. Rard[3,4] has reported osmotic coefficients at specified molality fractions as a function of the total molality m_T. The total molality is merely the sum of stoichiometric molalities of sodium sulfate and sulfuric acid. The reported osmotic coefficients, ϕ, are related to the mixed-basis osmotic coefficients, ϕ_{mix}, defined in equation (33) by:

$$\phi_{\mathrm{mix}} = 3m_T\phi/(2m_1 + 3m_2) \tag{41}$$

where m_1 and m_2 are equilibrium molalities of bisulfate and sulfate ions, respectively. The actual function fitted was thus not the osmotic coefficients on a mixed solution basis, since these values are not known until the exact amounts of all species present are known. The regression minimized deviations of the stoichiometric osmotic coefficients after multiplication of the ion-interaction equation for the mixed osmotic coefficients, equation (33), by the factor $(2m_1 + 3m_2)/3m_T$. This same fitting procedure was used for all other sets, including those from Stokes,[32] and for pure sodium sulfate and sulfuric acid.

All fits were done using a non-linear least squares regression routine. The convergence of the various fits was slow because of the multi-level iterative solution calculation employed for speciation as well as ion-interaction parameter convergence. The ion-interaction parameters define the activity coefficient ratio that in turn modifies amounts of species present at equilibrium and then the ion-interaction parameters, and so on.

Initial fits using the entire array of osmotic coefficients were quite poor in high-molality

regions, especially for high sulfuric acid mole ratios. Shortcomings here can be traced to the Reardon and Beckie[8] and Pitzer et al.[5] treatments of sulfuric in that they extend to only 6 mol·kg^{-1} sulfuric acid. The present osmotic coefficients for the mixtures extends to over mol·kg^{-1} total ionic strength in the sulfuric acid rich regions. Giving zero weight to osmotic coefficient values for the mixtures with molalities exceeding the range of applicability of treatments for sulfuric acid and sodium sulfate led to the following results. Initial fits using the Reardon and Beckie evaluation for sulfuric acid and the revised sodium sulfate parameters cited in table 1, led to an overall standard deviation of 0.0069. Substitution of the Pitzer et al. formulation provided essentially identical results with a standard deviation of 0.0070. Neither of these fits represents the experimental ϕ values to within the precision of the measurments or within an amount acceptable for a "good fit." As such, we found that treatments using constrained sulfuric acid ion-interaction parameters were not satisfactory.

Allowing optimization of the sulfuric acid parameters while keeping the parameters for sodium sulfate constrained to the results cited in table 1 and giving zero weight to molalities and ionic strengths outside of the range of the treatment of pure sodium sulfate, led to an overall standard deviation of 0.0026. The additional ion-interaction parameters that were optimized were: $\beta^{(0)}_{\mathrm{H1}}$, $\beta^{(1)}_{\mathrm{H1}}$, C^{ϕ}_{H1}, $\beta^{(0)}_{\mathrm{H2}}$, $\beta^{(1)}_{\mathrm{H2}}$, C^{ϕ}_{H2}, θ_{12}, and the ternary parameter $\psi_{12\mathrm{H}}$. The coefficients generated using this procedure are recommended as the low ionic strength set and are listed in table 3. The α_1 value used to represent the ionic strength dependence of the binary interactions of hydrogen with bisulfate ion and with sulfate ion, here and in the following section, was 2.0 as recommended by Pitzer.[13] Plots of the deviation between calculated and experimental results for mixtures considered in this treatment are shown in figure 4.

The complete set of osmotic coefficients for the mixtures was analyzed by allowing all interaction parameters to vary. To help retain a high quality of fit for pure sulfuric acid, representative values (osmotic coefficients) were calculated from Pitzer et al.[5] and Rard[31] up to 15 mol·kg^{-1} sulfuric acid. Also included in the regression were the ϕ values for sodium sulfate as outlined in the preceding section.

While other values of α_1 were tested for interaction of sodium ion with sulfate ion, including the common value 2.0, it was found that the best value was 1.4 for the combined system results. As discussed earlier, the best value of α_1 was found to be 1.7 for pure Na_2SO_4. The $\beta^{(2)}_{Na2}$ term was included for these fits using $\alpha_2 = 2.623$. Fits performed without the binary or ternary mixing parameters had such large uncertainties that they are not reported here. The complete set of ion-interaction parameters for the final chosen fit is presented in table 4, along with the corresponding standard deviation of each parameter. The overall standard deviation of the fit, employing all of the osmotic coefficients for sodium sulfate, sulfuric acid, and the mixtures formed from both, was found to be 0.0035. Representative figures showing deviations between calculated and experimental results are given in figure 5. Useful summaries of ion-interaction parameters for a wide variety of aqueous electrolytes have been published by Pitzer.[33] The derived ion-interaction parameters are within the general pattern of ionic interactions for species of similar structure and charge.

6. Discussion

The overall standard deviation of the low ionic strength fit of 0.0026 is only slightly lower than the standard deviation from the regression to the complete set of ϕ values (over 650 points) found to be 0.0035. The precision of the experimental osmotic coefficients is marginally lower than 0.001, although the accuracy of these results is about twice this value. Some limitations of the ion-interaction model are realized in the presently reported calculations. Specifically, the ion-interaction parameters do not represent the experimental values completely within known experimental uncertainties. However, the theoretical framework guides the form of the ion-interaction equations, and the range of applicability from infinitely dilute to well over saturation, and from pure sodium sulfate to pure sulfuric acid, makes this treatment extremely useful. Although the standard deviation for the entire set is outside experimental uncertainties, the value is low enough for this to be a "good" fit to the available results. Because calculations of other thermodynamic properties, including solubilities, require values well removed from investigated mole ratios, the importance of this global representation is immediately clear.

The present treatment is readily extended to more complex mixtures.

Increased precision of fit for $\{(1-y)H_2SO_4 + yNa_2SO_4\}(aq)$ could certainly be obtained by adding fourth-order interaction parameters (see Appendix H of reference 13), but their physical meaning would be questionable. Also, the introduction of $NaSO_4^-(aq)$ as an additional species with its equilibrium constant of formation might be considered. Values of $\ln K$ have been reported in the range 1.8 to 2.5.[6] Many additonal ion-interaction terms would be generated because of the increased interactions of all species with $NaSO_4^-(aq)$. While this array of additional parameters would presumably allow a better fit to the full array of ϕ values, its meaning would be very questionable because these terms were not required for pure $Na_2SO_4(aq)$. For the present purposes, however, application of the ion-interaction model in its present form has provided a very good representation of these ϕs, especially when it is considered that only 18 parameters were used to fit over 700 points.

Representative calculations of the speciation of solutions at smoothed values of the molality fraction and total molality are presented in table 5. Plots of osmotic coefficients and activity coefficient ratios for bisulfate dissociation are plotted in figure 6.

For the osmotic coefficents of certain mixtures, one finds shapes that are very different from those of pure electrolytes or of ideally dissociated solutions. The contributions to the measured osmotic coefficients from changing speciation is obvious in this plot. If sodium sulfate and sulfuric acid were both completely dissociated at all molalities and ionic strengths encountered, all curves in figure 6a would have the general shape defined by $y = 0$ and $y = 1$.

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REFERENCES

1. Goldberg, R.N.; Staples, B.R.; Nuttal, R.L.; Arbuckle, R. A bibliography of sources of experiment NBS special publication 485. 1977.

2. Bolsaitis, P.; Elliott, J.F. J. Chem. Eng. Data 1990, 35, 69.

3. Rard, J.A. J. Chem. Thermodynamics 1991, xx,yy.

4. Rard, J.A. J. Chem. Thermodynamics 1989, 21, 539.

5. Pitzer K.S.; Roy, R.N.; Silvester, L.F. J. Am. Chem. Soc. 1977, 99, 4930.

6. Millero, F.J.; Schreiber, D.R. Am. J. Sci. 1982, 282, 1508.

7. Hovey, J.K.; Hepler, L.G. J. Chem. Soc. Faraday Trans. 1990, 86, 2831.

8. Reardon, E.J.; Beckie, R.D. Geochim. Cosmochim. Acta 1987, 51, 2355.

9. Harvie, C.E.; Møller, N.; Weare, J.H. Geochim. Cosmochim. Acta 1984, 48,723.

10. Pabalan, R.T.; Pitzer, K.S. Geochim. Cosmochim. Acta 1988, 52, 2393.

11. Archer, D.G.; Wang, P. J. Phys. Chem. Ref. Data 1990, 19, 371.

12. Bradley, D.J.; Pitzer, K.S. J. Phys. Chem. 1979, 83, 1599.

13. Pitzer, K.S. Activity Coefficients in Electrolyte Solutions. Pitzer, K.S.:editor. CRC Press: Boca Raton. 1991, Chapter 3.

14. Dickson, A.G.; Wesolowski, D.J.; Palmer, D.A.; Mesmer, R.E. J. Phys. Chem. 1990, 94, 7978.

15. Pitzer, K.S. J. Solution Chem. 1975, 4, 249.

16. Friedman, H.L. Ionic Solution Theory. Wiley-Interscience: New York, 1962.

17. Harvie, C.E. Theoretical Investigations in Geochemistry and Atom Surface Scattering. PhD thesis, University of California, San Diego, 1981.

