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Liquidus Curves of $LiNO_3$(aq) Calculated from the Modified Adsorption Isotherm Model for Aqueous Electrolytes

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Abstract: The modified isotherm model, incorporating the Stokes-Robinson modification of the Brunauer-Emmett-Teller (BET) adsorption isotherm, is used to calculate the liquidus curve of $LiNO_3$(aq) including the eutectic points. The method described here represents a simplified approach to predict the liquidus curves with sparse information.

Keywords: Activity coefficients, aqueous electrolytes, Brunauer-Emmett-Teller (BET), absorption isotherm, eutectics, liquidus, lithium nitrate

INTRODUCTION

Robinson and Stokes (1) postulated that concentrated aqueous electrolytes may be viewed as an irregular arrangement of water around the electrolyte (a salt in the current paper); they applied the Braunauer-Emmett-Teller (BET) model for multi-layer gas adsorption (2) 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

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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 (4) 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 (5): 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 "BET" parameters, r (the number of hydration sites offered per particle of electrolyte) and c (defined as (ε/kT) where R is the ideal-gas constant, T is the absolute temperature, and ε is defined as the positive 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)), having reference states of liquid water and an (usually hypothetical) undercooled liquid (often a molten electrolyte); in this paper the term, two BET parameters, are r and c or ε. The MAI model is usually utilized by establishing a concentration region where the model is valid (usually $a_w < 0.3$ to 0.5) and treating the r and c or ε parameters as temperature-invariant or temperature variant constants for the system and the concentration region of interest.

The MAI model has been used in a number of studies, including the prediction of solute and solvent activities of $CaCl_2$(aq) (7), osmotic coefficients for NaOH(aq) (8), liquidus curves for NaOH(aq) (5), $NaNO_3$ (aq) (8), $AgNO_3$(aq) (9), NH_4NO_3(aq) (10), and vapor-liquid equilibria for HNO_3(aq) (11, 12). In these works the degree of solution ideality, described in terms of a_w (water activity) and x_w (water mole fraction) varied from reasonably ideal ($a_w \approx x_w$) to highly non-ideal ($a_w \neq x_w$).

The interest in molten salt hydrates for heat storage has renewed interest in MAI models. Voigt and Zeng (13) and Zeng and Voigt (14) added a temperature dependence on the BET r and c parameters. They built on the works of Stokes and Robinson, Abraham, and Ally and Braunsein 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 the temperature into consideration in BET r and c estimation greatly increases the precision of the estimate.

In previously referenced studies, our group has used the MAI model to predict liquidus curves for $AgNO_3$(aq) (a reasonably ideal liquid solution) (9), liquidus curves for NH_4NO_3(aq) (a reasonably ideal liquid solution but with several crystalline solid phases) (10), and vapor-liquid equilibria for HNO_3(aq) (a non-ideal liquid solution with several equilibrium hydrates) (11, 12). The current work focuses on use of the MAI model to generate liquidus curves for $LiNO_3$(aq) and comparison with experimental data; $LiNO_3$(aq) is a non-ideal liquid solution with one equilibrium hydrate ($LiNO_3 \cdot 3H_2O$) that must be taken into consideration in prediction of liquidus curves. The values of the two BET parameters for $LiNO_3$(ag) used in the current work are estimated as $r = 2.61$ and $\varepsilon = 4.88\ \text{kJ mol}^{-1}$; these parameters were extracted from vapor pressure data of Campbell et al. (15) and were treated as constants in all calculations reported here; these r and c or ε values are consistent with others reported in the literature (6, 14, 16).

RESULTS AND DISCUSSION

The following represent the essential equations of the MAI model as used in this paper.

Solid-Liquid Equilibria: Ice Formation

The relationship between water activity and solution temperature is

$$\ln a_w = \frac{\mathrm{L}_w}{R}\left[\frac{1}{T_m} - \frac{1}{T}\right] \tag{1}$$

where L_w is the latent heat of fusion ($6.009\ \text{kJ mol}^{-1}$), at T_m, the melting point (273.15 K) of pure ice (17), and T is the saturation temperature (K). The minor dependence of L_w on temperature is ignored.

The relationship between water activity and solute concentration is the Stokes-Robinson-BET model,

$$\frac{M_w m a_w}{1000(1 - a_w)} = \frac{1}{cr} + \frac{(c-1)}{cr} a_w \tag{2}$$

where m is the molality of $LiNO_3$(aq) and M_w is the molar mass of water at equilibrium conditions. Values of the BET parameters were extracted from vapor pressure data as indicated earlier. Solving Eqs. 1 and 2 simultaneously for m yields the equilibrium concentration from which the mole fraction of water, x_w, is readily obtained; results from application of Eq. 1 and 2 to the current problem, are shown as Curve B of Fig. 1.

Solid-Liquid Equilibria: $LiNO_3$(aq) Liquidus Curve

The relationship between the electrolyte activity (salt activity in the current paper) and solution temperature is

$$\ln a_s(x_s, T) = \frac{L_{ms}}{R}\left(\frac{1}{T_{ms}} - \frac{1}{T}\right) \tag{3}$$

Where a_s is the electrolyte activity, L_{ms} is the latent heat of fusion ($25.5\ \text{kJ mol}^{-1}$) at T_{ms} (523.15 K) the fusion temperature of $LiNO_3$ (18).

