

## Predicting Water Activity for Complex Wastes with Solvation Cluster Equilibria (SCE) - 12042

S. F. Agnew\*, J. G. Reynolds\*\*, C. T. Johnston\*\*\*

\*Columbia Energy and Environmental Services, Inc., Richland, WA 99354

\*\*Washington River Protection Solutions, Richland, WA 99354

\*\*\*Purdue University, West Lafayette, IN, 47906

### ABSTRACT

Predicting an electrolyte mixture's water activity, i.e. the ratio of water vapor pressure over a solution with that of pure water, in principle reveals both boiling point and solubilities for that mixture. Better predictions of these properties helps support the ongoing missions to concentrate complex nuclear waste mixtures in order to conserve tank space and improved predictions of water activity will help.

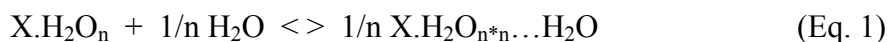
A new approach for predicting water activity, the solvation cluster equilibria (SCE) model, uses pure electrolyte water activities to predict water activity for a complex mixture of those electrolytes. An SCE function based on electrolyte hydration free energy and a standard Debye-Hückel (DH) charge compression fits each pure electrolyte's water activity with three parameters. Given these pure electrolyte water activities, the SCE predicts any mixture water activity over a large range of concentration with an additional parameter for each mixture vector, the multinarity. In contrast to ionic strength, which scales with concentration, multinarity is related to the relative proportion of electrolytes in a mixture and can either increase or decrease the water activity prediction over a broad range of concentration for that mixture.

### INTRODUCTION

Many-component electrolyte mixtures represent complex chemical systems with multiple ion-water and ion-ion interactions. Models that predict water activity (i.e. water vapor pressure) and electrolyte solubilities [1, 2] normally rely on very elaborate empirical fits to a measured solubility with a large number of parameters. As a result, there is often very little physical insight and such models do little more than interpolate measured solubilities.

The solvation cluster equilibria (SCE) approach incorporates a very physical basis with few parameters into its model. In spite of having few parameters, the SCE model appears to show predictive value for quite complex mixtures without the need for extensive sets of interaction parameters. In particular, the SCE shows that it can predict vapor pressure for boil-downs of complex mixtures of electrolytes.

The SCE describes solvation for an electrolyte X by means of a solvation cluster equilibrium with a fractional water as



with an equilibrium constant

$$K_h^n = [X.H_2O_{n+1}] / ((1-x_1)^n a_w) \quad (\text{Eq. 2})$$

$K_h$  is equilibrium constant for hydration eq 1  
 $x_1$  is the water mol fraction  
 $X.H_2O_n = (1-x_1)$  is the electrolyte mol fraction  
 $X.H_2O_{n^*n+1}$  is the mol fraction of water bound to  $n$  solvation clusters of  $n$  waters each  
 $n$  is the fractional hydration order for solvation cluster  $X.H_2O_n$   
 $a_w$  is the activity of water

Thus, each electrolyte is bound to  $n$  waters as a cluster and those clusters then bind whatever free water that is left over as in Fig. 1. With this approach, water activity is simply reduced from the water mol fraction  $x_1$  by the fraction of electrolyte clusters  $X.H_2O_{n^*n+1}$  as

$$a_w = x_1 (1 - X.H_2O_{n^*n+1}) \quad (\text{Eq. 3})$$

this sets the cluster water activity to

$$X.H_2O_{n^*n+1} = 1 - a_w / x_1 \quad (\text{Eq. 4})$$

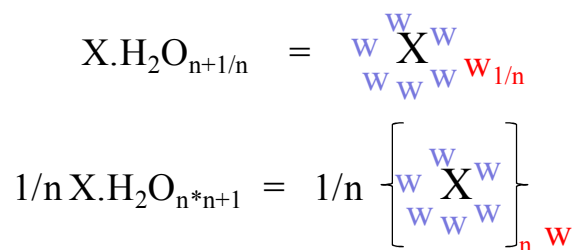


Fig. 1. Depictions of solvation cluster with either fractional weakly bound water to one cluster or as a water weakly bound to  $n$  ion clusters of  $n$  sites each.

This simple model lends itself to straightforward predictions of even complex mixtures of electrolytes.