18. Roger, P.S.Z.; Pitzer, K.S. J. Phys. Chem. 1981, 85, 2886.

19. Rard, J.A.; Miller, D.G. J. Chem. Eng. Data 1981, 26,33.

20. Gibson, R.E.; Adams, L.H. J. Am. Chem. Soc. 1933, 55, 2679.

21. Thompson, P.T.; Smith, D.E.; Wood, R.H. J. Chem. Eng. Data 1974, 19, 386.

22. Desnoyers, J.E.; de Visser, C.; Perron, G.; Picker, P. J. Solution Chem. 1976, 5, 605.

23. Pitzer, K.S.; Brewer, L. Thermodynamics, revision of Lewis, G.N.; Randall, M., McGraw-Hill: New York, 1961.

24. Robinson, R.A.; Stokes, R.H. Electrolyte Solutions, 2nd ed., Butterworths Scientific Publications: London, 1959.

25. Randall, M.; Scott, G.N. J. Am. Chem. Soc. 1927, 49,647.

26. Indelli, A. Ric. Sci. 1953, 23, 2258.

27. Downes, C.J.; Pitzer, K.S. J. Solution Chem. 1976, 5, 389.

28. Platford, R.F. J. Chem. Eng. Data 1968, 13, 46.

29. Platford, R.F. J. Chem. Eng. Data 1973, 18, 215.

30. Childs, C.W.; Platford, R.F. Aust. J. Chem. 1971, 24, 2487.

31. Rard, J.A. J. Chem. Eng. Data 1983, 28, 384.

32. Stokes, R.H. J. Am. Chem. Soc. 1948, 70, 874.

33. Pitzer, K.S. Activity Coefficients in Electrolyte Solutions. Pytkowicz, R.M.: editor. CRC Press: Boca Raton. 1979. Vol I, Chapter 7.

TABLE 1. Coefficients for equations of type (36) for the temperature dependence of the Pitzer parameters for sodium sulfate: $\beta^{(0)}_{\mathrm{Na2}}$, $\beta^{(1)}_{\mathrm{Na2}}$, and C^{ϕ}_{Na2} ($\alpha_1 = 1.7$).

Parameter	$p(298)$	b	c
$\beta^{(0)}_{\mathrm{Na2}}$	0.006536438 ± 0.00024	-30.197349 ± 1.1	-0.20084955 ± 0.022
$\beta^{(1)}_{\mathrm{Na2}}$	0.87426420 ± 0.0037	-70.014123 ± 8.9	0.2962095 ± 0.18
C^{ϕ}_{Na2}	0.007693706 ± 0.000054	4.5879201 ± 0.30	0.019471746 ± 0.0057

TABLE 2. Smoothed values for the osmotic coefficient ϕ and mean ionic activity coefficient $\gamma_{\pm}$ of aqueous sodium sulfate at (273.15, 298.15, 323.15, 348.15 and 373.15) K.

m	273.15 K		298.15 K		323.15 K		348.15 K		373.15 K	
$(\mathrm{mol \cdot kg^{-1}})$	ϕ	$\gamma_{\pm}$	ϕ	$\gamma_{\pm}$	ϕ	$\gamma_{\pm}$	ϕ	$\gamma_{\pm}$	ϕ	$\gamma_{\pm}$
0.0001	0.9868	0.9607	0.9868	0.9608	0.9869	0.9608	0.9869	0.9608	0.9869	0.9608
0.0010	0.9605	0.8846	0.9608	0.8849	0.9611	0.8851	0.9612	0.8853	0.9613	0.8854
0.0050	0.9195	0.7715	0.9212	0.7728	0.9222	0.7736	0.9229	0.7741	0.9234	0.7745
0.0100	0.8934	0.7026	0.8965	0.7047	0.8984	0.7061	0.8997	0.7070	0.9007	0.7077
0.0150	0.8755	0.6568	0.8799	0.6597	0.8827	0.6615	0.8846	0.6627	0.8859	0.6637
0.0200	0.8617	0.6222	0.8673	0.6257	0.8709	0.6279	0.8733	0.6294	0.8750	0.6305
0.0500	0.8116	0.5034	0.8236	0.5094	0.8310	0.5132	0.8360	0.5158	0.8396	0.5176
0.1000	0.7680	0.4102	0.7882	0.4186	0.8005	0.4237	0.8088	0.4272	0.8146	0.4297
0.2000	0.7179	0.3201	0.7505	0.3306	0.7701	0.3370	0.7828	0.3413	0.7917	0.3443
0.3000	0.6840	0.2708	0.7263	0.2823	0.7513	0.2893	0.7674	0.2938	0.7782	0.2970
0.4000	0.6573	0.2381	0.7077	0.2500	0.7371	0.2572	0.7558	0.2619	0.7682	0.2651
0.5000	0.6350	0.2143	0.6924	0.2264	0.7256	0.2337	0.7464	0.2383	0.7600	0.2415
0.6000	0.6158	0.1960	0.6795	0.2081	0.7160	0.2154	0.7386	0.2200	0.7532	0.2230
0.7000	0.5992	0.1814	0.6684	0.1934	0.7079	0.2006	0.7321	0.2052	0.7474	0.2081
0.8000	0.5846	0.1695	0.6590	0.1814	0.7011	0.1884	0.7266	0.1928	0.7426	0.1956
0.9000	0.5719	0.1596	0.6509	0.1713	0.6953	0.1782	0.7220	0.1824	0.7385	0.1851
1.0000	0.5609	0.1513	0.6441	0.1627	0.6905	0.1694	0.7182	0.1735	0.7352	0.1760
1.2000	0.5434	0.1381	0.6336	0.1489	0.6835	0.1551	0.7127	0.1589	0.7302	0.1611
1.4000	0.5312	0.1283	0.6269	0.1383	0.6792	0.1440	0.7095	0.1473	0.7271	0.1492
1.6000	0.5238	0.1209	0.6234	0.1300	0.6773	0.1351	0.7080	0.1380	0.7255	0.1395
1.8000	0.5209	0.1153	0.6228	0.1235	0.6775	0.1279	0.7080	0.1302	0.7250	0.1314
2.0000	0.5221	0.1112	0.6249	0.1182	0.6793	0.1219	0.7092	0.1237	0.7253	0.1244
2.2000	0.5272	0.1083	0.6293	0.1140	0.6826	0.1168	0.7113	0.1180	0.7261	0.1184
2.4000	0.5361	0.1064	0.6359	0.1107	0.6872	0.1125	0.7142	0.1131	0.7274	0.1130
2.6000	0.5486	0.1053	0.6445	0.1080	0.6930	0.1089	0.7176	0.1088	0.7289	0.1082
2.8000	0.5647	0.1051	0.6550	0.1060	0.6997	0.1057	0.7215	0.1049	0.7304	0.1038
3.0000	0.5841	0.1056	0.6674	0.1045	0.7074	0.1030	0.7257	0.1014	0.7319	0.0998
3.2000	0.6069	0.1068	0.6815	0.1034	0.7159	0.1007	0.7301	0.0982	0.7333	0.0961
3.4000	0.6329	0.1088	0.6973	0.1028	0.7251	0.0986	0.7347	0.0953	0.7345	0.0926
3.6000	0.6622	0.1114	0.7146	0.1026	0.7349	0.0968	0.7394	0.0926	0.7353	0.0894
3.8000	0.6946	0.1149	0.7335	0.1028	0.7454	0.0953	0.7441	0.0902	0.7359	0.0863
4.0000	0.7301	0.1191	0.7540	0.1033	0.7564	0.0940	0.7488	0.0878	0.7360	0.0834

TABLE 3. Low ionic strength set of Pitzer ion-interaction parameters for sodium bisulfate, sulfuric acid, and the various non-ideal mixing parameters θ and ψ at 298.15 K. These parameters are only valid to 4 mol·kg^{-1} sodium sulfate and 6 mol·kg^{-1} sulfuric acid.[a]

Parameter		σ
$\beta^{(0)}_{\mathrm{Na1}}$	0.0700838	0.00306
$\beta^{(1)}_{\mathrm{Na1}}$	0.3825196	0.02743
C^{ϕ}_{Na1}	−0.0053853	0.00030
$\beta^{(0)}_{\mathrm{H1}}$	0.1832845	0.00313
$\beta^{(1)}_{\mathrm{H1}}$	0.6423595	0.01670
C^{ϕ}_{H1}	0.0048954	0.00060
$\beta^{(0)}_{\mathrm{H2}}$	0.1990501	0.00534
$\beta^{(1)}_{\mathrm{H2}}$	−0.2712110	0.04564
C^{ϕ}_{H2}	0.0011043	0.00649
θ_{NaH}	0.0331661	0.00273
θ_{12}	−0.2151196	0.00830
ψ_{12H}	0.0605694	0.00404
ψ_{12Na}	−0.0061653	0.00105
ψ_{HNa1}	−0.0091358	0.00061
ψ_{HNa2}	0.0581395	0.00466

a These parameters were derived using the sodium sulfate parameters listed in table 1. The α_1 value was set equal to 2.0 for H1, H2, and Na1 B terms and 1.7 for Na2 B terms. σ values represent standard deviations. C^{ϕ} values are related to C values as described by equation (20).

