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Water and Mean Ionic Activities of Aqueous HNO_3 Solutions Calculated from an Extension of the Brunauer-Emmett-Teller (BET) Model

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The objective for this research was to employ the extended adsorption isotherm (EAI) to develop a predictive relationship between the activity of H_2O (a_w) and the mean ionic activity ($a_\pm$) of aqueous HNO_3. The EAI model is a calculative approach to the estimation of solutions for activities of highly non-ideal chemical systems and is the collective efforts of Stokes and Robinson, Abraham, and Ally and Braunstein. From previous works of the HNO_3-H_2O system by Rains et al., a predictive model of relevant aqueous phase activities was developed that only needs knowledge of composition and temperature of the HNO_3 solution.

Keywords activity coefficient; aqueous electrolyte; Brunauer-Emmett-Teller (BET); mean ionic activity; modified adsorption isotherm (MAI); nitric acid; Stokes-Robinson; water

INTRODUCTION

The purpose of this paper is to document and investigate a predictive relationship for the activity of H_2O (a_w) and the mean ionic activity ($a_\pm$) of aqueous HNO_3 solutions. This paper builds on previous works on the HNO_3-H_2O system by Rains et al. (1,2) The data used as a basis for this model development cover aqueous HNO_3 solutions at temperatures from 0 to 100°C and a wide range of concentrations (3–5). The data over this range of composition and temperatures agrees with predictions of the Extended Adsorption Isotherm (EAI) model quite well. Aqueous HNO_3 solutions are used for a variety of industrially-significant reactions and are an important reaction product of NO_x and H_2O in our atmosphere. A simple and robust predictive model of relevant aqueous phase activities is the goal of this activity and is of high interest.

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The calculational approach used in this paper is known as the Extended Adsorption Isotherm (EAI). Stokes and Robinson (6) postulated that concentrated aqueous electrolytes may be viewed as an irregular arrangement of water around the electrolyte (HNO_3 in the current paper); they applied the Brunauer-Emmett-Teller (BET) model from multi-layer gas adsorption (7) to describe the relationship of water activity (a_w) to concentrated electrolyte solutions. This work is usually referred to as the Stokes-Robinson application of the BET adsorption isotherm. The BET model is based on the postulate that a concentrated electrolyte solution could be viewed as an ionic lattice with irregularities introduced as a result of hydration. Abraham (8) later developed the corresponding relationship between the electrolyte activity and concentration for concentrated solutions using the BET model, confining the model to a binary (single salt and water) solution. Ally and Braunstein (9) extended the BET adsorption isotherm model for use with multiple electrolytes and a solvent; they also extended the model to evaluate excess properties and phase equilibria (10). The works of Stokes and Robinson, Abraham, and Ally and Braunstein are typically referred to as the Modified Adsorption Isotherm Model or the Ionic Lattice Model. The EAI Model is a simple approach to prediction of solution activities for highly non-ideal chemical systems and seeks to extend the MAI or Ionic Lattice Models. The EAI model allows the r and c parameters originally constant in the BET model to vary as functions of the water activity. In this paper the EAI model is shown to be in good agreement with experimental data over a wide range of temperatures and electrolyte concentrations.

BACKGROUND

The EAI Model contains two adjustable parameters (r and c); c is the positive difference between the molar enthalpy of "adsorption" of water on the electrolyte and the molar enthalpy of liquefaction of water and is typically

defined by $c = exp(\varepsilon/RT)$ with ε being the difference in the heat of adsorption and the heat of liquification of pure water, R being the ideal gas-law constant, and T being absolute temperature. The parameter r represents the number of "binding sites" for water on the electrolyte. A large body of experimental information supports the relationship between the water concentration (mole fraction or molality) and its activity in the MAI model (1,9–24). The MAI model restricts the range of applicability to concentration regions where r and c are relatively constant. The electrolyte activity (HNO_3 in this case) may be obtained from a Gibbs-Duhem-based expression developed by Abraham (8). The relationship between the electrolyte activity and its aqueous concentration in the MAI model is also supported by a number of studies (1,9,10,20–24). The MAI model provides a simple, robust representation of the thermodynamic phenomena for solvent-electrolyte systems. The MAI model has been used in previous investigations involving various nitrate solutions, aqueous HNO_3 solutions (1), aqueous solutions of $LiNO_3$ (24), $NaNO_3$ (20), $AgNO_3$ (22), and NH_4NO_3 (23). An extensive compilation of r and c values for various aqueous salt systems is presented by Marcus (25). Rains, Counce, and Spencer (2) defined c and r to be functions of a_w; incorporating the work of Rains, Counce, and Spencer, and this paper seeks to extend the previous MAI model with the new approach designated as the EAI model.

