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Liquidus Curves of $AgNO_3$(aq) Calculated from the Modified Adsorption Isotherm Model for Aqueous Electrolytes

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Summary. The *Brunauer-Emmett-Teller* (*BET*) adsorption isotherm as modified by *Robinson* and *Stokes* is used to calculate the liquidus curve of $AgNO_3$(aq) including the eutectic point and metastable phases. The simplified approach described here predicts the liquidus curves by using sparse data and readily available constants.

Keywords. Activity coefficients; Aqueous electrolytes; *Brunauer-Emmett-Teller* (*BET*); Adsorption isotherm, Eutectic.

Introduction

This paper demonstrates that the liquidus curve for $AgNO_3$(aq) calculated from the *Stokes-Robinson* application of the *Brunauer-Emmett-Teller* (*BET*) adsorption isotherm provides excellent agreement with experimental data. Based on *Ally* and *Braunstein*'s [1] statistical development of the ionic lattice model, the algebraic sign of the energy parameter, ε, is modified and used in the *Stokes-Robinson* (*BET*) model [2], in order to obtain the equation for calculating water activity. Solute activities are obtained from the expression developed by *Abraham* [3] using ε defined with the above noted modification. The values of the two *BET* parameters are calculated to be $r = 0.9$ and $\varepsilon = 0.65\,\mathrm{kJ\,mol^{-1}}$ from vapor pressure data [4] converted for use in the *BET* model by the method detailed by *Rains et al.* [5]. While these parameters may exhibit a small temperature dependence [6] and in some cases a concentration dependence [7], their values are kept constant in these calculations. The general thermodynamic treatment of *Ally* and *Braunstein* [8] provides the basis for the approach to calculating the liquidus curve. This approach to calculating solid–liquid equlibria is simplified by noting that the $AgNO_3$(aq)

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system apparently does not possess crystalline hydrates. The approach used in this paper is similar to that used sucessfully by *Ally* in a recent work [9].

Results and Discussion

Solid–liquid Equilibria: Ice Formation

At a given temperature, the chemical potential of ice in equilibrium with its saturated solution is given by $\mu_{\text{ice}} = \mu_w$, where μ_{ice} is the chemical potential of pure ice existing as a solid and μ_w is the chemical potential of water in the same solution which contains $AgNO_3$. This chemical potential equality may be expanded as shown in Eq. (1) where μ_w^* is the chemical potential of pure water at temperature T and one atmosphere pressure, a_w is the water activity in the solution, $AgNO_3(aq)$, 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, and T is the saturation temperature (K).

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

Differentiating Eq. (1) with respect to T^{-1}, rearranging and integrating gives Eq. (2) where $L_w = (h_w(\text{liquid}) - h_{\text{ice}}^*)$ 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 [10]. The slight temperature dependence of L_w is neglected.

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

Integration of Eq. (2) and rearrangement gives Eq. (3).

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

Water activity and water mole fraction are related in the *Stokes-Robinson-BET* model by Eq. (4) where $c = \exp(\varepsilon/RT)$, m is the molality of $AgNO_3(aq)$, and M_w is the molar mass of water at equilibrium conditions. Values of the *BET* parameters of $r = 0.9$ and $\varepsilon = 0.65\,\text{kJ mol}^{-1}$ were extracted from data by *Cambell et al.* [4].

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

By selecting a temperature in the range of interest, the equilibrium concentration, m, may be obtained by solving Eqs. (3) and (4) simultaneously. The mole fraction of water, x_w, is then readily obtained from the molality.

Solid–liquid Equilibria: $AgNO_3(aq)$ Liquidus Curve

At a temperature T the chemical potential of anhydrous $AgNO_3$ in equilibrium with its saturated solution can be described by $\mu_s^*(x_s = 1, T) = \mu_s^{\text{solution}}(x_s, T)$ where $\mu_s^*(x_s = 1, T)$ is the chemical potential of pure anhydrous $AgNO_3$ precipitate and $\mu_s^{\text{solution}}(x_s, T)$ is the chemical potential of $AgNO_3$ in a saturated solution at the same temperature. The chemical potential equality may be written as shown in Eq. (5) where $\mu_s^{\text{liq}}(x_s = 1, T)$ is the chemical potential of the hypothetical pure anhydrous liquid $AgNO_3$ precipitate at the same temperature.

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

Differentiation of Eq. (5) with respect to T^{-1} gives Eq. (6) where L_{ms} is the latent heat of fusion ($11.5\,\text{kJ mol}^{-1}$) and T_{ms} (482.15 K) the fusion temperature of $AgNO_3$ [10]. Again the minor temperature dependence of the enthalpy of fusion is neglected.

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

Integration of Eq. (6) and rearranging gives Eq. (7).