TABLE 4. Complete set of Pitzer ion-interaction parameters for sodium bisulfate, sulfuric acid, and the various non-ideal mixing parameters θ and ψ at 298.15 K. These parameters are valid over the entire range of mole ratios at infinitely dilute to supersaturated molalities.[a]

Parameter	value	σ
$\beta^{(0)}_{\mathrm{Na1}}$	0.0401956	0.00174
$\beta^{(1)}_{\mathrm{Na1}}$	0.6582967	0.02410
C^{ϕ}_{Na1}	−0.0014315	0.00013
$\beta^{(0)}_{\mathrm{H1}}$	0.2441330	0.00061
$\beta^{(1)}_{\mathrm{H1}}$	0.4065317	0.01728
C^{ϕ}_{H1}	−0.0050740	0.00005
$\beta^{(0)}_{\mathrm{H2}}$	0.0610849	0.00304
$\beta^{(1)}_{\mathrm{H2}}$	−0.0217880	0.04370
C^{ϕ}_{H2}	0.0277430	0.00282
$\beta^{(0)}_{\mathrm{Na2}}$	0.0087189	0.00068
$\beta^{(1)}_{\mathrm{Na2}}$	0.3849133	0.00938
$\beta^{(2)}_{\mathrm{Na2}}$	0.8319144	0.03006
C^{ϕ}_{Na2}	0.0070273	0.00014
θ_{NaH}	−0.0013853	0.00197
θ_{12}	−0.1352336	0.00204
ψ_{12H}	0.0155425	0.00227
ψ_{12Na}	−0.0011909	0.00048
ψ_{HNa1}	−0.0033964	0.00018
ψ_{HNa2}	0.0614402	0.00124

[a] The α_1 value was set equal to 2.0 for H1, H2, and Na1 B terms and 1.4 for Na2 B terms. σ values represent standard deviations. C^{ϕ} values are related to C values as described by equation (20).

TABLE. Representative speciation and smoothed osmotic coefficients at rounded mole ratios for the $\{(1-y)H_2SO_4 + yNa_2SO_4\}(aq)$ system.

	$(y = 0.0)$					$(y = 0.2)$					$(y = 0.4)$				
m_T	m_H	m_1	m_2	γ_{ratio}	ϕ	m_H	m_1	m_2	γ_{ratio}	ϕ	m_H	m_1	m_2	γ_{ratio}	ϕ
	$(mol \cdot kg^{-1})$					$(mol \cdot kg^{-1})$					$(mol \cdot kg^{-1})$				
0.1	0.127	0.073	0.027	0.223	0.673	0.093	0.067	0.033	0.224	0.683	0.063	0.057	0.043	0.220	0.699
0.2	0.246	0.154	0.046	0.142	0.662	0.178	0.142	0.058	0.147	0.667	0.116	0.124	0.076	0.146	0.676
0.3	0.366	0.234	0.066	0.102	0.664	0.261	0.219	0.081	0.109	0.663	0.169	0.191	0.109	0.110	0.666
0.4	0.486	0.314	0.086	0.079	0.669	0.345	0.295	0.105	0.085	0.663	0.221	0.259	0.141	0.088	0.661
0.5	0.607	0.393	0.107	0.063	0.676	0.429	0.371	0.129	0.070	0.665	0.273	0.327	0.173	0.073	0.658
0.6	0.730	0.470	0.130	0.052	0.684	0.515	0.445	0.155	0.059	0.669	0.325	0.395	0.205	0.062	0.656
0.7	0.853	0.547	0.153	0.044	0.693	0.600	0.520	0.180	0.050	0.673	0.378	0.462	0.238	0.054	0.656
0.8	0.978	0.622	0.178	0.038	0.703	0.686	0.594	0.206	0.044	0.678	0.430	0.530	0.270	0.048	0.656
0.9	1.103	0.697	0.203	0.033	0.713	0.773	0.667	0.233	0.039	0.684	0.483	0.597	0.303	0.043	0.657
1.0	1.229	0.771	0.229	0.029	0.723	0.859	0.741	0.259	0.035	0.690	0.536	0.664	0.336	0.039	0.659
1.5	1.865	1.135	0.365	0.017	0.781	1.294	1.106	0.394	0.023	0.728	0.799	1.001	0.499	0.026	0.675
2.0	2.505	1.495	0.505	0.012	0.846	1.723	1.477	0.523	0.017	0.773	1.053	1.347	0.653	0.021	0.700
2.5	3.137	1.863	0.637	0.010	0.916	2.135	1.865	0.635	0.014	0.824	1.289	1.711	0.789	0.018	0.730
3.0	3.755	2.245	0.755	0.008	0.991	2.526	2.274	0.726	0.013	0.878	1.501	2.099	0.901	0.016	0.763
3.5	4.354	2.646	0.854	0.007	1.068	2.891	2.709	0.791	0.012	0.931	1.689	2.511	0.989	0.016	0.795
4.0	4.930	3.070	0.930	0.007	1.146	3.231	3.169	0.831	0.012	0.984	1.850	2.950	1.050	0.016	0.825
4.5	5.485	3.515	0.985	0.007	1.223	3.548	3.652	0.848	0.013	1.033	1.989	3.411	1.089	0.017	0.852
5.0	6.019	3.981	1.019	0.007	1.299	3.845	4.155	0.845	0.013	1.079	2.108	3.892	1.108	0.018	0.876
5.5	6.534	4.466	1.034	0.007	1.373	4.125	4.675	0.825	0.014	1.121	2.210	4.390	1.110	0.019	0.896
6.0	7.032	4.968	1.032	0.007	1.443	4.391	5.209	0.791	0.016	1.159	2.298	4.902	1.098	0.020	0.912
7.0	7.986	6.014	0.986	0.008	1.575	4.892	6.308	0.692	0.020	1.224	2.444	5.956	1.044	0.025	0.937
8.0	8.899	7.101	0.899	0.009	1.692	5.371	7.429	0.571	0.025	1.276	2.563	7.037	0.963	0.030	0.954
9.0	9.783	8.217	0.783	0.011	1.795	5.843	8.557	0.443	0.035	1.317	2.667	8.133	0.867	0.037	0.963
10.0	10.653	9.347	0.653	0.014	1.885	6.322	9.678	0.322	0.050	1.349	2.765	9.235	0.765	0.046	0.968
11.0	11.518	10.482	0.518	0.018	1.963	6.816	10.784	0.216	0.077	1.376	2.861	10.339	0.661	0.057	0.968
12.0	12.387	11.613	0.387	0.025	2.031	7.333	11.867	0.133	0.127	1.398	2.960	11.440	0.560	0.073	0.965
13.0	13.271	12.729	0.271	0.037	2.091	7.875	12.925	0.075	0.230	1.419	3.063	12.537	0.463	0.093	0.959
14.0	14.175	13.825	0.175	0.059	2.145	8.438	13.962	0.038	0.452	1.437	3.175	13.625	0.375	0.120	0.950
15.0	15.103	14.897	0.103	0.100	2.194	9.018	14.982	0.018	0.971	1.453					

TABLE 5 (continued):

	($y = 0.5$)					($y = 0.6$)					($y = 0.8$)					($y = 1.0$)
m_T	m_H	m_1	m_2	γ_{ratio}	ϕ	m_H	m_1	m_2	γ_{ratio}	ϕ	m_H	m_1	m_2	γ_{ratio}	ϕ	ϕ
	($mol \cdot kg^{-1}$)					($mol \cdot kg^{-1}$)					($mol \cdot kg^{-1}$)					
0.1	0.050	0.050	0.050	0.215	0.710	0.037	0.043	0.057	0.210	0.722	0.017	0.023	0.077	0.195	0.754	0.793
0.2	0.090	0.110	0.090	0.143	0.684	0.067	0.093	0.107	0.138	0.693	0.029	0.051	0.149	0.125	0.719	0.752
0.3	0.129	0.171	0.129	0.108	0.671	0.095	0.145	0.155	0.104	0.677	0.040	0.080	0.220	0.094	0.698	0.726
0.4	0.168	0.232	0.168	0.087	0.662	0.122	0.198	0.202	0.084	0.666	0.052	0.108	0.292	0.075	0.682	0.706
0.5	0.207	0.293	0.207	0.072	0.657	0.150	0.250	0.250	0.070	0.658	0.064	0.136	0.364	0.062	0.669	0.689
0.6	0.245	0.355	0.245	0.062	0.652	0.178	0.302	0.298	0.060	0.651	0.075	0.165	0.435	0.053	0.658	0.676
0.7	0.284	0.416	0.284	0.054	0.650	0.206	0.354	0.346	0.052	0.646	0.087	0.193	0.507	0.046	0.649	0.665
0.8	0.324	0.476	0.324	0.048	0.648	0.234	0.406	0.394	0.046	0.642	0.099	0.221	0.579	0.041	0.641	0.656
0.9	0.363	0.537	0.363	0.043	0.646	0.262	0.458	0.442	0.042	0.639	0.111	0.249	0.651	0.036	0.635	0.648
1.0	0.402	0.598	0.402	0.039	0.646	0.290	0.510	0.490	0.038	0.636	0.123	0.277	0.723	0.033	0.630	0.642
1.5	0.597	0.903	0.597	0.027	0.652	0.430	0.770	0.730	0.026	0.634	0.185	0.415	1.085	0.022	0.617	0.625
2.0	0.783	1.217	0.783	0.021	0.668	0.564	1.036	0.964	0.020	0.644	0.246	0.554	1.446	0.016	0.620	0.626
2.5	0.954	1.546	0.954	0.018	0.691	0.686	1.314	1.186	0.017	0.661	0.299	0.701	1.799	0.014	0.634	0.641
3.0	1.102	1.898	1.102	0.016	0.716	0.788	1.612	1.388	0.015	0.681	0.339	0.861	2.139	0.012	0.654	0.668
3.5	1.227	2.273	1.227	0.016	0.741	0.868	1.932	1.568	0.015	0.702	0.363	1.037	2.463	0.012	0.675	0.704
4.0	1.328	2.672	1.328	0.016	0.764	0.926	2.274	1.726	0.015	0.721	0.369	1.231	2.769	0.013	0.694	0.749
4.5	1.406	3.094	1.406	0.016	0.783	0.963	2.637	1.863	0.015	0.737	0.358	1.442	3.058	0.014	0.710	
5.0	1.465	3.535	1.465	0.017	0.800	0.982	3.018	1.982	0.016	0.749	0.333	1.667	3.333	0.016	0.722	
5.5	1.507	3.993	1.507	0.018	0.813	0.985	3.415	2.085	0.017	0.758						
6.0	1.537	4.463	1.537	0.020	0.823	0.975	3.825	2.175	0.019	0.763						
7.0	1.565	5.435	1.565	0.023	0.836	0.928	4.672	2.328	0.023	0.765						
8.0	1.566	6.434	1.566	0.028	0.842	0.856	5.544	2.456	0.028	0.760						
9.0	1.550	7.450	1.550	0.033	0.842	0.770	6.430	2.570	0.034	0.749						
10.0	1.517	8.483	1.517	0.038	0.837	0.677	7.323	2.677	0.042	0.734						
11.0	1.286	9.714	1.286	0.034	0.792											
12.0	0.564	11.436	0.564	0.014	0.700											

Figure Captions:

Figure 1: Difference in experimental and fitted, equation (12), osmotic coefficients from a variety of sources for Na_2SO_4(aq) at 298.15 K as a function of the square root of molality: ▲, Rard and Miller[19]; △, Platford[28] ; ■, Downes and Pitzer[27] ; □, Gibson and Adams[20] (from vapor pressures); • Randall and Scott[25] (from freezing temperatures); o Indelli[26] (from freezing temperatures).

