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Application of Mixture Models to Solubility Calculations, Using Sodium Oxalate as an Example

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Abstract: The solubility of solids in nuclear waste impacts many separation processes including evaporator set-points, pressure drops in ion-exchange columns, as well as the washing and leaching of sludge. Scheffe and Cox type empirical mixture models have long been used to model crystal stability in nuclear waste glass melters, and this methodology has now started being employed to model solubility in aqueous nuclear wastes. The large amount of theory and data available for aqueous systems allows for the opportunity to evaluate mixture models for solubility calculations. In the present paper, it is shown that Scheffe type mixture models should be employed when the pure component is the standard state of interest whereas the Cox type mixture models should be employed when infinite dilution is the standard state. An example application is used to demonstrate that mixture models can be used to predict solubility, even across a phase boundary, when combined with the standard thermodynamic equations for the solubility product. The example employed is $Na_2C_2O_4$ solubility in aqueous $NaNO_3$ solutions, which can be thought of as a simplified high-level nuclear waste supernatant.

Keywords: Mixture model, nuclear waste, sodium oxalate, solubility

INTRODUCTION

The solubility of solids is important to many separation processes. Many chemicals are separated by either dissolution or precipitation, and the

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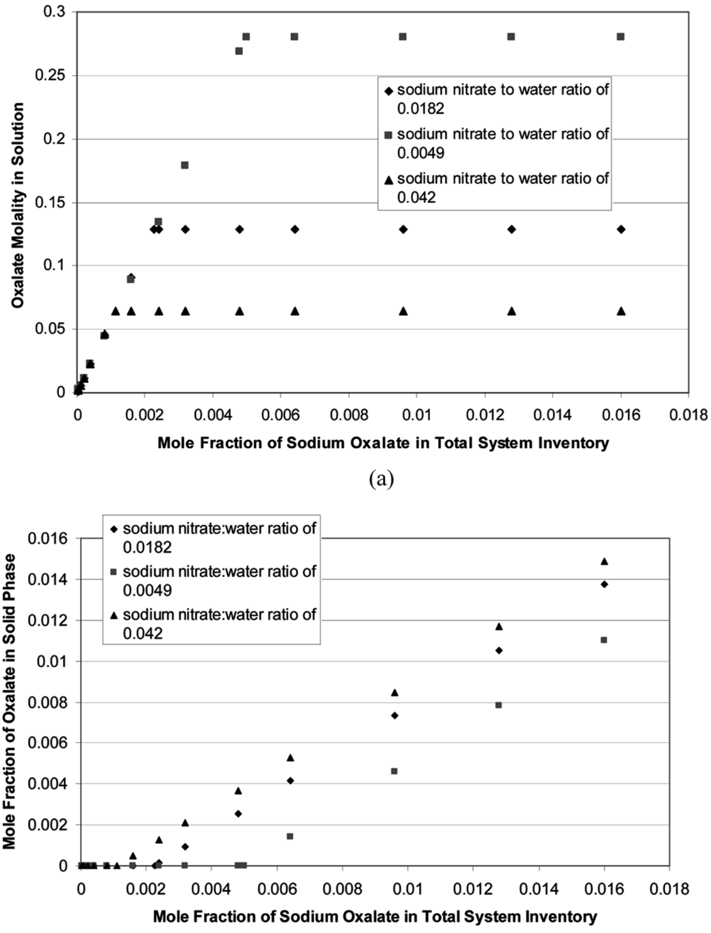
solubility of unwanted and wanted solids will impact the choice of media to perform the dissolution or precipitation reaction. The nuclear Waste Treatment and Immobilization Plant at the Hanford site in Washington State uses dissolution reactions to remove aluminum and semi-soluble salts such as sodium oxalate from sludge. The solubility of all components in these processes must be understood so that process flowsheets can accurately capture the fate of every waste component. Solid solubility also impacts performance of other waste separation processes because solids can foul ion-exchange columns, filters, and evaporators. Therefore, relatively simple models are needed to describe solid solubility in nuclear waste.

