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Liquidus Curves of NH_4NO_3 (aq) Calculated from the Modified Adsorption Isotherm Model for Aqueous Electrolytes

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Abstract: The Stokes-Robinson modification of the Brunauer-Emmett-Teller (BET) adsorption isotherm is used to calculate the liquidus curve of $NaNO_3$(aq) including the eutectic point and metastable phases. The method described here represents a simplified approach to predict the liquidus curves with sparse information and considers the presence of several crystalline solid phases of NH_4NO_3.

Keywords: Activity coefficients, aqueous electrolyte, Brunauer-Emmett-Teller (BET), absorption isotherm, eutectic

INTRODUCTION

In this paper it is demonstrated that the liquidus curve for NH_4NO_3(aq) calculated from the Stokes-Robinson application of the Brunauer-Emmett-Teller (BET) adsorption isotherm is in good agreement with experimental data. This is the second of 3 papers focusing on solutes exhibiting increasing competitiveness for water; the first of these demonstrated the applicability of the BET isotherm for $AgNO_3$ (1). The water activity equation is obtained from the Stokes-Robinson (BET) model (2), modified slightly in the algebraic sign of the energy parameter, ε, based on the statistical development of the ionic lattice model by Ally and Braunstein (3). The solute activities are

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obtained from the expression developed by Abraham (4). The values of the two BET parameters, estimated as $r = 1.63$ and $\varepsilon = 0.89\,\text{kJ mol}^{-1}$, were extracted from vapor pressure data of Campbell et al. (5) and kept fixed in all calculations despite the fact that they exhibit a small temperature dependence (6). The approach used here for calculating the liquidus curve (solid–liquid equilibria) is based on the general thermodynamic treatment of Ally and Braunstein (7) and takes into consideration the presence of several crystalline solid phases of NH_4NO_3. The approach used in this paper builds directly on previous work by Ally (8) and Rains and Counce (1).

RESULTS AND DISCUSSION

Solid–Liquid Equilibria: Ice Formation

The chemical potential of ice at a given temperature in equilibrium with its saturated solution is given by $\mu_{ice} = \mu_w$, where μ_{ice} is the chemical potential of pure ice (solid) and μ_w is the chemical potential of water in the same solution (containing NH_4NO_3). The above equality of chemical potential is elaborated as

$$\mu_{ice} = \mu_w^* + RT \ln a_w\,(T, p, x_w) \tag{1}$$

where μ_w^* is the chemical potential of pure water at temperature and one atmosphere pressure, a_w is the water activity in NH_4NO_3(aq), R is the ideal gas-law constant ($8.314 \times 10^{-3}\,\text{kJ mol}^{-1}\,\text{K}^{-1}$), x_w is the mole fraction of water, T is the saturation temperature (K), and p is pressure in atmospheres. After recognition that at constant pressure, $\mathrm{d}(\mu_w^*/T)/\mathrm{d}T^{-1} = h_w(\text{liquid})$ and $\mathrm{d}(\mu_w^*/T)/\mathrm{d}T^{-1} = h_{ice}^*$, rearrangement, differentiation Eq. (1) with respect to T^{-1}, and integration gives

$$R\int_{a_w=1}^{a_w} d\ln a_w = -\int_{T_m}^{T} (h_w(liquid) - h_{ice}^*)dT^{-1} = -\int_{T_m}^{T} L_w dT^{-1} \tag{2}$$

where $L_w = ((h_w(liquid) - h_{ice}^*)$ is the latent heat of fusion ($6.009\,\text{kJ mol}^{-1}$ and T_m is the melting point (273.15 K) of pure ice (9). The minor dependence of L_w on temperature is ignored. Integration of Eq. (2) and rearrangement gives

$$\ln a_w = \frac{L_w}{R}\left[\frac{1}{T_m} - \frac{1}{T}\right] \tag{3}$$

The relationship between water activity and solute molality by the Stokes-Robinson-BET model is

$$\frac{M_w m a_w}{1000(1 - a_w)} = \frac{1}{cr} + \frac{(c-1)}{cr} a_w \tag{4}$$

where $c = \exp(\varepsilon/RT)$, m is the molality of NH_4NO_3(aq), and M_w is the molar mass of water at equilibrium conditions. Values of the BET parameters of $r = 1.63$ and $\varepsilon = 0.89\,\text{kJ mol}^{-1}$ were extracted from data of Campbell et al. (5). Solving Eqs. (3) and (4) simultaneously for m yields the equilibrium concentration from which the mole fraction of water, x_w, is readily obtained.

Solid–Liquid Equilibria: NH_4NO_3(aq) Liquidus Curve

The chemical potential of anhydrous NH_4NO_3 in equilibrium with its saturated solution at a temperature T can be described by $\mu_s^*(x_s = 1, \text{T}) = \mu_s^{solution}(x_s,\ T)$ where $\mu_s^*(x_s = 1,\ T)$ is the chemical potential of pure anhydrous NH_4NO_3 precipitate and $\mu_s^{solution}\ (x_s, T)$ is the chemical potential of NH_4NO_3 in saturated solution at the same temperature. The equality in chemical potentials is written in expanded form as

$$\mu_s^*(x_s T) = \mu_s^{liq}(x_s = 1, T) + RT \ln a_s(x_s, T) \tag{5}$$

where $\mu_s^{liq}\ (x_s = 1,\ T)$ is the chemical potential of pure anhydrous liquid NH_4NO_3 at the same temperature. Again, after recognition that at constant pressure, $\text{d}(\mu_s^*/T)/\text{d}T^{-1} = h_s^{solid}$ and $\text{d}(\mu_s^{liq}/T)/\text{d}T^{-1} = h_s^{liquid}$, rearrangement, differentiation of Eq. (5) with respect to T^{-1} and integration gives

