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Thermodynamics of Acetic Acid (aq) Calculated from the Modified Adsorption Isotherm Model for Aqueous Electrolytes

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Abstract: The modified adsorption isotherm model, incorporating the Stokes-Robinson modification of the Brunauer-Emmett-Teller (BET) adsorption isotherm, is used to calculate the activity of the organic acid and water, and the liquidus curve. This is the first known use of the modified adsorption isotherm for estimation of thermodynamic information for aqueous organic acid solutions and one of few works using the model for predicting information for aqueous acids in general. The method described here represents a simplified approach to estimating thermodynamic properties. The model offers some improvement over regular solution theory, but perhaps more importantly offers a method for adjusting thermodynamic properties in the presence of other components in the future. While other models such as UNIQUAC may prove to be more accurate, this model provides satisfactory results with more ease.

Keywords: Acetic acid, activity coefficients, adsorption isotherm, aqueous electrolytes, Brunauer-Emmett-Teller (BET), eutectic, liquidus curve

INTRODUCTION

The removal of acetic acid from aqueous mixtures of nitric acid and various metal salts is being studied. An understanding of the solution

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thermodynamics is key to making appropriate separation process decisions supporting that study and is the focus of the current work. In this study, the thermodynamics of binary mixtures of acetic acid and water are studied to provide a baseline for future work.

Robinson and Stokes (1) postulated that concentrated aqueous electrolytes may be viewed as an irregular arrangement of water around the electrolyte (an acid in the current paper). They applied the Braunauer-Emmett-Teller (BET) model for multi-layer gas adsorption (2) to describe the water activity (a_w) in concentrated electrolyte solutions. This work is usually referred to as the Stokes-Robinson application of the BET adsorption isotherm. Abraham (3) later developed the corresponding relationship between the electrolyte activity and molality for concentrated solutions using the BET model, confining the model to a binary (single salt and water) solution. Ally and Braunstein (5) 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 (4). The works of Stokes and Robinson, Abraham, and Ally and Braunstein are referred to collectively in this work as the Modified Adsorption Isotherm (MAI) model. The MAI model utilizes two parameters, r (the number of hydration sites offered per particle of electrolyte) and c (defined as $e^{\varepsilon/RT}$, where R is the ideal gas constant, T is the absolute temperature, and ε is defined as the difference between the molar enthalpy of "adsorption" of water on the ionic compound and the molar enthalpy of liquification of water, adopting the terminology of Marcus) (6). The MAI model has reference states of liquid water and liquid CH_3COOH (often a hypothetical molten electrolyte). In this paper the MAI parameters are r and c (or ε); thus the term "MAI parameters" is equivalent to BET parameters used in other places in the literature. The MAI model may be utilized by establishing a concentration region where the model is valid (usually $a_w < 0.2$ to 0.5) and treating the r and c (or ε) parameters as temperature-invariant or temperature variant parameters for the system and concentration region of interest.

Although acetic acid is usually treated as a single component, it can actually be two components consisting of hydrogen and acetate ions in the dilute region, but it can largely be taken to be a single molecule at high concentrations. Despite this behavior which sets acetic acid apart from strong inorganic acids, the MAI model predicts the behavior of the organic acid in water well. The effectiveness of the MAI model on partially ionized organic acids gives way to modeling systems containing these acids as well as systems in which a strong acid and weak acid are present.

The interest in molten salt hydrates for heat storage has renewed interest in modified models. Voigt and Zeng (7) and Zeng and Voigt (8) 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 and 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. In general, taking temperature into consideration in BET estimation of *r* and *c* greatly increases the precision of the estimate.

An extensive list of MAI parameters has been recently compiled for a number of aqueous salt solutions by Marcus (6). Ally (9) and Ally and Braunstein (4) have used the MAI model to correlate thermodynamic properties for aqueous NaOH solutions. For aqueous acid solutions, the MAI model has been used for correlation of phase equilibrium data for aqueous H_2SO_4 solutions by Trudelle et al. (10) and for aqueous HNO_3 solutions by Rains and Counce (11,12). To complement previous work with strong acids, the current work with a weak acid is presented utilizing the MAI model to correlate phase-equilibrium data involving aqueous CH_3COOH solutions.

