Thermodynamic Modeling of Electrolyte Precipitation from Aqueous Solutions

John C. Telotte
Department of Chemical Engineering
FAMU/FSU College of Engineering
Tallahassee, FL 32316

The ability to selectively precipitate one of several electrolytes from an aqueous solution by the addition of a miscible organic solvent is a problem of both theoretical and practical interest. The solubility of an electrolyte in simple organic solvents typically is orders of magnitude less than its aqueous solubility. By studying the solubility of an electrolyte in a mixed solvent, the nature of the influence the organic species has on the hydration of the electrolyte can be determined. This can be used as a tool to understand local composition effects in aqueous solutions. On the more practical side, the difference in solubility of similar electrolytes in mixed solvents can be used to design highly selective separation operations. The separation of KI and KIO_3 was demonstrated by Hull and Owens (1975), and the separation of KBr and $KBrO_3$ by Alfassi and Feldman (1976). Other systems have been studied, and consideration of overall design for these "solventing out" processes has been addressed by Alfassi (1985).

While a full understanding of the phenomena that determine this phase behavior is a long-term goal, some progress has been made in modeling the behavior of simple systems (Alfassi and Mosseri, 1984) of a single electrolyte in a binary solvent. A two-parameter expression does an adequate job of describing the amount of electrolyte that is precipitated from a saturated aqueous solution by the addition of a miscible organic solvent. This approach, however, is essentially just a curvefit of the experimental data and does little to offer any insight into the basic thermodynamics involved. Moreover, the range of applicability of Alfassi and Mosseri's expression is limited. This paper details a more fundamental scheme that can describe the single electrolyte solubility behavior both with greater accuracy and fewer parameters.

Theory

The general approach followed here is to develop a model for the "excess solubility" of the electrolyte in the solvent mixture. The excess solubility is defined as

$$\ln x_1^E = \ln x_{1,M} - \theta_2 \ln x_{1,2} - \theta_3 \ln x_{1,3} \tag{1}$$

Several points should be made about this excess solubility to clarify matters. First, the $x_{1,2}$ and $x_{1,3}$ terms are reference solubilities of the electrolyte in the two solvents. In many cases, these would be used simply as the solubilities in the pure solvents at the system temperature and pressure. There are, however, cases in which this is either impossible or undesirable. Such is the case for the problem of interest here. The θ_i are solute-free fractions that sum to one. The choice of weighting factor used (volume, surface area, etc.) is made to improve data correlation.

More importantly, this excess solubility is not an excess property in the classical thermodynamic sense (Van Ness and Abbott, 1982). The mathematical structure of this function is the same as typical excess functions, the excess solubility is zero at the reference compositions of each of the solvents. The value of this analysis is that we have a large body of knowledge available on useful forms for excess properties of binary mixtures. The technique used here essentially reduces the ternary problem to a pseudobinary one: i.e., the ternary mixture is considered as a mixture of the solute and the solvent. The solvent can have variable composition, but we account for much of the solvent composition effect on the solid solubility by having the reference solubility vary with composition.

We have found that for most problems involving the solubility of a solid in a mixed solvent that the optimal choice for the description of the solvent composition is the solute-free volume fraction (Ibeh, 1987; O'Callaghan, et al., 1988) and that tact will be followed here.

As with a normal excess function, the definition of the excess solubility requires the specification of the reference solubilities in the two solvents. In the situation addressed here, we find that the solubilities of the salts in the organic solvents are several orders of magnitude lower than the aqueous solubilities. In many cases, the solubility in the organic is a quantity that is either not known or difficult to measure. Further, the physical process required for the separation of the mixed salts would involve the addition of the organic solvent to the aqueous solution. The volume of organic solvent required for 99% recovery of a particular salt is typically four times the volume of the initial solution. Thus, if the salt is labeled as species 1, water as species 2, and the organic solvent as species 3, we are typically interested in situations where

$$x_3/(x_2 + x_3) < 0.8 \qquad (2)$$

So that there is no real need to attempt to describe the solubility behavior in solvent mixtures that are nearly pure species 3.

The above factors lead us to develop an alternative reference solubility for the salt in the organic solvent. We shall use the general expression.

$$\ln x_1^E = \ln x_{1,M} - \theta_2 \ln x_{1,2} - \theta_3 \ln S_3 \qquad (3)$$

where S_3 is the reference solubility that must now be specified. In developing a means to calculate S_3, it is only necessary to notice the similarity of the present situation and those that normally warrant the introduction of a Henry's-law-type reference state. Figure 1 shows the graphical technique that can be used to obtain S_3. Algebraically, this is simply

$$\ln S_3 = \ln x_{1,2} + \lim_{\theta_3 \to 0} (\partial \ln x_{1,M}/\partial \theta_3)_{T,P} \qquad (4)$$

The slope of the solubility curve required above will be given by the symbol Δ for future convenience. If Eqs. 3 and 4 are combined, the excess solubility is then given by

$$\ln x_1^E = \ln (x_{1,M}/x_{1,2}) - \theta_3 \Delta \qquad (5)$$

This form allows one to calculate the excess solubility from experimental data for correlation purposes. This equation would be solved for $x_{1,M}$, when a model has been developed for the excess solubility to predict the solubility behavior in a mixture.