$$\begin{aligned} R\int_1^{a_s} d\ln a_s(x_s, T) &= \int_{Tms}^{T} (h_s^{solid}(x_s = 1, T) - h_s^{liquid}(x_s = 1, T))dT^{-1} \\ &= -L_{ms}\int_{Tms}^{T} dT^{-1} \end{aligned} \tag{6}$$

where L_{ms} is the latent heat of fusion (6.13 kJ mol^{-1}) and T_{ms} (442.8 K) the fusion temperature of NH_4NO_3 (10). Similar information may be obtained from reference (11). Some additional complexity must be introduced due to the several crystalline forms of NH_4NO_3 that must be considered; information on these phase transitions is presented in Table 1. The L_{ms} may be adjusted to include the heats of transition encountered along the liquidus curve by $L_{ms} + \sum L_{T,i}$ where $L_{T,i}$ is the appropriate heat of transition. The above integration

Table 1. Phase transition data (11)

Transition	Temperature (K)	$L_{T,i}$ or L_{ms} (kJ/mol)
Phase V-IV	255	0.50
Phase IV-III	305.3	1.67
Phase III-II	357.4	1.31
Phase II-I	398.4	4.29
Phase I-Liquid	442.8	6.13

must now be considered as in several steps. Completing the integration of Eq. (6) from T_{ms} to $T > T_{II\text{-}I}$ and slight rearrangment gives

$$\ln a_s(x_s, T) = \frac{L_{ms}}{R}\left(\frac{1}{T_{ms}} - \frac{1}{T}\right) \tag{7}$$

which is valid from the melting point to the first phase transition, occurring at 398.4 K. Another version of Eq. (7) is valid from the first phase transition temperature of 398.4 K to the second phase transition temperature at 357.4.

$$\ln a_s(x_s, T) = \ln a_s(x_s, T)_{II-I}\left[\frac{L_{ms} + L_{T,II-I}}{R}\right]\left(\frac{1}{T_{II-I}} - \frac{1}{T}\right) \tag{8}$$

where $L_{T,II-I}$ is the enthalpy of transition to phase II from phase I at $T = T_{II-I}$. The succeeding estimates of a_s proceed similarly. The solute activity in the Stokes-Robinson-BET model is obtained from Abraham (4) and Ally and Braunstein (7) as

$$\frac{\lambda(1 - x_s)}{x_s(1 - \lambda)} = \frac{r}{c} + \frac{r(c - 1)\lambda}{c} \tag{9}$$

where $\lambda = a_s^{1/r}$, x_s is the stoichiometric mole fraction of the salt, and r and ε retain the same identities and values as in Eq. (4). The composition of the

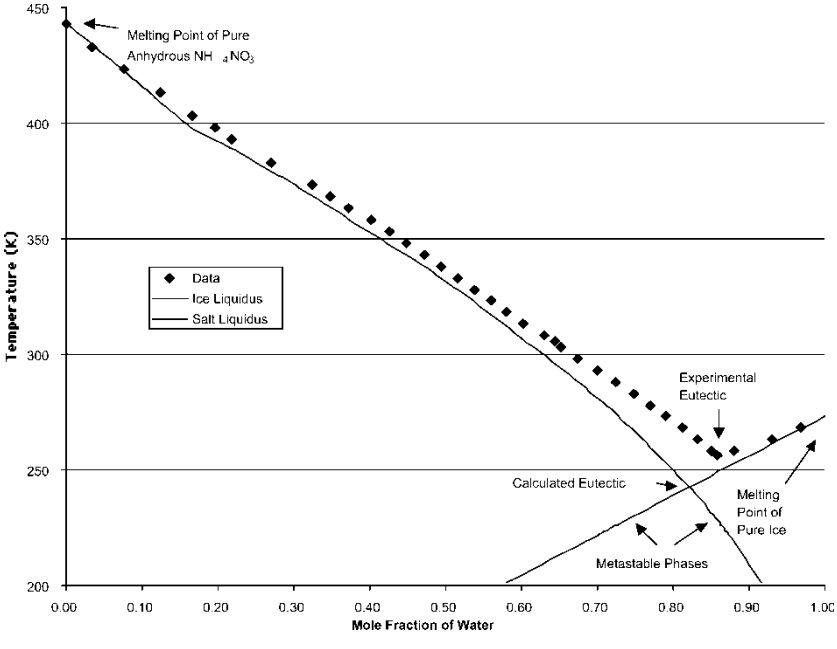

Figure 1. Liquidus curve from pure water (ice) to pure anhydrous liquid NH_4NO_3 (aq) at its melting point; comparison of predicted against sparse experimental data by Linke and Seidell (13).

liquidus curve is given by x_s when Eq. (7) and (9) are satisfied simultaneously at a given temperature. Metastable liquidus compositions are calculated in the same way by proceeding to temperatures lower than the eutectic point.

It should be noted that since the Stokes-Robinson-BET model provides a free energy function which is extensive and homogeneous in the mole numbers, its chemical potentials satisfy the Gibbs-Duhem relationship automatically (3, 12).

The predicted liquidus curves show good agreement, with experimental data of Linke and Seidell (13) (Fig. 1), especially in the location of the eutectic point. The freezing point depressions are given by the loci of points corresponding to the liquidus curve for water. Agreement with experimental data and reasonable location of the eutectic point justifies ignoring the temperature dependence of the enthalpy terms L_w and L_{ms}.

The ability of the Stokes-Robinson adsorption isotherm to predict the liquidus curve of water in dilute solution is interesting. Ally and Braunstein (14) and Ally (15) 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 (15). In the dilute solution regime, the excess properties are negligible, 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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