METHOD AND RESULTS

The values of the two MAI parameters for CH_3COOH (aq) used in the current work are estimated as $r = 0.72$ and ε as a function of temperature (Table 2); these parameters were extracted from data of Freeman and Wilson (13) at 372.8 K, 412.6 K, 462.1 K, and 502.9 K. The value of the r parameter is the average value of the calculated r values taken from the linear portion of the BET plot for each temperature.

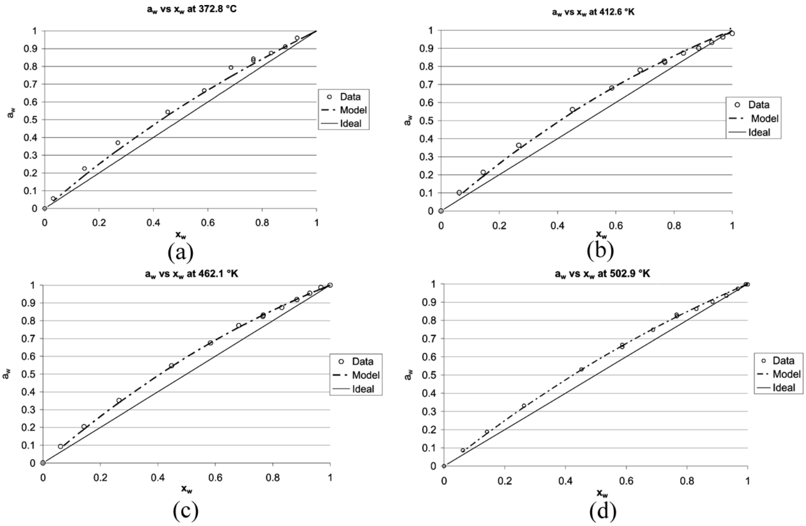
$$\frac{M_w m a_w}{1000(1 - a_w)} = \frac{1}{cr} + \frac{(c-1)}{cr} a_w \tag{1}$$

The BET (MAI) equation is shown above as equation (1) where m is the molality of CH_3COOH (aq), and M_w is the molar mass of water at equilibrium conditions. The r parameter is treated as a constant that is independent of temperature and is taken from water activity range of 0.2 to 0.5. The c (or ε) parameters were determined to be more precise by calculating them from a correlation of Henry's Constant. Henry's Law is defined as activity divided by mole fraction of water.

$$a_w = K_H x_w \tag{2}$$

This equation can be inserted into equation (1), and when the limit as x_w approaches 0, the BET model equation is simplified.

$$\lim_{x_w \to 0} \frac{a_w}{x_w} = \frac{1}{cr} \tag{3}$$



(a) (b)

(c) (d)

Figure 1. Activity as a function of water composition for the aqueous CH_3COOH system 372.8° K, 412.6° K, 462.1° K, and 502.9° K. Solid line represents ideal behavior. Data is from Freeman and Wilson (13).

While Henry's Constant is for values when x_w goes to zero, because it is a linear relationship as shown by Fig. 1, c can be determined by using the r value previously obtained from the MAI model equation and Henry's Constant at the same temperature. Table 2 shows the ε to deviate with temperature. This dependence on temperature is accounted for in the ε values used in the activity calculations. The validity of the MAI model with the above r and ε parameters was established by comparison with the data of Freeman and Wilson (13) at temperatures ranging from 372.8 to 502.9 K. A comparison of a_w predicted by the MAI model from the above r and ε parameters with data of Freeman and Wilson and ideal models ($a_w = x_w$) is presented in Fig. 1 for each set of data. This comparison of calculated activities to those obtained experimentally by Freeman and Wilson shows the accuracy of the calculated parameters. This MAI model was then used to predict freezing points of aqueous CH_3COOH solutions and compared with the data from Barr (14) in Fig. 2 to demonstrate the usefulness of the parameters as well as their accuracy at temperatures much lower than that of the original data.