Since Stokes and Robinson proposed the BET adsorption isotherm model, numerous studies have sought to improve its precision. One of Anderson's (26) modifications to the BET model is to add a third parameter, which allows for the heat of adsorption to be less in each consecutive layer of hydration. This was originally coupled with the idea that r must be an integer to truly be the hydration number. Stokes and Robinson (27) revisited their original model and suggested an improvement based on characterizing the energy of adsorption in each consecutive layer. Nesbitt (28) proposed a modification of the model, which is based on an extension to the Debye-Huckel theory, like the most common models used today. Both Stokes and Robinson and Nesbitt recognized that the r parameter was not identical with a tightly bound hydration number. Rains, Counce and Spencer (2) showed how the r and c parameters in the HNO_3-H_2O system change with composition and how the variability of these parameters can be rationalized from the system chemistry; r was found to vary from near three where the $HNO_3(H_2O)_3$ complex is prevalent to one where the HNO_3H_2O complex dominates to near zero as the water content approaches zero. Voigt and Zeng (21) and Zeng and Voigt (29) added a temperature dependence on the BET r and c parameters. They built on the works of Stokes and Robinson, Abraham, and Ally and Braunstein, successfully generated phase diagrams, and calculated other thermodynamic information for ternary (two electrolytes and water) mixtures. They have successfully predicted several new eutectic temperatures and compositions. Clegg and Simsonson (30) extended the work of Ally and Braunstein (10) by developing equations for solute and solvent activities for a single solvent and an infinite number of solutes.

This paper seeks to investigate a model whereby r and c parameters are determined from vapor-liquid information and applied for predictions of water and mean ionic activities for the HNO_3-H_2O system. The paper seeks to determine and examine a base-line EAI Model for the HNO_3-H_2O system. Both Clegg and Brimblecomb (31) and Brandani and Brandani (32) have produced Pitzer-type models for the HNO_3-H_2O system and report model data differences most apparent in at high HNO_3 mole fractions (>0.6 to 0.7).

THEORY

The activity of H_2O is estimated, assuming ideal-gas behavior, as

$$a_w = \frac{P_W}{P_W^0} \tag{1a}$$

where a_w is the (rational) activity of H_2O, P_W is the H_2O vapor pressure of the solution, and P_W^0 is the vapor pressure of pure water at the pertinent temperature. The activity of HNO_3 is estimated, again assuming ideal-gas behavior, as

$$a_{HNO_3} = \frac{P_{HNO_3}}{P_{HNO_3}^0} \tag{1b}$$

where a_{HNO_3} is the rational activity of HNO_3, P_{HNO_3} is the HNO_3 vapor pressure of the solution and $P_{HNO_3}^0$ is the vapor pressure of pure HNO_3 at the pertinent temperature.

The equilibrium between gaseous and aqueous phase HNO_3 may be described as

$$HNO_3(g) \rightleftharpoons H^+(aq) + NO_3^-(aq) \tag{2}$$

where g and aq are gaseous and aqueous species, respectively. The equilibrium constant for reaction (2), again assuming ideal gas behavior, is

$$K_{H_X} = \frac{a_{H^+} a_{NO_3^-}}{P_{HNO_3}} = \frac{a_\pm^2}{P_{HNO_3}} \tag{3}$$

where P_{HNO_3} is the partial pressure of HNO_3 over the solution, and $a_\pm, a_{H^+}$ and $a_{NO_3^-}$ are the mean ionic activity, hydrogen activity, and nitrate activity (mole fraction basis). The equilibrium constant, K_{H_X}, is available from Clegg and

Brimblecombe (31) in units of atm^{-1} (K_{H_X} =851.3 atm^{-1} at 25°C).

$$\ln(K_{H_X}) = \left[386 - \frac{3020}{T} - 71\ln(T) + 0.131(T) - 0.421 \times 10^{-4}(T^2)\right] \quad (4)$$