Empirical mixture models of the Scheffe (1) and Cox type (2) have long been used to model crystal solubility in nuclear waste glass (3–6). The most common solubility parameter modeled in waste glass with mixture models is the liquidus temperature, which is the highest temperature at which a crystal is stable in the melt. The use of empirical mixture models for many-component nuclear waste glass is necessary because there is insufficient thermodynamic data for the melt phases to calculate the solubility using traditional thermodynamic methods (5,7). For aqueous solutions, however, more complicated thermodynamic models are generally used because of the copious amount of theory and data available to develop those types of models (8). Nonetheless, mixture models have started to gain popularity for use in solubility problems in aqueous nuclear wastes (9–11), presumably because of the simplicity of the models.

The strong understanding of solubility in aqueous solutions affords the opportunity to compare empirical mixture models with traditional thermodynamic models to determine if there is any physical meaning behind the coefficients and to determine the most efficient way to use mixture models.

The soluble concentration of constituents in solution can change significantly when crossing phase boundaries. This principal can be demonstrated with the $Na_2C_2O_4$-$NaNO_3$-H_2O system, as shown in Figs. 1a and 1b. These figures show the oxalate concentration in solution (Fig. 1a) or the mole fraction of sodium oxalate in the solid phase (Fig. 1b) as a function of the fraction of sodium oxalate inventory in the mixture. The fraction of sodium oxalate in the inventory is used as the dependent variable in the figures because inventory is what is typically tracked in chemical process flowsheets (12). Thus, it is convenient to calculate solubility from inventory. The soluble and solid phase concentrations in Fig. 1 were calculated directly from the solubility product (K_{sp}; Equation (1)) using the data at 323.15 K reported by Kol'ba et al. (13) for three selected ratios of sodium nitrate to water



(a)

(b)

Figure 1. (a) Oxalate solubility as a function of sodium oxalate fraction in the total inventory of the system; (b) Oxalate solubility as a function of sodium oxalate fraction in the total inventory of the system.

in the mixtures.

$$K_{sp} = \frac{(X_{Na^+})^2 (X_{C_2O_4^{2-}})}{1} = \frac{K_{eq}}{(\lambda_{Na^+})^2 (\lambda_{C_2O_4^{2-}})} \tag{1a}$$

$$X_{Na^+} = Sodium\ Molality \tag{1b}$$

$$X_{C_2O_4^{2-}} = Oxalate\ Molality \tag{1c}$$

$$\lambda_{Na^+} = Sodium\ Activity\ Coefficient \tag{1d}$$

$$\lambda_{C_2O_4^{2-}} = Oxalate\ Activity\ Coefficient \tag{1e}$$

Molality is moles of analyte per kilogram of water. Inspecting Fig. 1a indicates that the concentration of liquid phase sodium oxalate is equal to the quantity of sodium oxalate added to the system up to a certain point (the saturation point) and then is constant from that point on. The saturation point is affected by the sodium nitrate to water ratio in the mixture. Conversely, Fig. 1b shows that there are no sodium oxalate solids in the system until a certain quantity of sodium oxalate is reached (the saturation point), but the quantity of solids equals the quantity of sodium oxalate added to the system past that point. The saturation point equals the K_{sp} when solid sodium oxalate is present.

These figures indicate that the impact of one mixture component (sodium oxalate) on the soluble concentration of oxalate is very simple and linear, a slope of one below the saturation point and a slope of zero above the saturation point. The saturation point does depend on the mixture composition, as indicated by the change in the locations of the break in the lines in Fig. 1 as a function of sodium nitrate to water ratio. These breaks in the soluble oxalate concentration observed in Fig. 1a occur because a phase boundary has been reached at the break in the line (the K_{sp}), as indicated by the appearance of sodium oxalate solid at the same point in Fig. 1b. Predicting solubility across a phase boundary is a known difficulty of simple polynomials like the Scheffe (1) and Cox (2) mixture models (14–15). The purpose of the present work is to develop a method to predict soluble concentrations of constituents when crossing a phase boundary using simple mixture models.