## METHODOLOGY

Predicting water activity involves four fundamental solvation phenomena [3]:

- 1) Colligative, the dilution of species due to atomicity;  
 –ion association reduces atomicity;
- 2) Ion hydration, the bonding of water to ions (inner) and water to those inner waters;
- 3) Long range electrostatic charge compression, i.e. the Debye-Hückel factor;
- 4) A mixture of electrolytes has single multinary factor,  $Q_f$ , depending on proportion of ions and due to long-range coupling of electrostatic and ion hydration forces;

Colligative effects provide a basis for so-called ideal solution predictions and for pure electrolytes, colligative effects often dominate water activity reduction. Solutions whose water activity derives only from water mol fraction are termed ideal. Such ideal solution properties scale solely on atomicity or number of species, which is the sum of ions and neutrals. Dissolution

of electrolytes or any species in water decreases water activity by simple mol fraction or colligative effects.

Ion hydration involves both strong and weak binding of water. Inner ion hydration is usually due to strong binding between ion and water, i.e. binding that is significantly stronger than water binds to itself. Secondary or outer shell hydration is usually due to weak binding between ion inner and outer waters although some ions can have weak inner shell binding as well. Often outer hydration is termed an intermediate range force [2] since it acts at a distance from the parent ion. However, the SCE approach focuses on an average of all weakly bound waters associated with both inner and outer shell ion hydration. Weakly bound water is that water bound to ions with strength on the same order as water is bound to itself.

Long-range forces between unlike ions results in a compressive solvation force and such unlike-ion attraction or *Debye-Hückel* (DH) charge compression acts over a long range as in Fig. 2. The DH charge compression necessarily decreases ion free energy, increases electrolyte solubility, and therefore *increases* water activity. Like water from a sponge, DH compression impacts ion hydration indirectly by affecting solution free energy. As a result, DH charge compression does not depend on the nature of ion hydration, only on ion charges and separation.

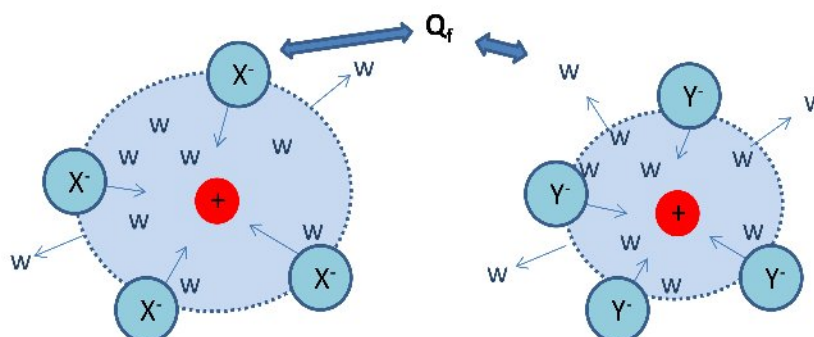


Fig. 2. Debye-Hückel charge compression *squeezes* water out of a solvation sphere thereby increasing water activity for a mixture. That water comes from those weakly bound in the electrolyte solvation sphere and therefore reduces the amount of bound water. However, the number and binding strength of sites does not change.

Each of the two system activity factors, DH charge compression and ion hydration, are averages for an entire electrolyte mixture. These two factors average differently but are both linked to the same water activity and its derivatives with composition. This different scaling of long range coupling of system variables results in a mixture correction,  $Q_f$ , termed mixture multinarity.

There is also short-range ion-ion interaction, i.e. ion association, which can also be important. For example, sodium phosphate is highly associated [4] showing an effective range of  $\nu$  (colligative factor or ion number) from 1.7 to 2.2 instead of 4.0 expected for complete dissociation. Sodium phosphate and other electrolyte associations do not appear to change significantly over the range of sodium in Hanford concentrates, 5.0 to 12.0 m. Therefore the SCE accounts for ion association by adjustment of  $\nu$  for the colligative effect but SCE does not scale  $\nu$  with composition.

Predicting water activity in Hanford electrolyte solutions needs to consider all these effects: colligative, electrolyte hydration, Debye-Hückel charge compression, and multinarity. Since

colligative and multinary effects account for much of ion-ion interaction, the SCE model does not include additional ion association parameters for these mixtures. This neglect is not always appropriate for all electrolyte mixtures but seems to work quite well here.