The following represent the essential equations for this paper in which the MAI model are utilized.

Solid-liquid equilibria: Ice formation

The relationship between water activity and solution melting temperature is

$$\ln a_w = \frac{L_w}{R}\left[\frac{1}{T_m} - \frac{1}{T}\right] \tag{4}$$

where L_w is the latent heat of fusion (6.009 kJ mol^{-1}), at T_m, the melting point (273.15 K) of pure ice (15), and T is the saturation temperature (K). The heat of solution was modified to account for dimerization effects, and was found to make no significant change in results. The minor dependence of L_w on temperature is ignored.

Values of the MAI parameters were extracted from vapor pressure data; as indicated earlier, activity was found and the MAI parameters were extracted from the BET (MAI) plot. Solving Eqs. (1) and (4) simultaneously for m with varying temperature yields the equilibrium concentration from which the mole fraction of water, x_w, is readily obtained; results for application of Eq. (1) and (4) to the current problem, are shown as the dotted line in Fig. 2.

Solid-liquid equilibria: CH_3COOH (aq) liquidus curve

The relationship between the electrolyte activity (acetic acid activity in the current paper) is

$$\ln a_e(x_e, T) = \frac{L_{me}}{R}\left(\frac{1}{T_{me}} - \frac{1}{T}\right) \tag{5}$$

Where a_e is the electrolyte activity, L_{me} is the latent heat of fusion (11.23 kJ mol^{-1}) at T_{me} (289.73 K) the fusion temperature of CH_3COOH (16). The solute activity is obtained from Abraham (3)

$$\frac{\lambda(1-x_e)}{x_e(1-\lambda)} = \frac{r}{c} + \frac{r(c-1)\lambda}{c} \tag{6}$$

where $\lambda = a_e^{1/r}$, x_e is the stoichiometric mole fraction of the electrolyte, and r and ε retain the same identities and values as in Eq. (1).

The composition of the liquidus curve is given by x_e when Equation (5) and (6) are satisfied simultaneously at a given temperature. Metastable liquidus compositions are calculated in the same way by proceeding to temperatures lower than the prevailing liquidus temperature; results from application of Eq. (5) and (6) to the current problem are the solid line in Fig. 2. The “water curve” proved to have no significant deviation from the data, while the “salt curve” deviation from the data was slightly more pronounced. The model for the “water curve” had a deviation of a mere two degrees. The ideal curve deviated by approximately two and half degrees. The "acid curve" deviated for the model by only one and a half degrees on average while the ideal curve deviated three and eight-tenths of a degree from the model. The predicted eutectic differed by three degrees K and a mole fraction of 0.023. The slight deviation of the model to the data is believed to be caused by the use of the simplified equation for solid liquid curve, and not error in the r and ε parameters. This conclusion is based on the fit for the "water curve" which is also dependent on the r and ε parameters as well as accuracy of the predicted activities for the temperature range of 372.8 to 502.9 K. The slight deviation was excepted since the areas of interest were those of very high and low concentrations of acetic acid and not the concentrations between.

CONCLUSIONS

This is the first known use of the modified adsorption isotherm for estimation of thermodynamic information for aqueous organic acid (acetic acid) solutions and one of few works using the model for predicting information for weak aqueous acids in general. The activity of water (a_w) estimated by the MAI model is plotted as a function of the mole fraction of water (x_w) as "Model" curve in Fig. 1; in this figure, the "ideal" curve represents an ideal solution where $a_w = x_w$. The slight deviation between these 2 curves indicates that the solution behaves slightly different than ideal. The MAI model better represents the data than the ideal model. This difference between ideal and non-ideal predictions is expected to become more pronounced as a third ionizing component is added; where it is anticipated that the MAI model will be most useful. The addition of various salts as well as nitric acid to aqueous acetic acid solutions generally results in a "salting out" (increase in activity for the acetic acid and a decrease in water activity) (16). The *r* and ε parameters obtained from this work for aqueous acetic acid solutions is compared to those of aqueous nitric and sulfuric acid solutions in Table 1. Comparison of the r parameters in Table 1 is especially significant, agreeing with expectations