The next task to address is the forms that can be used to model the excess solubility. One reason for invoking this entire procedure is that we should be able to use the functional forms of typical free-energy models to represent the excess solubility. However, when using a reference solubility like S_3, the models must be recast in unsymmetric form. In this work, we use a Redlich-Kister expansion for the excess solubility that has been properly normalized. This is simply

$$\ln x_1^E = t_2 \theta_3^2 + t_3 \theta_3^3 + \cdots \qquad (6)$$

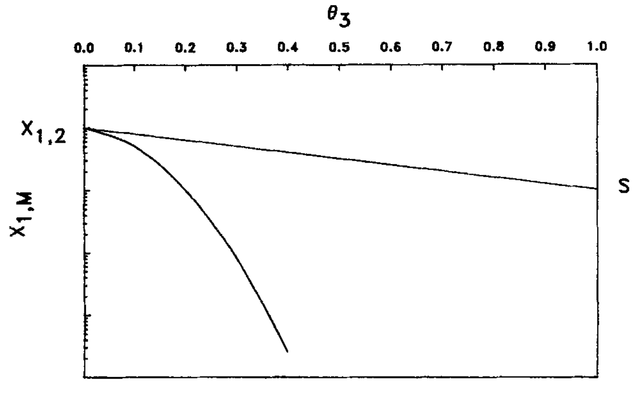

Figure 1. Definition of the Henry's-law-type reference solubility, S_3.

Combination of Eqs. 5 and 6 generates the form required to correlate experimental data that are presented as mole fraction solubilities.

$$\ln (x_{1,M}/x_{1,2}) = \theta_3 \Delta + t_2 \theta_3^2 + t_3 \theta_3^3 + \cdots \qquad (7)$$

For small values of θ_3, the excess function terms (t_2, t_3, etc.) may not even be required to correlate experimental data (O'Callaghan et al., 1988). This is the reason that the Henry's-constant-type reference state was chosen for component three.

The data of Alfassi and Mosseri (1984) are presented in terms of the fraction of the salt precipitated, f, upon addition of aliquots of the organic solvents. This fraction precipitated can be related to the mole fraction solubilities used in this work as

$$\ln (x_{1,M}/x_{1,2}) = \ln (1 - f) + \ln x_2 - \ln (1 - x_{1,2}) \qquad (8)$$

Combination of Eqs. 7 and 8 leads to the general result that could be used to correlate the experimental data in the situations of interest

$$\ln (1 - f) = \ln (1 - x_{1,2}) - \ln x_2 + \theta_3 \Delta + t_2 \theta_3^2 + t_3 \theta_3^3 + \cdots \qquad (9)$$

To make this result slightly simpler to use, x_2 is expressed in terms of the solute free volume fractions, and it is assumed that $x_3 \simeq 1 - x_2$ (in the cases of interest here, we have $x_2 + x_3 > 0.994$). The final result that will be used is then

$$\ln (1 - f) = \ln (1 - x_{1,2}) - \ln [\gamma \theta_2/(\gamma \theta_2 + \theta_3)] + \theta_3 \Delta + t_2 \theta_3^2 + t_3 \theta_3^3 + \cdots \qquad (10)$$

The first two terms on the righthand side of Eq. 11 require a knowledge of the salt solubility in pure water and the solvent composition. The third term is determined from solubilities in mixed solvents that are mainly water, and the other terms are added to improve the model performance as the amount of organic solvent is increased. In practice, we can correlate the data as presented by Alfassi and Mosseri (1984) without even a knowledge of $x_{1,2}$.

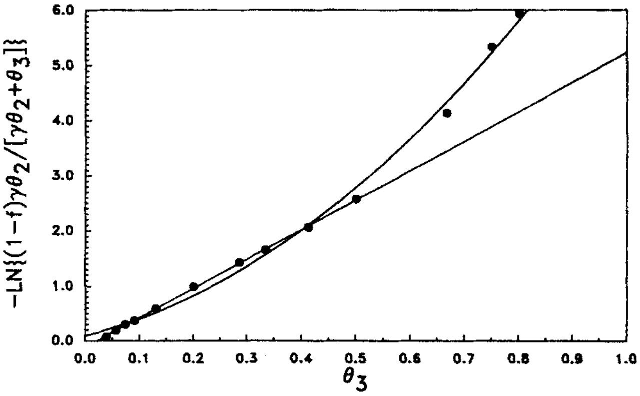

Figure 2. Potassium iodate precipitation data analyzed according to Eq. 10.