The $Na_2C_2O_4$-$NaNO_3$-H_2O system is used in this study because oxalate ($C_2O_4^{2-}$) is a major component of Hanford nuclear waste (16), and its solubility has many impacts on tank waste processing (17). Sodium nitrate is one of the most prevalent salts in nuclear waste, so the $Na_2C_2O_4$-$NaNO_3$-H_2O system can be thought of as a simplified nuclear waste system.

SCHEFFE AND COX MIXTURE MODELS AND THEIR RELATIONSHIPS TO STANDARD STATES USED IN CHEMISTRY

The Scheffe 1st and 2nd order mixture models (1) are shown in Equations (2) and (3), respectively. In these equations, y is the response of interest (soluble oxalate concentration in this paper), x_i and x_j are the mole fraction of each constituent, q is the number of constituents in the mixture, while a_i and $b_{i,j}$ are first and second order empirically determined coefficients.

$$y = \sum_{i=1}^{q} a_i x_i \tag{2}$$

$$y = \sum_{i=1}^{q} a_i x_i + \sum_{1<j=1}^{q} b_{i,j} x_i x_j \tag{3}$$

Hrma (18) noted that the Scheffe mixture models are consistent with the Gibbs-Duhem equation used in physical chemistry. He also noted that the a_i coefficients in Equation (2) are the partial molar properties of the constituents. An ideal mixture in chemistry (e.g., Raoult's Law) is one where the mixture behaves as a mechanical mixture of the mixture components (19). The function used to describe ideal mixtures is exactly the same as Equation (2) (19). Hence, Equation (2) represents an ideal mixture.

The Cox mixture models are given by Equations (4) and (5) (2):

$$y = B_o + \sum_{i=1}^{q} a_i x_i \tag{4}$$

$$y = B_o + \sum_{i=1}^{q} a_i x_i + \sum_{1<j=1}^{q} b_{i,j} x_i x_j \tag{5}$$

where B_0 is the value of y at a reference mixture composition. The values of the a_i and $b_{i,j}$ coefficients in the Cox mixture models differ from the Scheffe mixture models in that the totals in the summations in Equations (4) and (5) equal zero for the reference mixture (2). The Cox mixture models have the same predictive ability and regression statistics as the identical order Scheffe mixture models (20), but provide information of how the response (y) changes with respect to a candidate reference mixture.

One advantage of the Cox mixture model parameterization is that the Student's t test and associated p statistic can be used to determine the statistical significance of the a_i and $b_{i,j}$ coefficients. In regression, the p statistic is used to determine if a component has a statistically significant response, and is used to reduce the number of terms applied to the model (21). Models with excessive numbers of terms have artificially high correlation coefficient squared (R^2) values (22). The p statistic cannot be used for the Scheffe model, but can be used for the Cox model (23).

The concept of standard mixture used in the Cox mixture model is comparable to the concept of standard state used in thermodynamics; the primary difference being that in thermodynamics each component has its own standard reference state rather than having a reference mixture as a standard state (19). Thus, in thermodynamics there are as many reference states as components, but the Cox mixture model has only one standard state. The most common standard reference state employed is the pure component. The Scheffe mixture models (Equations (2) and (3)) are appropriate when the pure component standard states are used, however the Cox mixture model can only have one reference mixture at a time. The a_i coefficients in Equation (2) are the property values for the pure component.

Another common standard state for a component is infinite dilution in a solvent (19). Infinite dilution is usually used as the reference state when the component cannot exist as a pure component under the conditions of interest (19). An example is sodium oxalate dissolved in water. Liquid water can be a pure compound at ambient temperatures, but pure sodium oxalate is not a liquid at ambient temperatures. Therefore, infinite dilution is used as the reference state for sodium oxalate dissolved in water because infinite dilution is a physically possible state for sodium oxalate at ambient temperature. When infinite dilution in a single solvent is used for the standard state for all solutes, as is typically the case for electrolytes at ambient temperature (19), the Cox mixture model can be used with the reference mixture (in Equations 4 and 5) being the pure solvent. The Cox model can be used in this case because all components are referenced to the same mixture, the pure solvent. Thus, the choice of mixture model depends on the choice of reference state if the concept of standard state is to be retained in mixture models.