The relationship between water activity and solution composition in the Stokes-Robinson-BET model may be expressed as

$$\frac{a_w(1-x_w)}{x_w(1-a_w)} = \frac{M_w m_E a_w}{1000(1-a_w)} = \frac{1}{cr} + \frac{(c-1)}{cr}a_w \quad (5)$$

where x_W and m_E are the mole fraction of H_2O and molality of the electrolyte (HNO_3), and M_w is the molar mass of water at equilibrium conditions. Defining the individual terms of Eq. (5) to be equivalent to $f(a_W)$,

$$f(a_W) = \frac{1}{cr} + \frac{(c-1)}{cr}a_w \quad (6)$$

Taking the first derivative of Eq. (6) with respect to a_w

$$f'(a_W) = \frac{(c-1)}{cr} \quad (7)$$

Combining Eqs. (6) and (7), the equations for c and r are obtained,

$$c = \frac{f'(a_W)}{[f(a_W) - a_W f'(a_W)]} + 1 \quad (8)$$

and

$$r = \frac{(c-1)}{cf'(a_W)} \quad (9)$$

The corresponding electrolyte activity to the water activity may be obtained by use of the classical Gibbs Duhem equation or a version of this incorporating the Stokes-Robinson-BET model (8),

$$\frac{\lambda(1-x_E)}{x_E(1-\lambda)} = \frac{r}{c} + \frac{r(c-1)\lambda}{c} \quad (10)$$

where $\lambda = (a_E^{BET})^{1/r}$, a_E^{BET} is the BET activity of the electrolyte, x_E is the stoichiometric mole fraction of the electrolyte, and r and c retain the same identities and values as in Eq. (5).

METHOD AND PROCEDURE

The aqueous HNO_3-H_2O system has some unique characteristics that make it especially attractive for study. Nitric acid does not have a solubility or miscibility limit in water; this allows application of the BET-based models at solute concentrations much higher than typical of such models. There are several distinct molecular species formed in concentrated HNO_3 as its degree of dissociation declines, including HNO_3, $HNO_3(H_2O)$ and $HNO_3(H_2O)_3$. Like H_2O, HNO_3 is capable of forming strong hydrogen bonds and forms an azeotrope with H_2O at about approximately 68 wt% HNO_3 (38 mole% HNO_3). These considerations make the H_2O-HNO_3 system challenging to model.

The data utilized to parameterize this present study are compiled from the literature sources of Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4). The pure-component vapor pressures of HNO_3 are from the individual references, except at 100°C, where the data of the Thermodynamic Research Center, TRC, (33) is used. The pure-component vapor pressure of H_2O is from Weast (34). The data described is referred to as the compiled literature database. The intention for the selection of this specific data set was that it was simply the most available and commonly used for chemical engineering purposes.

The modeling procedure begins with the solution temperature, composition and the vapor pressure of pure H_2O and HNO_3 and involves

1. the iterative solution of Eq. (11),

$$f(aW) = 1.7985a_W^3 - 2.3071a_W^2 + 1.1754a_W + 0.0187 \quad (11)$$

to determine a_W and $f(a_W)$, (2) calculation of $f'(a_W)$, r and c, (3) and estimation of λ and a_E^{BET}, (see "Results and Discussion" for a detailed explanation and derivation of Eq. (11)).

The calculated activities are then compared with experimental quantities.

RESULTS AND DISCUSSION

Figure 1 uses the Stokes-Robinson-BET model of Eqs. (5) and (6) to illustrate the relationship between $f(a_w)$ and water activity, a_w, based on the compiled literature database, (the same data are shown in Fig. 2 except presenting a generalized correlation of the data as well). In Fig. 1 each data subset, divided by literature source and temperature, is found in the plot legend. As can be seen from Fig. 1, the data with similar temperatures but from different researchers are in agreement. In general $f(a_w)$ appears to increase slightly with temperature. Each data subset of Fig. 1 was then fitted with a third order polynomial as a function of a_w and later the r and c parameters determined based on this generalized correlation using Eqs. (8) and (9).

In an attempt to generalize the results of this study the entire $f(a_w)$ data was correlated as a function of water

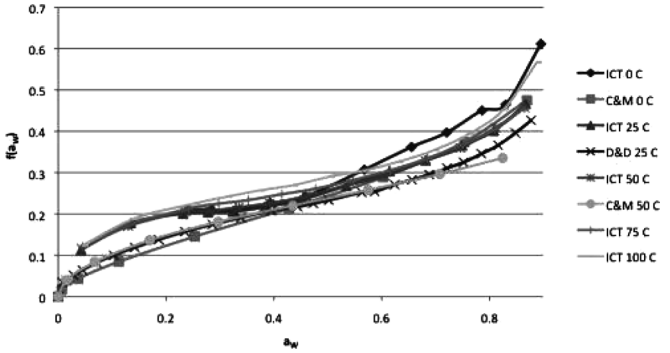

FIG. 1. Isothermal data displaying the experimental rational water activity and the experimental $f(a_w)$. Sources of this database are Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