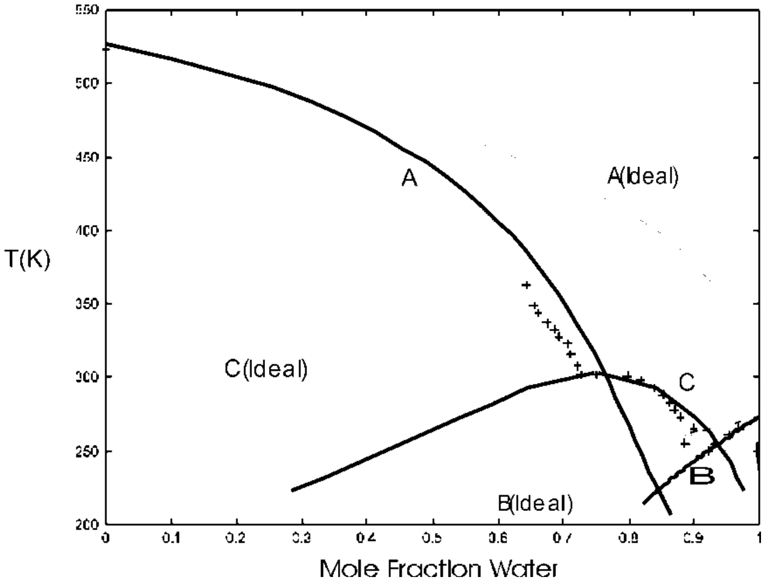

Figure 1. Liquidus curve from pure water (ice) to pure anhydrous liquid $LiNO_3$(aq) at its melting point; comparison of predicted against sparse experimental data by Linke and Seidell (19).

The solute (electrolyte) activity is obtained from Abraham (3)

$$\frac{\lambda(1-x_s)}{x_s(1-\lambda)} = \frac{r}{c} + \frac{r(c-1)\lambda}{c} \tag{4}$$

where $\lambda = a_s^{1/r}$, x_s is the stoichiometric mole fraction of the salt, and r and c retain the same identities and values as in Eq. (2). The composition of the liquidus curve is given by x_s when Equations (3) and (4) 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; the results from the application of Eq. (3) and (4) to the current problem are shown in Curve A of Fig. 1.

Solid-Liquid Equilibria: $LiNO_3 \cdot 3H_2O$(aq) Liquidus Curve

Alley and Braunstein (4) provide the following differential equation representing the solubility

$$Rd\ln a_s a_w^j = [-L_{SHj}(T) + \bar{H}_s^E(T_j) + j\bar{H}_w^E(T_j)]d(1/T) \tag{5}$$

curve of the j_{th} hydrate, written in terms of excess properties, where the excess enthalpies are defined as

$$\bar{H}_w^E = \frac{c\varepsilon[1 - rs - a_w]}{c(1 - rs) - 2a_w(c - 1) - 2} \tag{6}$$

and

$$\bar{H}_s^E = \frac{c\varepsilon r[rs(\lambda - 1) + 1]}{rs(c - 2) - 2rs(1 - c) - c} \tag{7}$$

and L_{SHj} is 36.4 kJ/mole at the fusion temperature of 303.05 K (18) and s = m/55.51. The activities in Eq. (5) are relative to pure liquid standard states (real in the case of water and hypothetical in the case of the salt). Equation (5) may be integrated between the limits of the j_{th} hydrate melting point (T_j, x_j) and any point on the liquidus curve (T, x); the above equation is exact only at the melting point of the salt. Equation (5) is solved by trial and error, similar to that recommended by Ally and Braunstein (4); results for application of Eq. (5) to the current problem are shown as Curve C in Fig. 1.

CONCLUSIONS

The predicted liquidus curves from predictions of the MAI model show good qualitative agreement, with experimental data (Fig. 1), especially in the location of the eutectic points. The liquidus curve is located by following curve A from the freezing point of $LiNO_3$ to the intersection of curves A and C (a eutectic point), then following curve C to the intersection of curves C and B (another eutectic point) and following curve B (the ice curve) to the freezing point of water.

The ideal curves where the activities from Eqs. (1), (3), and (5) are approximated as the mole fractions are shown as dotted lines in Fig. 1. Curve A (Ideal) is the idealized liquidus curve coresponding to curve A; curves B (Ideal) and C (Ideal) are the idealized versions of curves B and C, respectively. The qualitative deviation between the idealized curves and the MAI model generated curves, where non-ideality is accounted for, show the importance of the MAI model. Agreement of the MAI model with experimental data and the reasonably close estimation of the eutectic point justify ignoring the temperature dependence of the enthalpy terms L_m, L_{SHj}, and L_{ms}.

The ability of the MAI model to predict the liquidus curve of water in dilute solution is interesting. Ally and Braunstein (20) and Ally (7) have investigated the concentration regime over which the Stokes-Robinson adsorption isotherm applies before showing signs of deterioration. In this regard the predicted and experimental osmotic coefficients provide a good indication of the validity of the model (7). 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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