Figure 2: Difference in experimental and fitted, equation (12), osmotic coefficients ϕ for Na_2SO_4(aq) at various temperatures as a function of the square root of molality. (a) (T=273.15K): □, Platford[29] ; •, Randall and Scott[25] (freezing temperatures); o, Indelli[26] (freezing temperatures); (b) (T=288.15K): o, Childs and Platford[30]; (c) (T=323.15K): o, Pabalan and Pitzer[10]; (d) (T=348.15K): o, Pabalan and Pitzer[10]; (e) (T=372.75K): o, Pabalan and Pitzer[10];

Figure 3: Smoothed values of properties for Na_2SO_4(aq) at various temperatures as a function of the square root of molality: (a) osmotic coefficients ϕ; (b) $\ln \gamma_{\pm}$. Temperatures are as follows: —, 273.15 K; — · —, 298.15 K; - - - -, 323.15 K; — —, 348.15 K; · · · ·, 373.15 K.

Figure 4: Low ionic strength differences between experimental and fitted, equations (33) and (38), osmotic coefficients for $(1-y)H_2SO_4$(aq)+yNa_2SO_4(aq) at 298.15 K as a function of the square root of molality: (a) y=0.12471: •, Rard[3](referenced to $CaCl_2$); o, Rard[3](referenced to NaCl) (b) y=0.24962: •, Rard[3](referenced to $CaCl_2$); o, Rard[3](referenced to NaCl) (c) y=0.37439: •, Rard[3](referenced to $CaCl_2$); o, Rard[3](referenced to NaCl) (d) y=0.500 □, Rard[4](referenced to $CaCl_2$); •, Rard[4](referenced to NaCl) o, Stokes[32](referenced to NaCl) (e)y=0.55595: o, Rard[4](referenced to $CaCl_2$) (f)y=0.70189: o, Rard[4](referenced to $CaCl_2$) (g)y=0.84920: o, Rard[4](referenced to NaCl) (h) y=0.0: •, Rard[31]; o, Pitzer et al.[31]

Figure 5: High ionic strength (complete set) differences between experimental and fitted, equations (33) and (38), osmotic coefficients for $(1-y)H_2SO_4$(aq)+yNa_2SO_4(aq) at 298.15 K as a function of the square root of molality: (a) y=0.12471: •, Rard[3](referenced to

$CaCl_2$); o, Rard[3](referenced to NaCl) (b) y=0.24962: •, Rard[3](referenced to $CaCl_2$); o, Rard[3](referenced to NaCl) (c) y=0.37439: •, Rard[3](referenced to $CaCl_2$); o, Rard[3](referenced to NaCl) (d) y=0.500 □, Rard[4](referenced to $CaCl_2$); •, Rard[4](referenced to NaCl) o, Stokes[32](referenced to NaCl) (e)y=0.55595: •, Rard[4](referenced to $CaCl_2$) o, Rard[4](referenced to NaCl) (f)y=0.70189: o, Rard[4](referenced to NaCl) (g)y=0.84920: o, Rard[4](referenced to NaCl) (h) y=0.0: o, Rard[31]; •, Pitzer et al.[31] (i) y=1.0: ▲, Rard and Miller[19]; △, Platford[28] ; ■, Downes and Pitzer[27] ; □, Gibson and Adams[20] (from vapor pressures); • Randall and Scott[25] (from freezing temperatures); o Indelli[26] (from freezing temperatures).

Figure 6: Smoothed values of properties for $(1-y)H_2SO_4(aq)+yNa_2SO_4(aq)$ at rounded molality fractions m_T as a function of the square root of the total molality: (a) osmotic coefficients; (b) $\ln \gamma_{ratio}$ for bisulfate dissociation. Values of y are denoted by: —, $y = 0$; — · —, $y = 0.2$; - - - -, $y = 0.4$; — —, $y = 0.6$; · · · ·, $y = 0.8$; — · · —, $y = 1.0$.

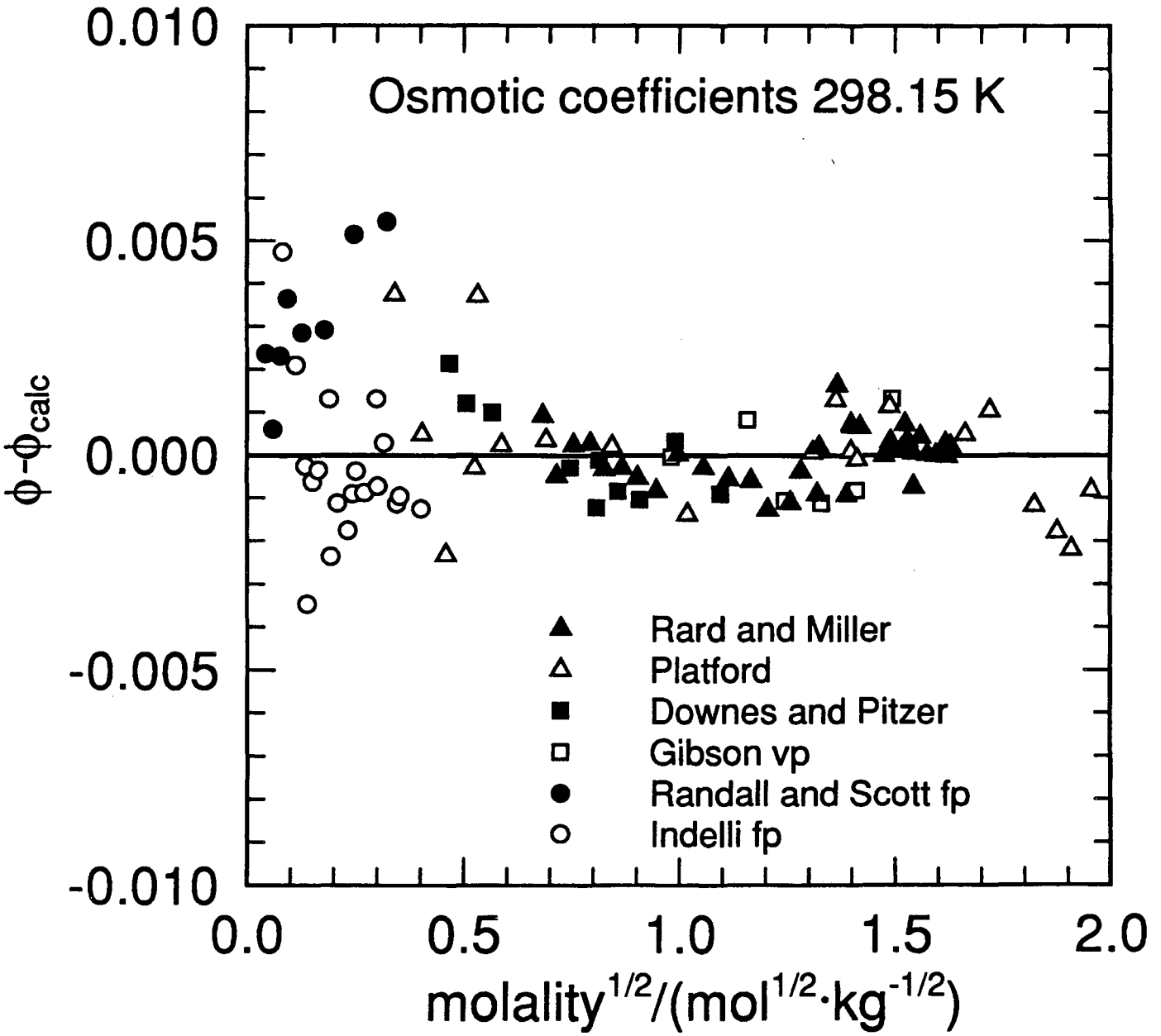

Osmotic coefficients 298.15 K
0.010
0.005
0.000
-0.005
-0.010
0.0
0.5
1.0
1.5
2.0
$\phi-\phi_{calc}$
molality$^{1/2}$/(mol$^{1/2}$·kg$^{-1/2}$)
Rard and Miller
Platford
Downes and Pitzer
Gibson vp
Randall and Scott fp
Indelli fp