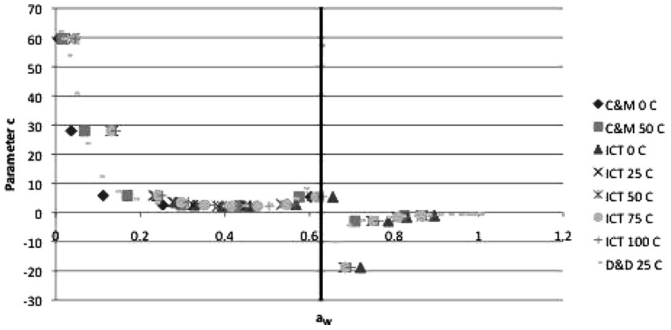

FIG. 3. Parameter c calculated from experimental data vs. a_W. Sources of this database are Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

activity. This correlation is presented in Eq. (11) and illustrated in Fig. 2.

$$f(aW) = 1.80a_W^3 - 2.31a_W^2 + 1.18a_W + 0.019 \qquad (11)$$

In Figs. 3 and 4 the r and c parameters are calculated from experimental data and are presented. In general it may be noted that the c parameter switches from + to – at a water activity of ~0.6. Since the EAI Model requires that c be a positive number this appears to limit the model to water activities less than or equal to ~0.6 which is consistent with the general range of application for the underlying Stokes-Robinson-BET model. Henceforward this paper will restrict the EAI Model to water activities less than or equal to ~0.6. Mason indicates from density measurements that there is a continuous change of waters of hydration from one, (at low water concentrations), to eleven at high water concentrations. Mason also mentions that the hydrate with three waters of hydration has been isolated. In the BET-based models, the water associated with the acid molecule is to be adsorbed, (or in an association shell). Whether it is associated by adsorption or hydration, the species in question has an effectively larger molecular weight and different properties, (e.g., vapor pressure), which would cause variation in the activity coefficient. Thus there seems to be support to asserting that the parameter in the current BET-based model describing the number of solvent molecules associated with a solute molecule is variable and continuous (35).

Using the correlation of Eq. (11), generalized values of r and c for data of this study were calculated using Eqs. (7–9) to re-estimate the water activity by Eq. (5). The estimated rational water activity is compared with the experimental value in Fig. 5 where good agreement is noted.

Figures 6 and 7 display parameters r and c based on the correlation of $f(a_w)$ as a function of a_W of Eq. (11). Here, the relationship holds as the data collapses to one singular line due to the Stokes-Robinson-BET model where r and c are the functions of the calculated water

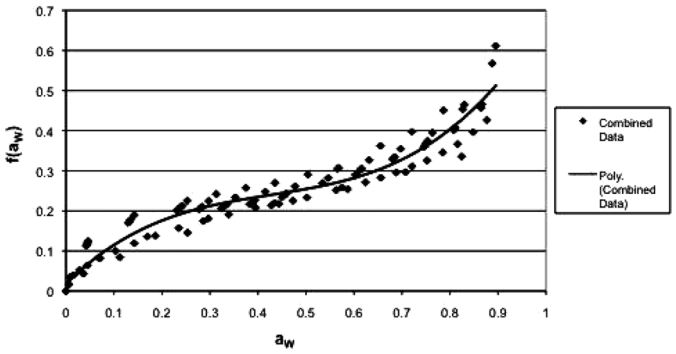

FIG. 2. Data displaying the experimental rational water activity and the experimental $f(a)$ as well as 3rd order polynomial fit of the data. Sources of this database are Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

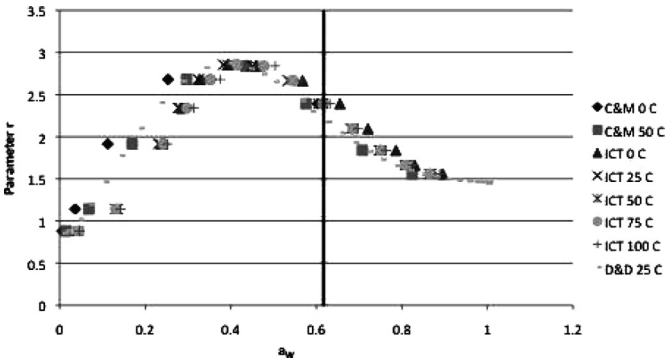

FIG. 4. Parameter r calculated from the experimental data vs. a_W. Sources of this database are Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