Table 1. Constants for the modified adsorption isotherm adopted to various aqueous acid solutions

Aqueous Acid	*r*	ε (kJ mol^{-1})	Source
Acetic Acid	0.72	0.57	Current work
Nitric Acid	2.66	5.08	(11)
Nitric Acid	2.42	3.78	(11)
Sulfuric Acid	3.8	8.37	(10)

Table 2. Calculated c, r, and K_H values at 372.8°K, 412.6°K, 462.1°K, and 502.9°K from Freeman and Wilson (13)

T(°K)	r_{calc}	K_H	Mε (KJ·mol^{-1})	c
372.8	0.75	1.24	0.36	1.12
412.6	0.71	1.22	0.49	1.14
462.1	0.69	1.19	0.58	1.16
502.9	0.71	1.13	0.86	1.23
	r_{avg} 0.72		ε_{avg} 0.57	

for aqueous acetic acid being weakly hydrated while these values for nitric and sulfuric acid are consistent with these species being strongly hydrated in aqueous solutions.

The liquidus curves from predictions of the MAI model show qualitative agreement with experimental data (Fig. 2). The predicted minimum freezing point is within approximately 0.023 with the experimental mole fraction of water and approximately three degrees Kelvin. The liquidus curve is located by following the "acid curve" from the freezing point of CH_3COOH to the intersection of the "acid curve" and "water curve" (a eutectic point), then following the "water curve" back to the freezing point of water. Results suggest that the BET (MAI) model can be applied to systems containing weak organic acids. It is also believed, based on

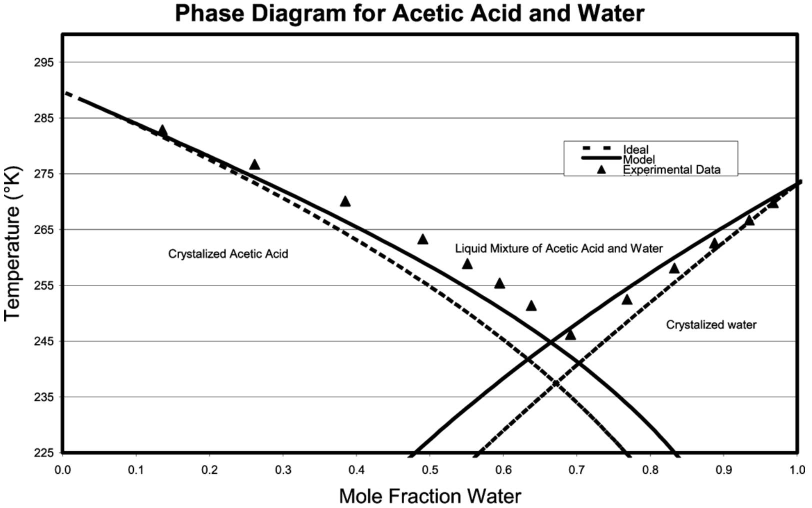


Figure 2. Liquidus curve from pure water (ice) to pure anhydrous liquid CH_3COOH (aq) at its melting point; comparison of predicted against experimental data by Barr and Newsham (14).

results, the BET (MAI) approach could also likely be used to model systems containing compounds of both strong and weak ionizing properties.

The ability of the MAI model to predict the liquidus curve of water in dilute solution is interesting. Ally and Braunstein (4) and Ally (9) have investigated the concentration regime over which the Stokes-Robinson adsorption isotherm applies before showing signs of deterioration. In the dilute solution regime, the excess properties are negligibly small, so even if the model is inaccurate in this region, it does not have a significant bearing on the derived properties, i.e. the liquidus curve in this case.

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