CHEMICAL POTENTIAL AND RELATIONSHIP WITH MIXTURE MODELS

Per standard texts (19), the solubility of a solid phase in solution is described by the equilibrium constant (K_{eq}). The K_{eq} depends on the change in Gibbs Free Energy (ΔG) of the system according to Equation:

$$K_{eq} = \exp\left(\frac{\Delta G}{-RT}\right) \tag{6}$$

where R is the Universal Gas Constant and T is temperature in Kelvin (19). The solubility product changes with composition because the partial molar Gibbs Energy of the reactants changes with composition (19). Substituting Equation (1) into Equation (6) and solving for oxalate would indicate that oxalate solubility is dependent on temperature. A mixture model that predicts solubility as a function of composition is only valid at a single fitted temperature, unless temperature is introduced into Equations 2 through 5 (20).

The total Gibbs Energy (G) of the solution is the sum of the partial molar Gibbs energies (μ_i) of the components, including both reactants and products (19):

$$G = \sum m_i \mu_i \tag{7}$$

In Equation 7, m_i is the number of moles or mass in the system. Note that Equation 7 has the same form as Equation 2, as partial molar properties should, but has one difference. This difference is that the total quantity of each component is used rather than mole fraction because energy is an extensive variable that depends on the size of the system.

In traditional thermodynamic calculations, the partial molar Gibbs Energy, also called the chemical potential, is modeled as a function of composition by Equation 8:

$$\mu_i = \mu_i^\circ + RT \ln(X_i \lambda_i) \tag{8}$$

where $\mu_i{}^\circ$ is the Gibbs energy at the standard state and λ_i is the activity coefficient for the compound. The effects of mixing on the system are calculated through the activity coefficients in Equation 8.

The ΔG in Equation 6 is the change in total G from the chemical reaction. For solid-liquid equilibrium, the ΔG reflects both the change in the quantity of the solid, and also the energy content of the liquid as components are added or subtracted from the liquid phase. Given that the quantity of the liquid or the solid portion can be infinitely large, the total energy of the system depends on the size of the system. Therefore, the soluble concentration of a constituent cannot be directly modeled as a function of fraction of total system inventory, and a way to use mixture models to calculate soluble concentrations must be developed.

While the use of mixture models to predict soluble concentration as a function of composition through the activity coefficients has been normal, recent authors have started to directly model soluble concentrations with mixture models (9–10). Therefore, a method to use these models in conjunction with the inventories tracked by flowsheets is needed, and developed in the next section.

ALGORITHM FOR EMPLOYING MIXTURE MODELS TO CALCULATE SOLUBLE CONCENTRATION FROM TOTAL INVENTORIES

In this section a Cox mixture model will be developed that directly describes the soluble concentration of oxalate as a function of solution composition. A method to use this model to calculate soluble concentrations from total inventories will also be developed, where the total inventory is the quantity of the constituents in both solid and liquid phases. Total inventory rather than solution composition needs to be the input to the solubility algorithm because the solution concentration would already be known if the solution composition were known. Nonetheless, as will be shown below, a model that predicts solution oxalate concentration from solution mole fraction is needed as part of the algorithm to calculate solution concentration from total inventory.