The straight line is calculated assuming all t_i terms are zero and the curve uses t_2 as nonzero. Data from Alfassi and Mosseri (1984).

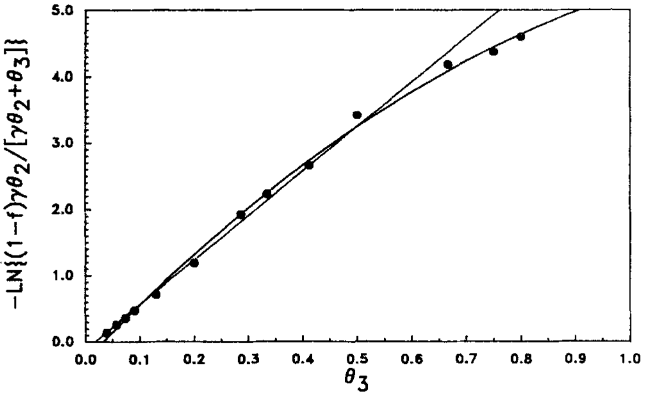

Figure 3. Potassium Sulfate precipitation data analyzed according to Eq. 10.

The straight line is calculated assuming all t_i terms are zero and the curve uses t_2 as nonzero. Data from Alfassi and Mosseri (1984).

Results

The application of Eq. 11 is shown in Figures 2 and 3. Figure 2 shows the data for KIO_3 in propylamine–water mixtures. Here, we have plotted $\ln(1-f) + \ln[\gamma\theta_2/(\gamma\theta_2 + \theta_3)]$ vs. θ_3. We see that, for $\theta_3 < 0.5$, the data fit well with a straight line. This corresponds to neglecting all of the t_i terms in Eq. 10. Thus, this is equivalent to an ideal solution model based on a Henry's-law reference for the solubility in propylamine. To extend the correlation to $\theta_3 = 0.8$ (where the fraction precipitated is 99%), we require the addition of the t_2 term, the curve on the figure. Not shown is the line fit to the data using both t_2 and t_3 terms. This gives quantative reproduction of the data over the entire solvent composition range.

The same type of analysis has been performed for K_2SO_4 in the propylamine–water solvent system. The results, shown in Figure 2, are similar to those for potassium iodate in this solvent mixture. Here, we find that the linear fit is excellent over an even broader solvent composition range.

We find that, by using only one adjustable parameter, Δ, we are able to correlate the precipitation data better than was done previously with two parameters (k and V_c of Alfassi and Mosseri) and that it is possible to correlate the data over any desired composition range by simple extension of our model. We have not presented our analysis of the rest of the data generated by Alfassi and Mosseri, but the results are similar. This is to be expected as the correlation constants reported by those investigators were nearly equal for all of the systems they studied.

Notation

f = fraction of solute precipitated
P = pressure
S_i = reference solubility in solvent i based on the solvent Henry's-law reference state
t_i = constant in excess solubility model
T = temperature
V_i = molar volume of species i
x_i = mole fraction of species i
$x_{i,M}$ = mole fraction solubility of species i in the mixture
$x_{i,j}$ = mole fraction solubility of species i in solvent j

Greek letters

$\gamma = V_2/V_3$, ratio of the solvent molar volumes
Δ = limiting value of the solubility curve
θ_i = solute-free volume fraction of solvent i

Superscript

E = "excess" property

Literature Cited

Alfassi, Z. B., "The Separation of Electrolytes by a 'Solventing-Out' Process," *AIChE J.*, **31,** 506 (Mar. 1985).

Alfassi, Z. B., and L. Feldman, "The Preparation of Carrier Free Radiobromide: The Separation of $KBrO_3$ and KBr Using an Organic Solvent," *Int. J. App. Radiation Isot.*, **27,** 125 (1976).

Alfassi, Z. B., and S. Mosseri, "Solventing Out of Electrolytes From Their Aqueous Solution," *AIChE J.*, **30,** 874 (Sept., 1984).

Hull, D. R., and C. W. Owens, "Separation of KI and KIO_3 Using 1,4 Dioxane," *Radiochem. Radioanal. Lett.*, **21,** 39 (1975).

Ibeh, C., "Solubility of Benzoic Acid Derivatives in Ethanol–Water Solutions," D.E. Thesis, Louisiana Tech Univ. (1987).

O'Callaghan, C., G. Bertrand, N. Book, J. Telotte, and O. Sitton, "The Solubility of Glucose in Aqueous Ethanol Solutions at Various Temperatures," *J. Chem. Engr. Data*, submitted (1988).

Van Ness, H. C., and M. M. Abbott, *Classical Thermodynamics of Non-electrolyte Solutions*, McGraw-Hill, New York (1982).

Manuscript received Sept. 12, 1988, and revision received June 14, 1989.