Fig. 1

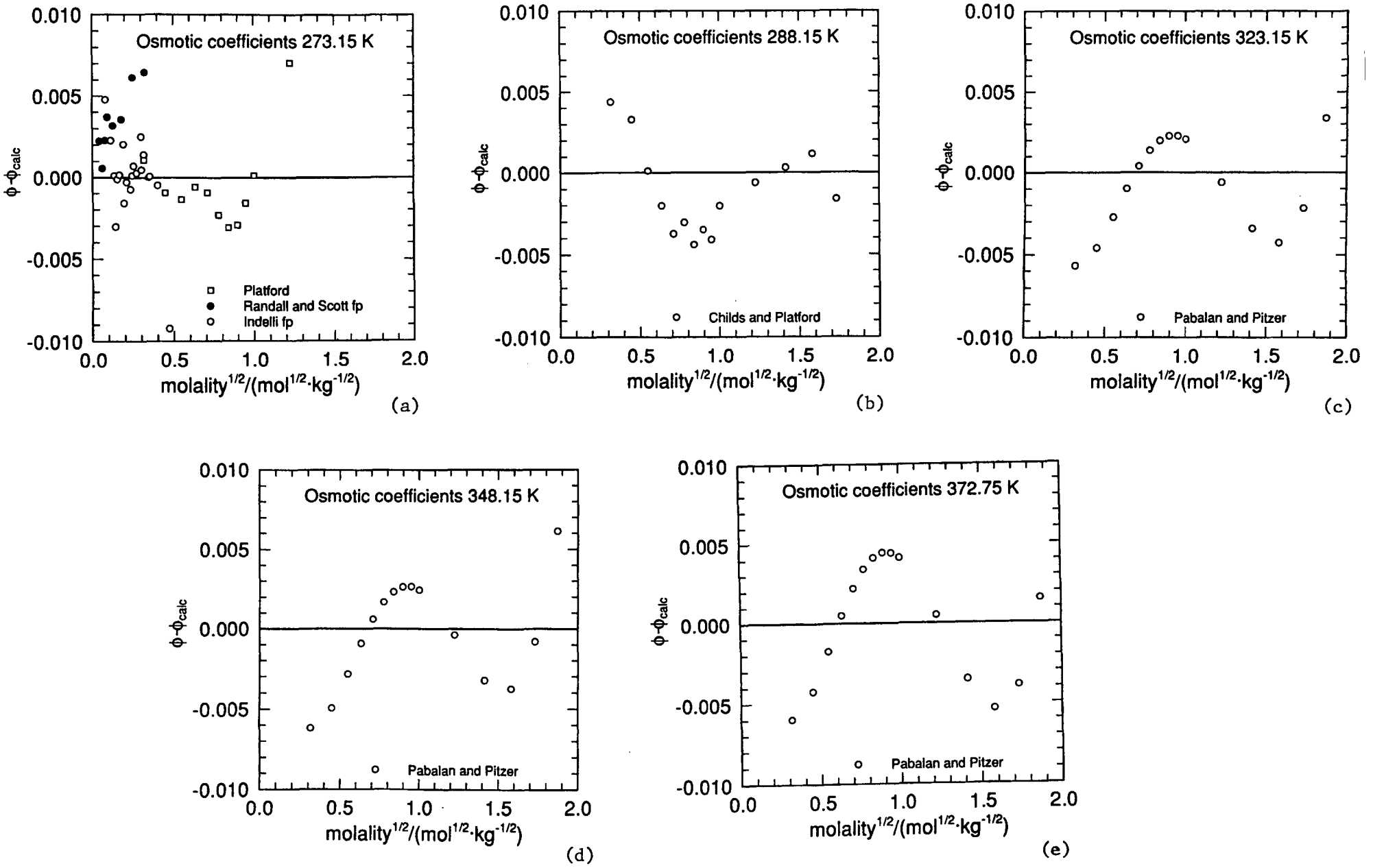
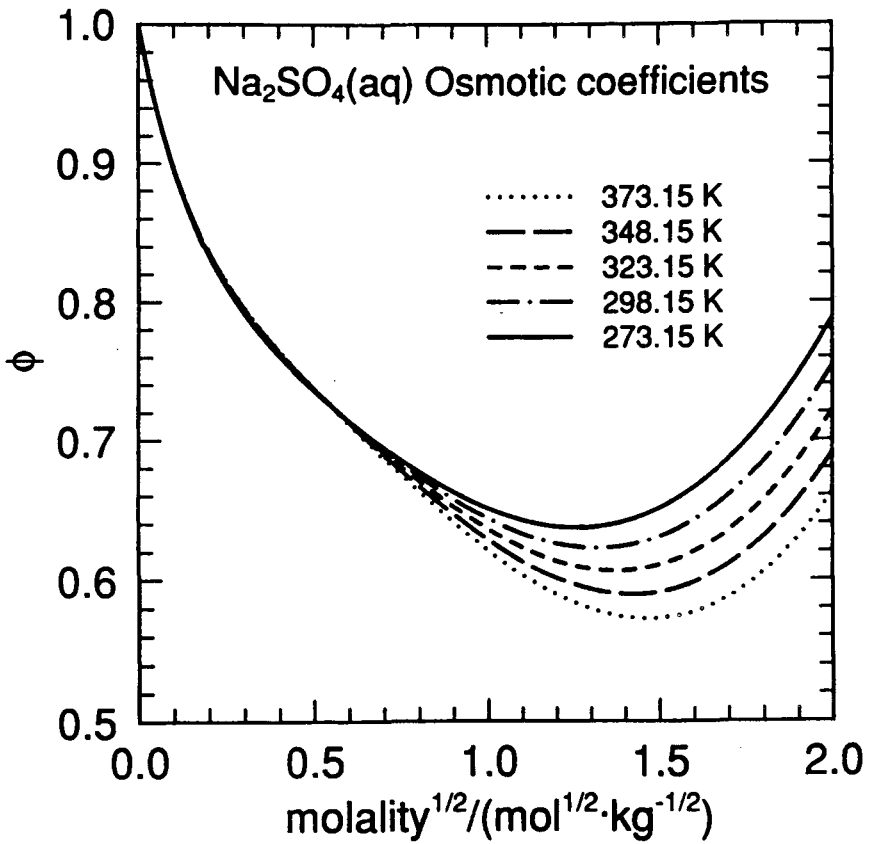
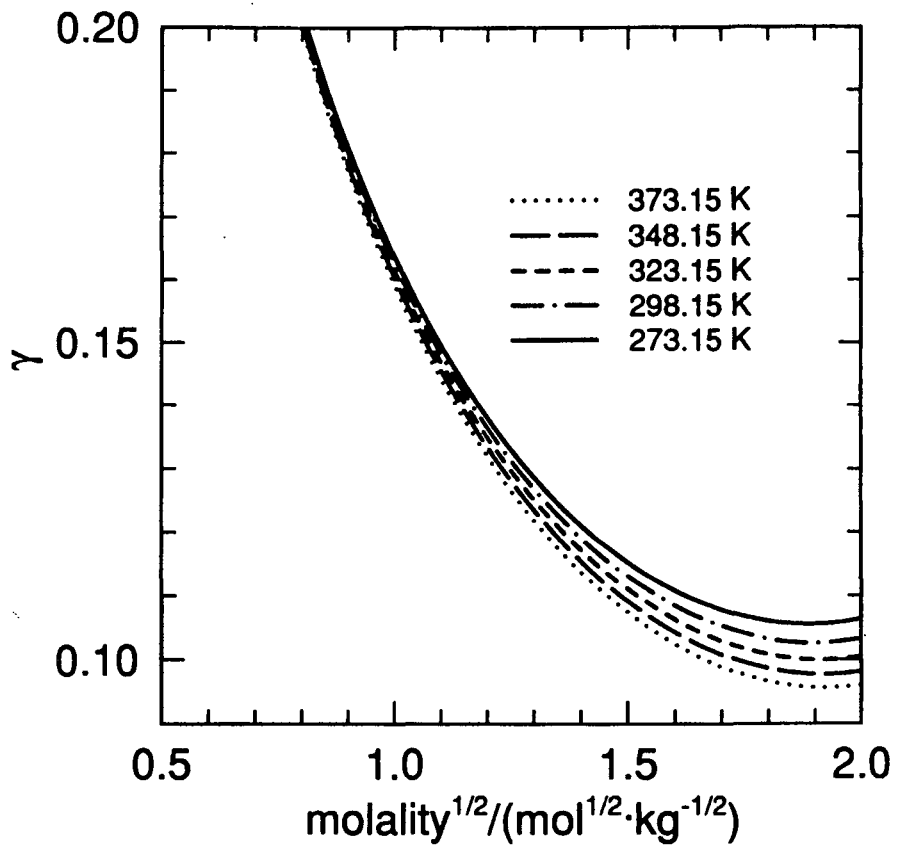

Osmotic coefficients 273.15 K
Platford
Randall and Scott fp
Indelli fp
(a)
Osmotic coefficients 288.15 K
Childs and Platford
(b)
Osmotic coefficients 323.15 K
Pabalan and Pitzer
(c)
Osmotic coefficients 348.15 K
Pabalan and Pitzer
(d)
Osmotic coefficients 372.75 K
Pabalan and Pitzer
(e)
$\phi-\phi_{calc}$
molality$^{1/2}$/(mol$^{1/2}$·kg$^{-1/2}$)
0.010
0.005
0.000
-0.005
-0.010
0.0
0.5
1.0
1.5
2.0