A 1st and 2nd order Cox mixture model (Equations 4 and 5) was fit to the soluble oxalate concentration in equilibrium with solid sodium oxalate at 323.15 Kelvin (data from reference (13)), as a function of mole fraction of sodium oxalate, sodium nitrate, and water in the solution mixture. The initial full 2nd order model included all cross-product terms ($Na_2C_2O_4{}^*H_2O$, $Na_2C_2O_4{}^*NaNO_3$, $NaNO_3{}^*H_2O$). The reference state (B_o) for this regression was pure water (standard state of infinite dilution), which means that a_{H2O} must equal zero because the summations in Equations 4 and 5 can only equal zero at infinite dilution if $a_{H2O} = 0$. The model coefficients and associated regression statistics, determined by least-squares regression of the data, are shown in Table 1. The R^2 of both the 1st and full 2nd order fits to the data was 0.999, calculated per the method of Marquardt and Snee (24). All model components in the 1st order model had effects that were statistically different from zero ($p < 0.1$). Two model components in the 2nd order model were found to have p statistics >0.10, a_{NaNO3} and $a_{Na2C2O4,NaNO3}$. Therefore, a reduced 2nd order model was fit to the data, eliminating the $a_{Na2C2O4,NaNO3}$ model component. The a_{NaNO3} component became highly significant when that 2nd order term was removed (p value went from 0.322 to 0.004), and all other model components remained statistically significant. The results of the reduced 2nd order Cox mixture model are also shown in Table 1. These results indicate that there are two significant 2nd order interactions when modeling the oxalate molality (Table 1). Nonetheless, the large R^2 for the 1st order model (0.999) indicates that adding these two coefficients is effectively unnecessary. This conclusion is also supported by Fig. 2, which shows that both the first and second order models predict the experimental data of Kol'ba et al. (13) well. In fact, it is nearly impossible to distinguish the difference between the first and reduced second order mixture models in Fig. 2. Therefore, only the first order model will be used for the remainder of this paper.

Now with a model of oxalate solubility as a function of solution composition, an iterative method is developed to use this model for calculating oxalate solubility from the total inventory of all components.

Table 1. Coefficients and statistics for the fit of equations (4) and (5) to the oxalate solubility data from Kol'ba et al. (13)

	1st order cox model (equation (3))		Full 2nd order cox model (equation (4))		Reduced 2nd order cox model (reduced equation (4))	
Coefficient	Value	P statistic	Value	P statistic	Value	P statistic
B_o	0.002879	–	−0.00021	–	−0.00021	–
$a_{Na2C2O4}$	55.500544	4.93×10^{-40}	122.0278	6.04×10^{-11}	114.5988	8.06×10^{-25}
a_{NaNO3}	−0.0065127	2.54×10^{-07}	−0.00207	0.322	−0.00458	0.004
$b_{Na2C2O4,\ NaNO3}$	–	–	−5.88149	0.158	–	–
$b_{Na2C2O4,\ H2O}$	–	–	−66.5046	4.12×10^{-08}	−59.0299	2.59×010^{-21}
$b_{NaNO3,\ H2O}$	–	–	0.005197	0.069	0.008544	1.69×10^{-04}
R^2	0.999	–	0.999	–	0.999	–

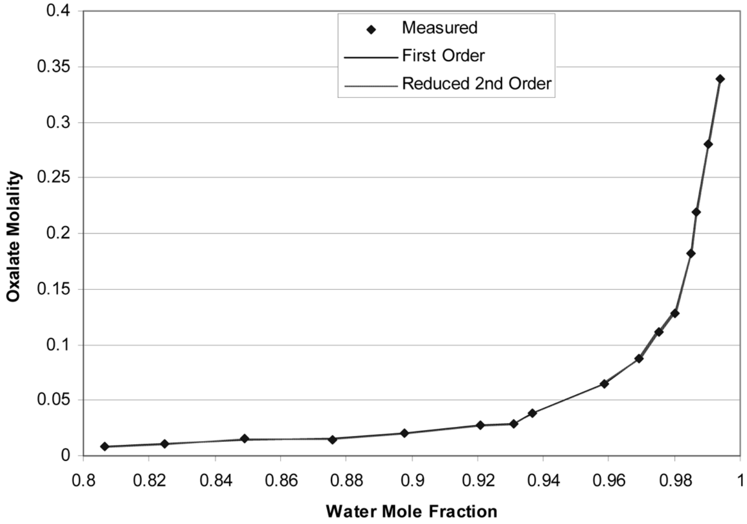


Figure 2. Comparison of measured oxalate molality (13) to that predicted by Equations (4) and (5) with coefficients from Table 1.