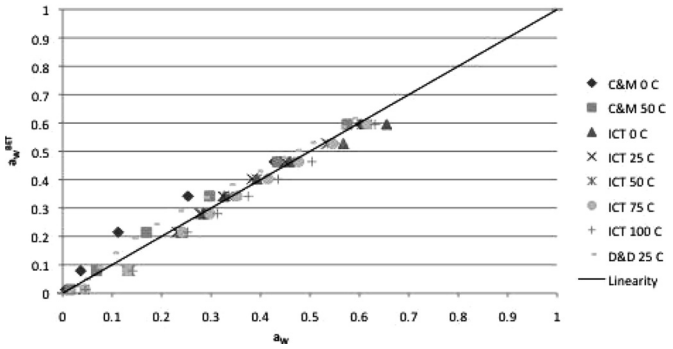

FIG. 5. The experimental rational water activity vs. the calculated rational water activity based on Eq. (11). Sources of this database are Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

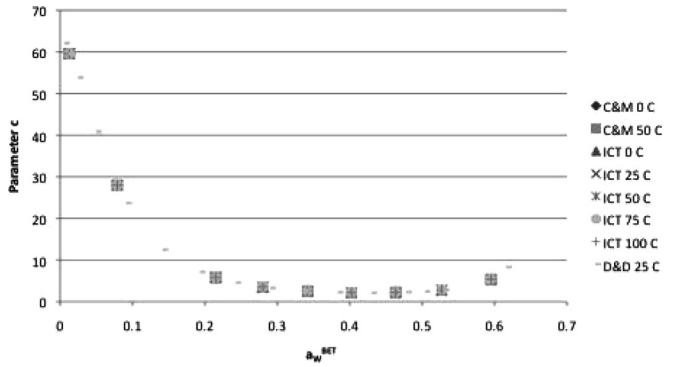

FIG. 6. The calculated parameter c vs. the calculated water activity, both based on Eq. (11). Sources of this database are Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

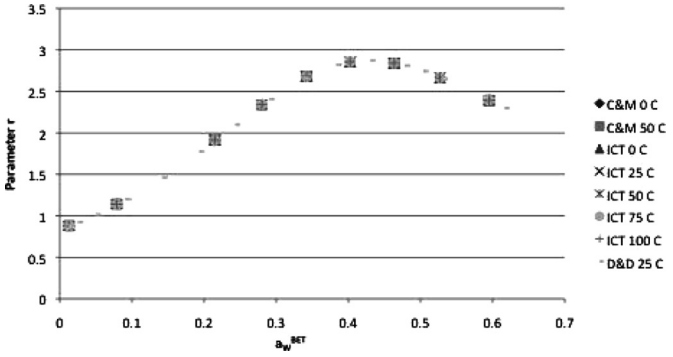

FIG. 7. The calculated parameter r vs. the calculated water activity, both based on Eq. (11). Sources of this database are Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

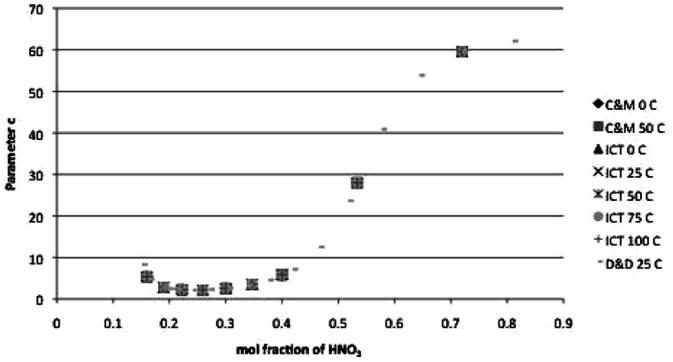

FIG. 8. Isothermal data of the calculated nitric acid activity and the experimental rational nitric acid activity.

activity, save for the model constraint imposed by restricting the water activity to less than of equal to ~0.6. Recalling Figs. 3 and 4, where the parameters r and c were plotted against the experimental rational water activity, the generalized model (based on Eq. (11)) retains consistency with the r, c, and a_W values calculated from experimental data.

Recalling Figs. 3 and 4, where the rational activity was plotted against the parameters r and c, the model still shows signs of consistency with the rational activity.

Not only does this model hold that c and r are functions of activity, but as can be seen in Figs. 8 and 9, the parameters r and c prove to be functions of composition as assumed when deriving Eqs. (6–9).