The SCE model regresses each pure electrolyte water activity to a function of three SCE parameters,  $K_i$ ,  $n_i$ , and  $v_i$ , and then each electrolyte mixture vector has a  $Q_f$ . The parameters  $K_i$  and  $n_i$  are the equilibrium constant and hydration order for weakly bound water,  $v_i$  is the electrolyte colligative factor (or ion number), and  $Q_f$  is the multinary for a given mixture vector.

$$a_w = \frac{1}{\frac{1}{x_1} + \prod K_i^{f_i n_i} (1-x_1)^n \gamma_{DH}^n} \quad (\text{Eq. 5})$$

$$a_w = \frac{1}{1 + \frac{\sum v_i m_i}{55.51} + \left( \frac{1}{1 + \frac{\sum v_i m_i}{55.51}} \right)^n \prod (K_i \gamma_{iDH})^{f_i n_i}} \quad (\text{Eq. 6})$$

$$\ln \gamma_{DH} = Q_f \sum f_i \frac{n_i}{n} \gamma_{iDH} = Q_f \sum f_i \frac{n_i}{n} \frac{z_{i+} z_{i-} A_\gamma}{(I_i m_i)^{1/2} + 1} \quad (\text{Eq. 7})$$

$m_i$  is the molality of electrolyte  $i$

$f_i = x_i / (1-x_1)$  is the mol electrolyte fraction of electrolyte  $i$

$\gamma_{DH}$  is defined by Eq. 7 as the effective DH factor

$A_\gamma = 1.1723$  at 25 C is the dimensionless Debye-Huckel constant

$z_{i+}$ ,  $z_{i-}$  are the formal ion charges for electrolyte  $i$

$I_i$  is the ionic strength factor for electrolyte  $i$ ,  $I_i = (z_{i+}^3 + z_{i-}^3) / (z_{i+} + z_{i-})$

$n = \sum f_i n_i$  is the average hydration order for an electrolyte mixture

Table I. SCE parameters for listed electrolytes. [ $\Delta g_h = -RT \ln(K_h)$ ,  $T = 298.15$  K]

Electrolyte	$K_h$	$n$	$v_{\text{eff}}$	$\Delta g_h$ kJ/mol	$\Delta G_{\text{sol}}^a$ kJ/mol
NaOH	7.53	6.14	2.46	-5.00	-39.6
NaAl(OH) <sub>4</sub>	5.78	6	2.00	-4.35	-33.2 <sup>b</sup>
Na <sub>2</sub> Al <sub>2</sub> O(OH) <sub>6</sub>	7.61	7.0	3.00	-5.03	-64.4 <sup>b</sup>
NaCl	7.49	4.21	2.00	-4.99	-9.07
Na <sub>2</sub> CO <sub>3</sub>	9.4	12.61	3.00	-5.56	-4.93
NaNO <sub>2</sub>	4.58	3.11	1.85	-3.77	-9.47
NaNO <sub>3</sub>	9.09	11.53	1.69	-5.47	-6.14
Na <sub>2</sub> SO <sub>4</sub>	5.17	6.05	1.90	-4.07	7.60
Na <sub>3</sub> PO <sub>4</sub>	9.75	6	1.70	-5.64	-15.7

<sup>a</sup> Literature values except as indicated.

<sup>b</sup> Estimated.

## RESULTS AND DISCUSSION

Figure 3 shows an SCE regression with measured [4] NaOH  $a_w$  along with the ratio of that prediction and measurement. Also shown are the SCE  $a_w$  upon setting  $\gamma_{DH} = 1$ , i.e., setting the DH free energy to zero, is the ion hydration equilibrium alone reduces water activity significantly. This shows the ion hydration balance with DH compressive force that results in the observed water activity for NaOH.