This total inventory includes both dissolved and precipitated sodium oxalate. The following steps were developed to achieve this goal:

1. Calculate the mole fraction of water, sodium oxalate, and sodium nitrate in the system inventory.
2. Choose a starting assumption for fraction of the sodium oxalate that is in the liquid phase. For this paper, the starting assumption was that all of the sodium oxalate was in the liquid phase, but this is not required.
3. From the fraction of sodium oxalate in the liquid phase derived from Step 2, calculate the mole fraction of water, sodium oxalate, and sodium nitrate in the liquid phase. When all of the oxalate in the system is dissolved, this mole fraction is the same as the mole fractions calculated in Step 1.
4. Calculate the soluble concentration of oxalate in molality units using the mole fractions of each constituent in the liquid phase from Step 3.
5. Calculate the dissolved concentration of oxalate in molality units using Equation (4) with the coefficients reported in Table 1 and the liquid phase mole fractions from Step 3.
6. Compare the oxalate concentrations calculated in Steps 4 and 5. If they are the same, then the assumed partitioning of oxalate between the solid and liquid phase is correct, or at least as correct as can be obtained using the model. If they are not the same, a new guess for

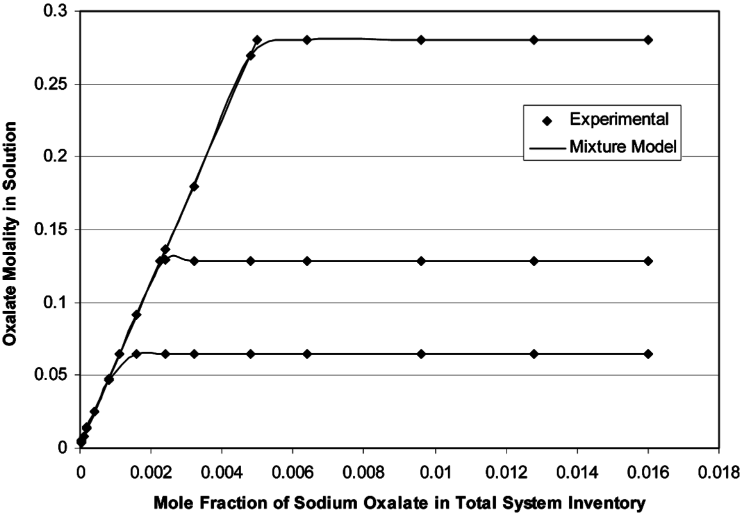


Figure 3. First order mixture model fit of the oxalate solubility calculated from measured solubility products at three representative $NaNO_3$:H_2O ratios.

the fraction of the oxalate in the liquid phase in Step 2 is taken and Steps 2 through 6 repeated until Steps 4 and 5 are identical. A suitable numerical method for optimizing the fraction of oxalate in the liquid phase (Step 2) can be used by minimizing the difference between the results calculated in Steps 4 and 5. In the present study, the Newton method was used within a Microsoft Excel® spreadsheet via the Solver® function.

Figure 3 compares the results of the prediction of oxalate concentration in the datasets presented in Fig. 1a with those calculated using Steps 1 through 6. As can be seen, the model was able to easily reproduce the experimental data. It should be pointed out that during development, the model was only directly fit the experimental data in Fig. 3 at the point where the line breaks on the graph (the saturation point), yet the model was able to predict all of the data points well. The results confirm that mixture models can be used to accurately predict solubility from total system inventory for simple systems, such as the $Na_2C_2O_4$-$NaNO_3$-H_2O system.