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

The *Stokes-Robinson-BET* model solute activities are obtained from *Abraham* [3] and *Ally* and *Braunstein* [8] as given in Eq. (8) where $\lambda = a_s(1/r)$, x_s is the mole fraction of the salt on a stoichiometric basis, and r and ε are the same entitites as in Eq. (4).

$$\frac{\lambda(1 - x_s)}{x_s(1 - \lambda)} = \frac{r}{c} + \frac{r(c - 1)\lambda}{c} \tag{8}$$

At a given temperature Eqs. (7) and (8) are satisfied simultaneously and the composition of the liquidus curve is given by x_s. By proceeding to temperatures lower than the eutectic point, the metastable liquidus compositions are calculated in the same way.

The chemical potentials in the *Stokes-Robinson-BET* model automatically satisfy the *Gibbs-Duhem* relationship since the model provides a free energy function which is extensive and homogeneous in mole numbers [1, 11].

The predicted liquidus curves for water and $AgNO_3$ show very good agreement with available experimental data [12] as shown in Fig. 1. The freezing point depressions are given by the loci of points corresponding to the liquidus curve for water. The model's good agreement with experimental data along with the correct location of the eutectic point justifies ignoring the temperature dependence of the enthalpy terms L_w and L_{ms}.

The good performance of the *BET* adsorption isotherm to predict the liquidus curve of water in the dilute solution is particularly interesting. *Ally* and *Braunstein* [13] and *Ally* [14] have examined the concentration regimes over which the *BET* adsorption isotherm may be applied before a deterioration in accuracy. A good indicator of the validity of the model is comparison of predicted and experimental osmotic coefficients [14] and verification of parameter constancy [7]. In the dilute solution derived properties such as the liquidus curve are not greatly affected by the neglibly small excess properties. For this reason the model may still perform well in the dilute solution where it may be inaccurate. This procedure, while restricted

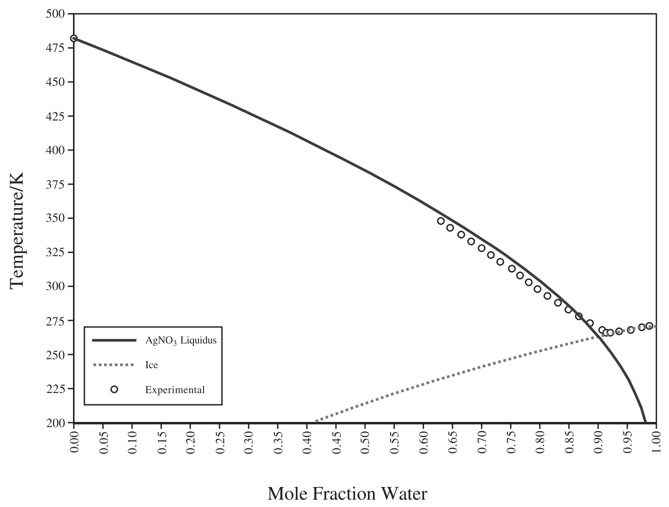

Fig. 1. Liquidus curve from pure water (ice) to pure anhydrous liquid $AgNO_3$(aq) at its melting point; comparison of predicted against sparse experimental data by *Linke* and *Seidell* [12]

to ideal eutectic systems, has the difficulty that the parameters and transition enthalpies are taken to be temperature independent. However, in cases where the determination of the parameters of the respective binary systems is easier than the determination of the binary phase diagram or if they are already known with sufficient accuracy then this procedure is very promising in the construction of eutectic phase diagrams.

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References

[1] Ally MR, Braunstein J (1998) J Chem Thermodyn **30**: 49
[2] Stokes RH, Robinson R (1948) J Am Chem Soc **70**: 1870
[3] Abraham M (1981) J Chim Phys **78**: 57
[4] Cambell AN, Fishman JB, Rutherford G, Schaefer TP, Ross L (1956) Can J Chem **34**: 151
[5] Rains WO, Counce RM, Spencer BB (1999) Chem Eng Comm **171**: 169
[6] Braunstein H, Braunstein J (1971) J Chem Thermodyn **3**: 419
[7] Rains WO, Counce RM (2000) Ind Eng Chem Res **39**: 236
[8] Ally MR, Braunstein J (1993) Fluid Phase Equilibria **87**: 213
[9] Ally MR (2000) Monatsh Chem **131**: 341
[10] International Critical Tables **3**: 372
[11] Braunstein J, Ally MR (1996) Monatsh Chem **127**: 269
[12] Linke WF, Seidell A (1965) Solubilities, Inorganic and Metal-Organic Compounds, vol II, 4th edn American Chemical Society, Washington DC
[13] Ally MR, Braunstein J (1996) Fluid Phase Equilibria **120**: 131
[14] Ally MR (1999) J Chem Eng Data **44**(4): 792