Fig. 2

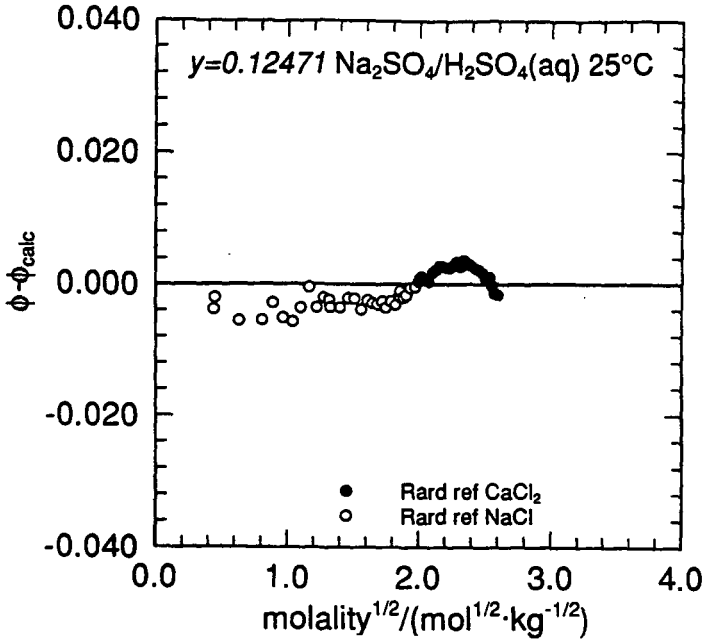

Na2SO4(aq) Osmotic coefficients
373.15 K
348.15 K
323.15 K
298.15 K
273.15 K
φ
1.0
0.9
0.8
0.7
0.6
0.5
0.0
0.5
1.0
1.5
2.0
molality1/2/(mol1/2·kg-1/2)

(a)

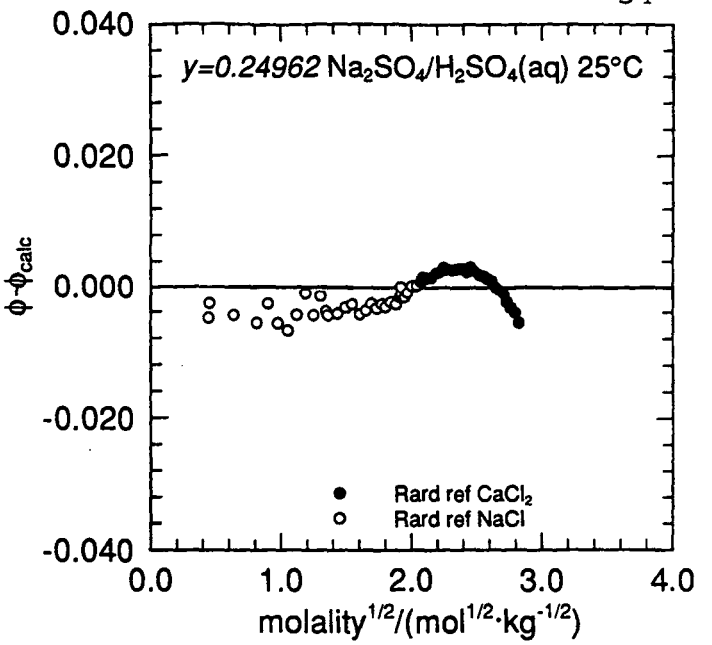

373.15 K
348.15 K
323.15 K
298.15 K
273.15 K
γ
0.20
0.15
0.10
0.5
1.0
1.5
2.0
molality1/2/(mol1/2·kg-1/2)

(b)

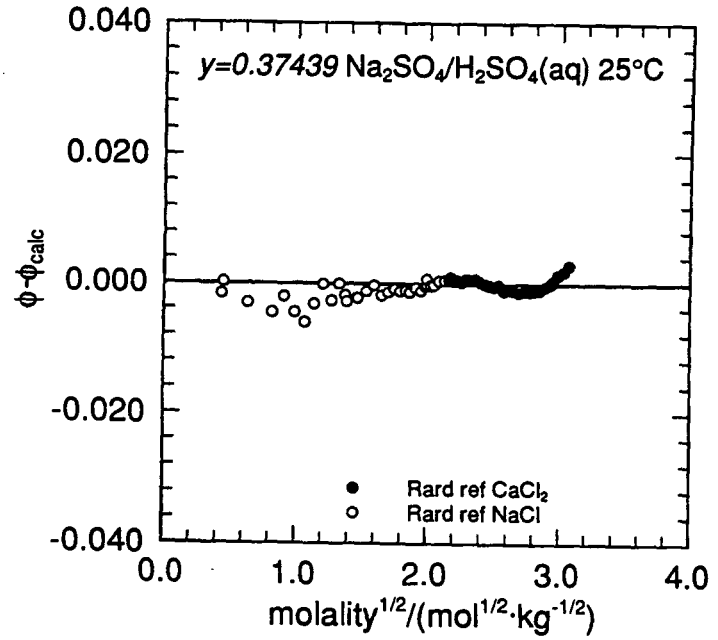
Fig. 3


y=0.12471 Na2SO4/H2SO4(aq) 25°C
Rard ref CaCl2
Rard ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

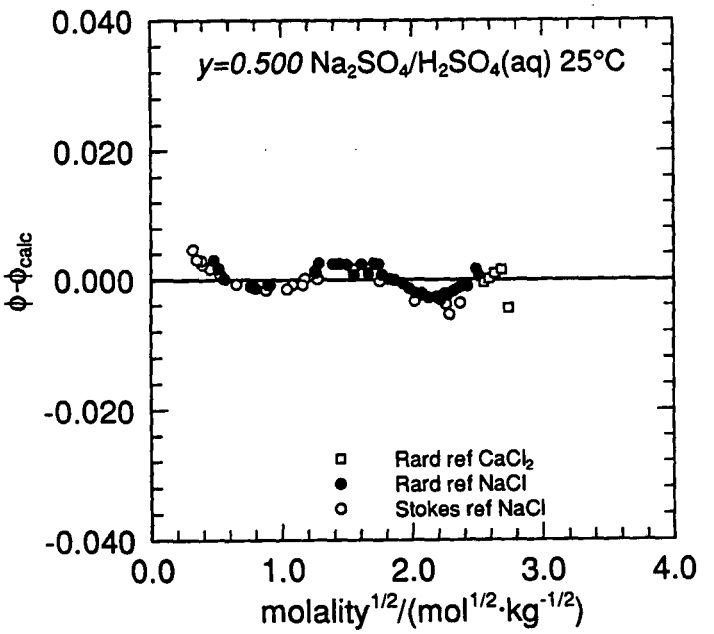
(a)


y=0.24962 Na2SO4/H2SO4(aq) 25°C
Rard ref CaCl2
Rard ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

(b)

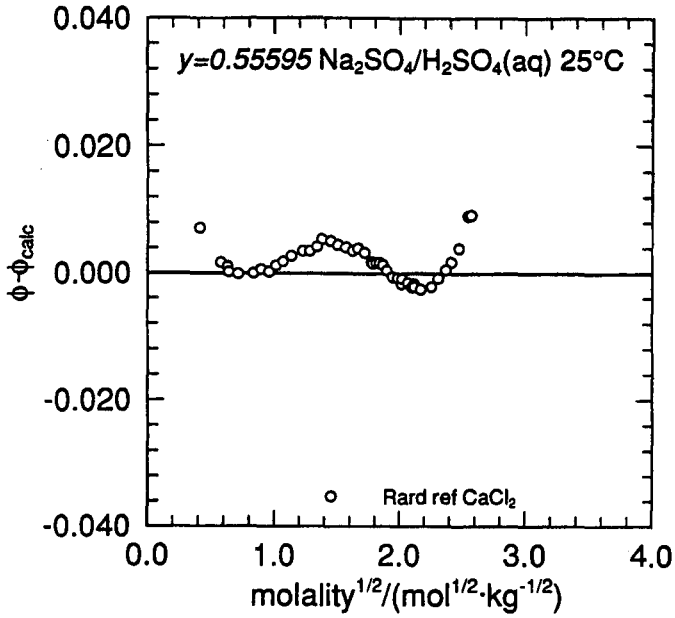

y=0.37439 Na2SO4/H2SO4(aq) 25°C
Rard ref CaCl2
Rard ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

(c)

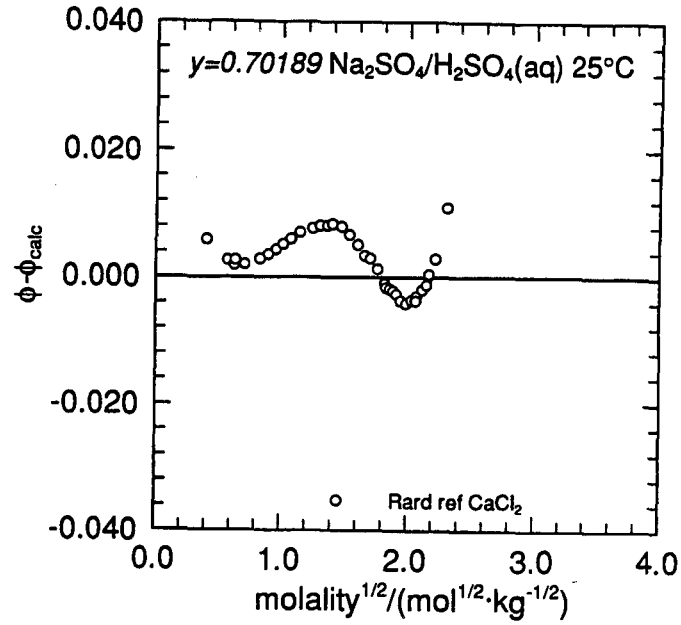

y=0.500 Na2SO4/H2SO4(aq) 25°C
Rard ref CaCl2
Rard ref NaCl
Stokes ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

(d)