Because the calculated values were in good agreement, the generalized values of r and c were used with Eq. (10) to estimate the BET HNO_3 activity, $a^{BET}_{HNO_3}$. The results of the $a^{BET}_{HNO_3}$ calculation are compared with the rational nitric acid activity extracted from the compiled database and presented in Fig. 10. Although the isotherms are densely packed, the curves for the corresponding temperatures ascend from 0°C to 100°C.

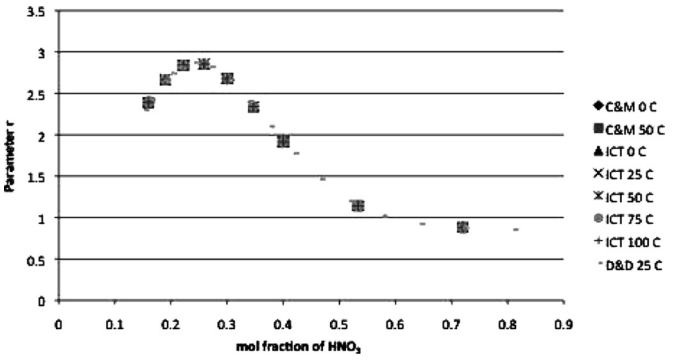

FIG. 9. Isothermal data of the calculated nitric acid activity and the experimental rational nitric acid activity.

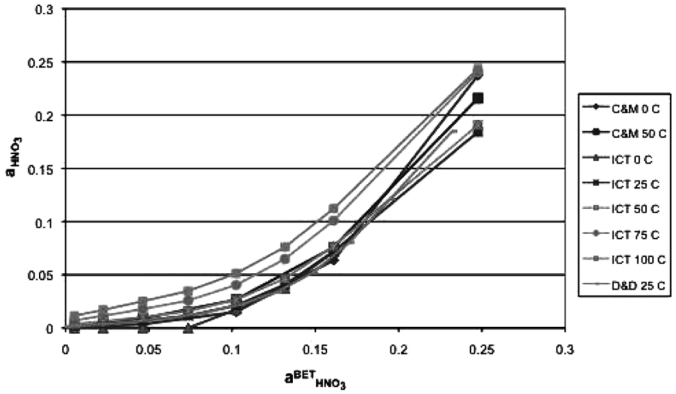

FIG. 10. The calculated nitric acid activity, based on Eq. (11), vs. the experimental rational nitric acid activity. Sources of this database are Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

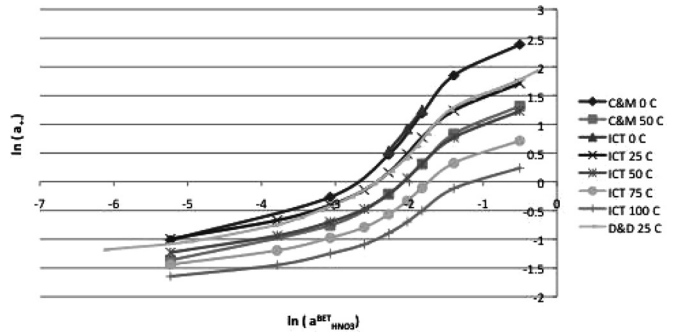

FIG. 11. The calculated BET activity vs. the experimental nitric acid ionic activity, both based on Eq. (11). Input conditions are consistent with database conditions of Taylor [ICT] (5) at 0, 25, 50, 75, and 100°C, the entire data of Davis and DeBruin [D&D] at 25°C (3) and the entire data of Clavelin and Mirabel [C&M] at 0 and 50°C (4).

In Fig. 11 the calculated $a^{BET}_{HNO_3}$ values were then compared with the mean ionic nitric acid activity extracted from the compiled database via Eqs. (3) and (4). Although the isotherms are again densely packed, the ionic activity of our database appears to be related to the BET HNO_3 activity by a well-defined family of curves.

Notable in Fig. 11 is the distribution of the isotherms, generally increasing as a function of temperature and $a^{BET}_{HNO_3}$. Also, the temperatures from the discrete data sources correspond to one another.

CONCLUSIONS

With knowledge of the isothermal temperature of the aqueous HNO_3 solution, composition, and the component partial pressures, estimates of the water activity appear predictable and a clear relationship between the BET activity and the rational and ionic activities for the nitric acid-water system can be seen. The results agree regardless of the data source. It appears that any model coming from this work is likely to apply at water activities below ~0.6.

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