DISCUSSION AND LIMITATIONS

The present paper has shown that mixture models can be used to accurately predict the solubility of oxalate at a given temperature in a given matrix

($Na_2C_2O_4$-$NaNO_3$-H_2O). The author has found mixture models to be successful for other phases, temperatures, and systems to which it has been applied, as have others in the literature (9–11). The limitation of this mixture model for sodium oxalate solubility is that it is only applicable to this blend of components and at 323.15 K. In order to use the model for more complicated systems, such as nuclear wastes that have many electrolytes and a range of possible temperatures, more composition variables need to be included, and temperature needs to be included in Equations (4) and (5) (25). Choi et al. (10) have generated an example of a mixture model of sodium nitrate solubility in a many-component system.

In many instances, there is simply insufficient information to develop a mixture model that contains all of the components of interest in the system. In such cases, it might be possible to make assumptions, guided by chemical theory, about the effects of certain components. For instance, the present model might be extended to more complicated nuclear waste solutions by assuming that the effect of all monovalent strong electrolytes in waste (NaOH, $NaNO_2$, $NaAl(OH)_4$, ect.) have the same effect on oxalate solubility as sodium nitrate. In this case, the mole fractions of those components can be summed together with sodium nitrate and multiplied by the coefficients determined for sodium nitrate in Table 1. While the effect of these other monovalent electrolytes are known to be somewhat different than sodium nitrate (comparing the results in (13) to (26)), the difference might be small enough for model accuracy to be within the desired range. Debeye-Huckel theory of electrolyte solutions predicts only a small difference between monovalent ions on solubility, though the difference increases as the total solution ionic strength increases (8).

The challenges with inclusion of temperature and larger composition ranges can be avoided by using traditional thermodynamic models. These models use theory to predict the interactions of components on solubility (8). Traditional thermodynamic models have previously been successfully used to model sodium oxalate solubility in complex solutions, including nuclear waste (17,27–28). Thermodynamic models can be tested more rigorously than mixture models because they simultaneously reconcile a number of thermodynamic parameters, in addition to just solubility. These parameters include: temperature (13,29), density (30), heat of dissolution (31), measured activity coefficients (32) and stability of other reactions that involve the same components of interest (33).

The mixture models developed in the present paper have usage in three applications: The first is where only solubility in a given solution matrix is of interest, and no other thermodynamic parameters are desired or necessary. In these instances, mixture models have been especially useful when the end user does not have the skill or patience to learn and apply the more complicated traditional thermodynamic methods.

The second application for mixture models is for cases where traditional thermodynamic models are too computationally intensive for the given application. This is the case for a dynamic flowsheet used at the Hanford Waste Treatment Plant, which must calculate solubility in hundreds of vessels at six minute time intervals while simulating many years of operation. For this flowsheet, traditional thermodynamic models slowed the iterative solution of the mass balance down to unacceptable levels, so faster mixture models were employed. The third application is for matrices where there is simply too little thermodynamic data available to develop traditional thermodynamic models. An example of this is the prediction of crystallization of molten nuclear waste glass (5).

CONCLUSIONS

The present paper has demonstrated that mixture models can be used to predict solubility in aqueous solution from the total system inventory. This method is effective even when the desired composition crosses a solid: liquid phase boundary. The method is to fit a 1st or 2nd order mixture model to the soluble concentration of the analyte of interest as a function of solution composition. The fraction of the analyte in the inventory that reports to the liquid phase is then optimized iteratively until the concentration calculated by the mixture model and the K_{sp} (Equation (1)) are the same. The resulting fraction in the liquid phase corresponds to the concentration of the analyte at equilibrium.

An example of this method was applied to sodium oxalate solubility in aqueous sodium nitrate solutions. A Cox mixture model was fit to published solubility data, setting the reference state to the pure solvent to make it equivalent to the standard state used for electrolytes in aqueous solution. The regression results, shown in Table 1, indicate that there are two statistically significant second order terms. The effect of these 2nd order terms is small, however, as indicated by the small residuals (Fig. 2) and large R^2 values (Table 1) observed for the first order model fit of the data.

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