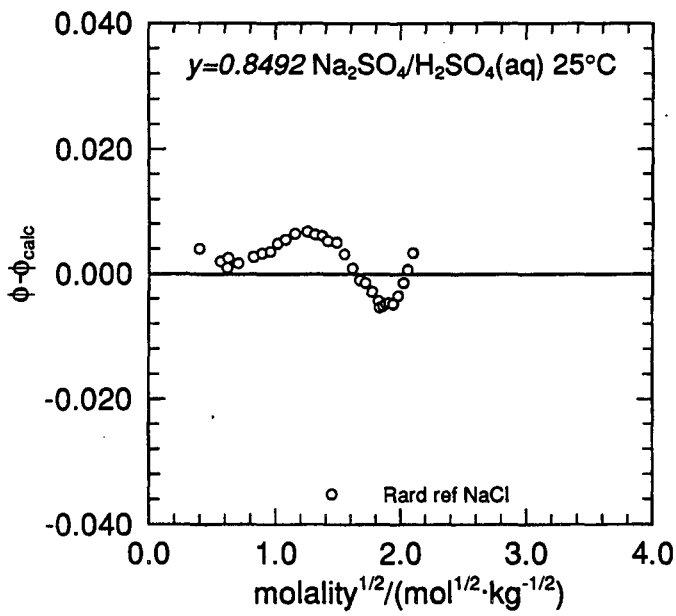
Fig. 4



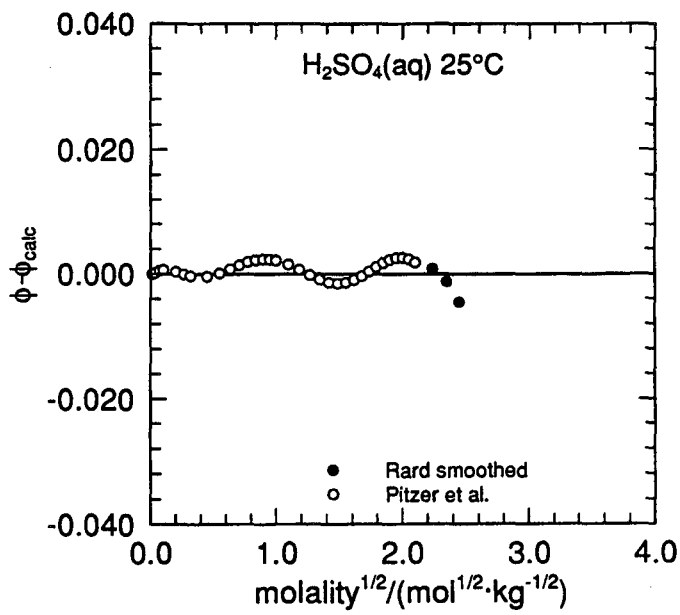
(e)



(f)

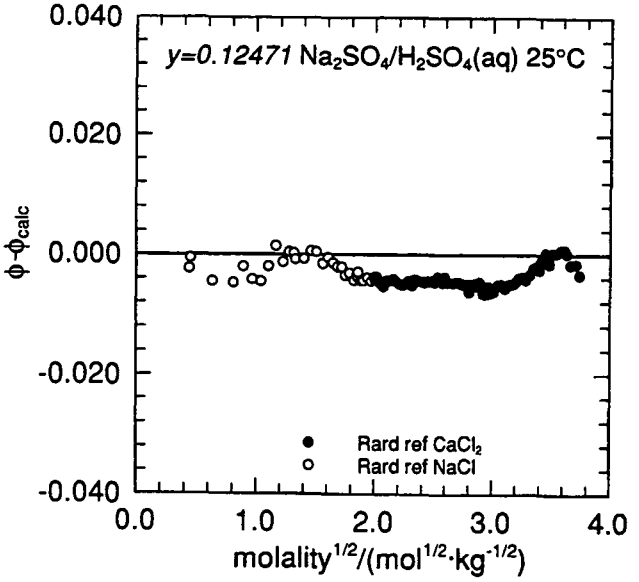


(g)

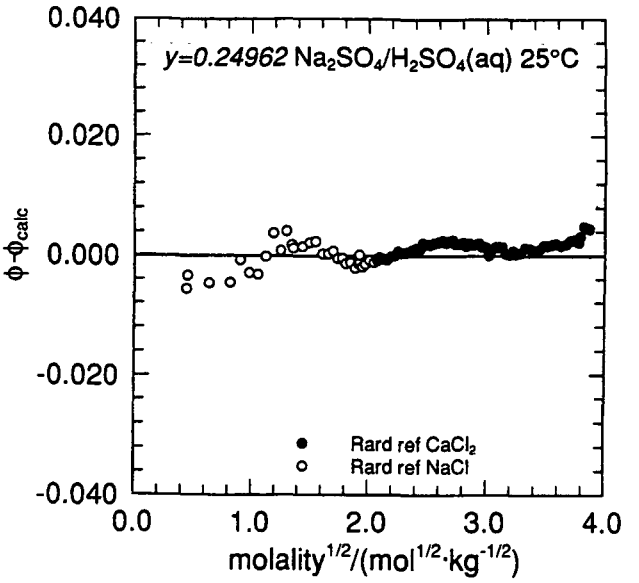


(h)

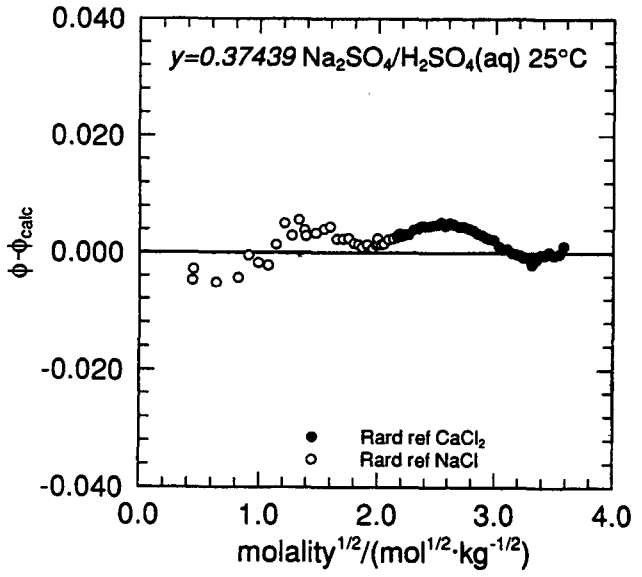
Fig. 4, continued


y=0.12471 Na2SO4/H2SO4(aq) 25°C
Rard ref CaCl2
Rard ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

(a)


y=0.24962 Na2SO4/H2SO4(aq) 25°C
Rard ref CaCl2
Rard ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

(b)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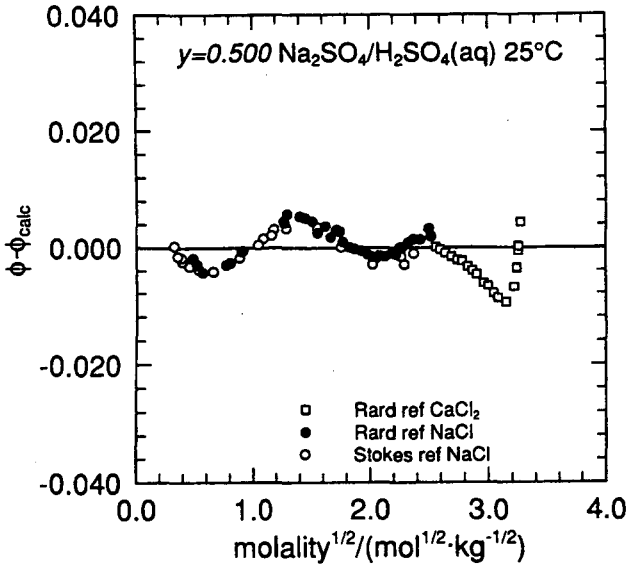
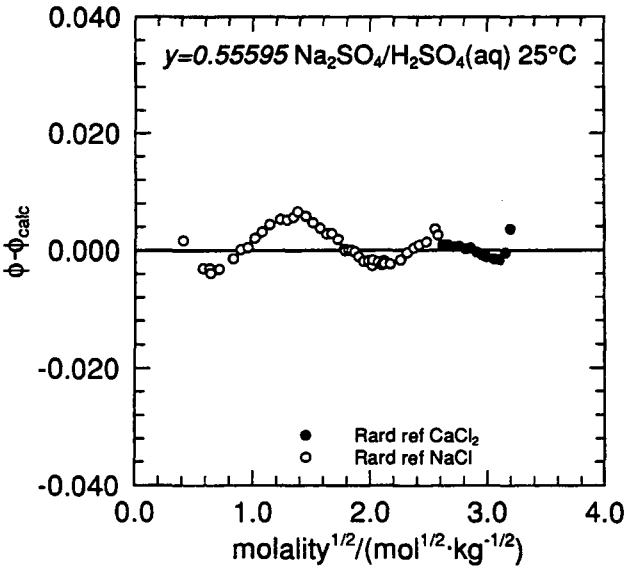
Rard ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

(c)


y=0.500 Na2SO4/H2SO4(aq) 25°C
Rard ref CaCl2
Rard ref NaCl
Stokes ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

(d)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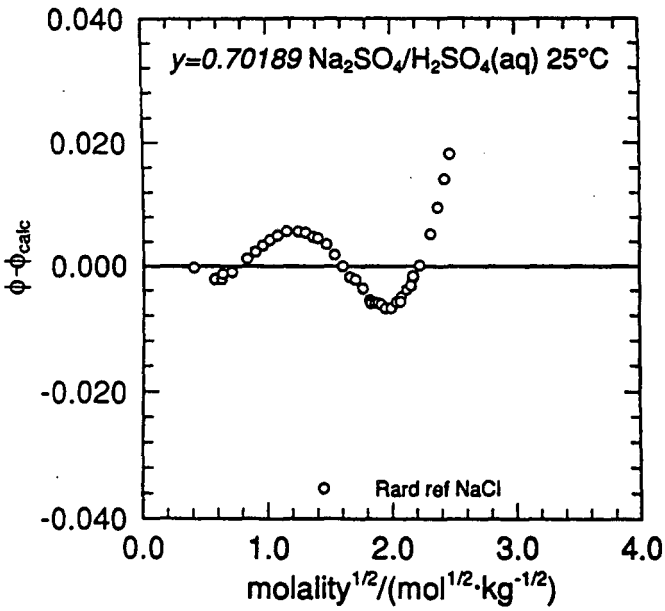
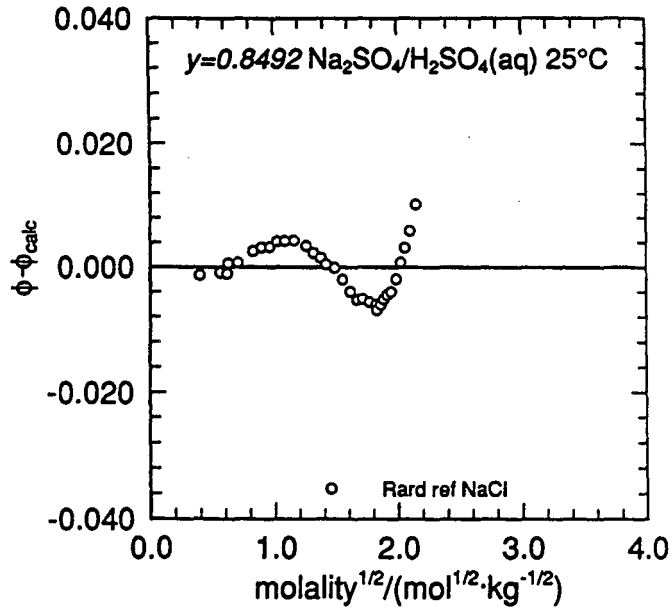
Rard ref CaCl2
Rard ref NaCl
φ-φcalc
molality1/2/(mol1/2·kg-1/2)

(e)

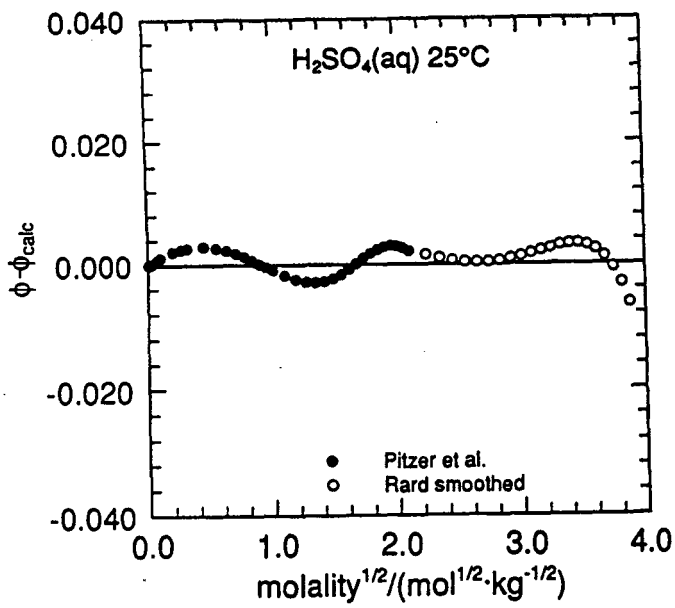
Fig. 5



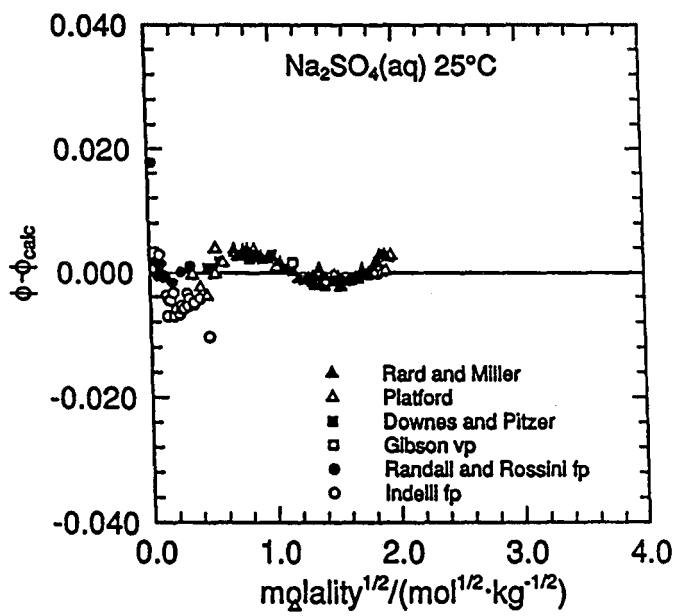
(f)



(g)

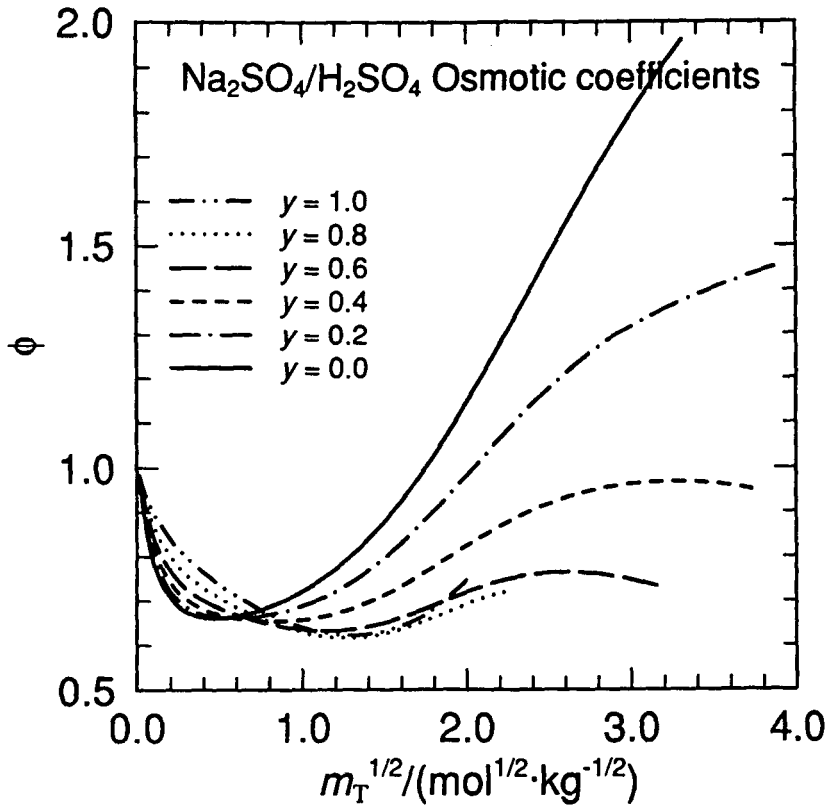


(h)

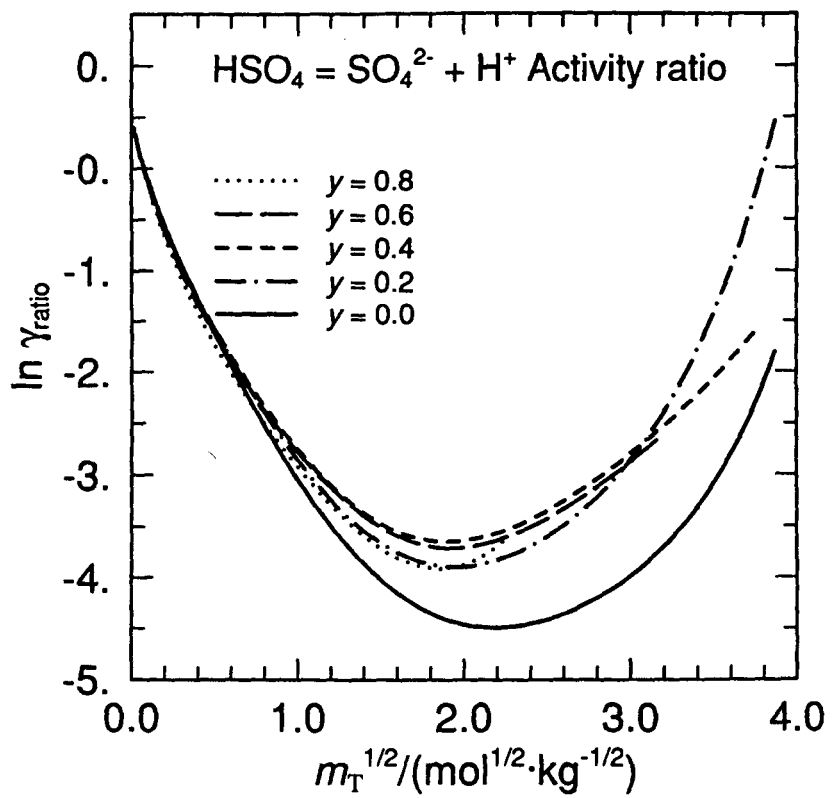


(i)

Fig. 5 continued


Na2SO4/H2SO4 Osmotic coefficients
y = 1.0
y = 0.8
y = 0.6
y = 0.4
y = 0.2
y = 0.0
φ
2.0
1.5
1.0
0.5
0.0
1.0
2.0
3.0
4.0
mT1/2/(mol1/2·kg-1/2)

(a)


HSO4 = SO42- + H+ Activity ratio
y = 0.8
y = 0.6
y = 0.4
y = 0.2
y = 0.0
ln γratio
0.
-0.
-1.
-2.
-3.
-4.
-5.
0.0
1.0
2.0
3.0
4.0
mT1/2/(mol1/2·kg-1/2)

(b)

Fig. 6

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