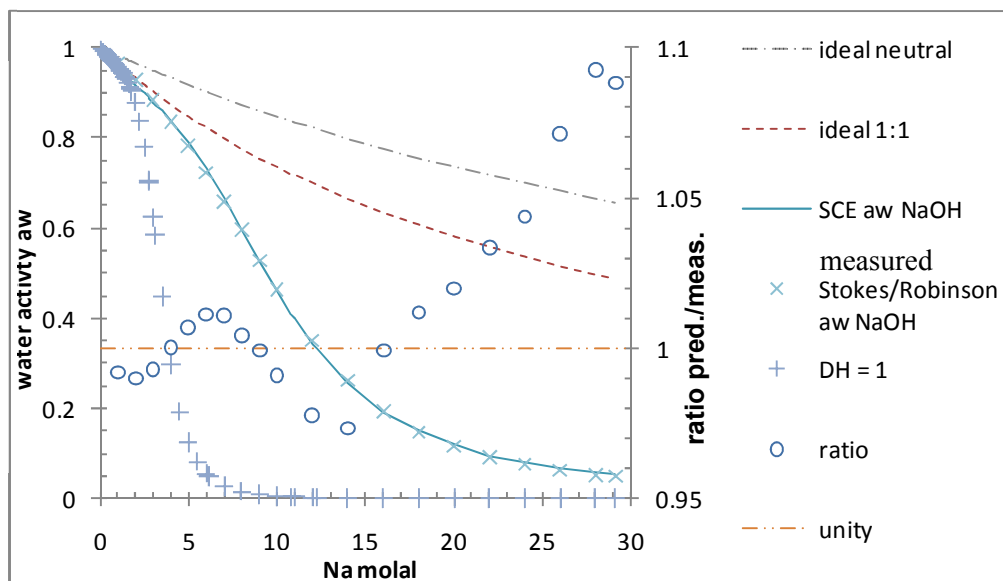


Fig. 3. Measured water activity ( $a_w$ ,  $\times$ ) versus regressed SCE  $a_w$  for NaOH, left scale, and the ratio pred./meas. (right scale,  $o$ ). Also shown are SCE  $a_w$  predictions for NaOH with  $\gamma_{DH} = 1$  ( $a_w$ ,  $+$ ), i.e., setting DH charge compression free energy to zero, and ideal  $a_w$  for neutral and 1:1 electrolyte.

Figure 4 shows the SCE fits for the electrolytes  $\text{NaNO}_3$  and Figs. 5-7 show combinations of electrolytes NaOH,  $\text{NaNO}_2$ , and  $\text{NaAl}(\text{OH})_4$ . The SCE function represents the water activity of these electrolytes over the ranges of their respective solubilities with just three parameters for each electrolyte shown in Table I. For the mixtures, a multinary provides a final adjustment for each mixture vector. Since the SCE model is physically based on reaction orders and free energies, even though each electrolyte has a limited solubility range, the SCE function still presents a reasonable albeit approximate  $a_w$  over a very wide molality range.

The multinarities vary between 0.5 and 1.5 and depend only on the relative amounts of electrolytes, not on their concentrations. Thus unlike ionic strength, which has a well-defined role in predicting electrolyte activity for mixtures, the multinary has an equally important alternate role in predicting water activity for electrolyte mixtures within the SCE. Accurate water activity predictions for a mixture necessarily mean accurate predictions of solution free energy

from the Gibbs-Duhem integration. Given a mixture free energy, the solubilities of each electrolyte then follow.

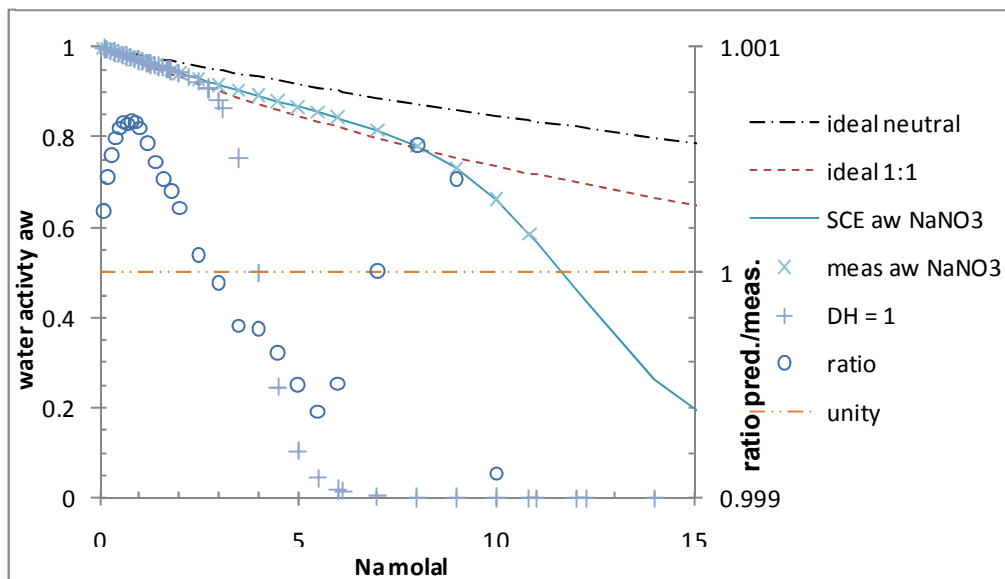


Fig. 4. The measured (x) versus SCE regressed water activities for NaNO<sub>3</sub> as function of molality, and the ratio pred./meas. (right scale, o). Note that the effective ion number differs from that of the fully dissociated 1:1 electrolyte. Also shown are SCE a<sub>w</sub> predictions for NaOH with  $\gamma_{DH} = 1$  (a<sub>w</sub>, +), i.e., setting DH charge compression free energy to zero, and ideal a<sub>w</sub> for neutral and 1:1 electrolyte.

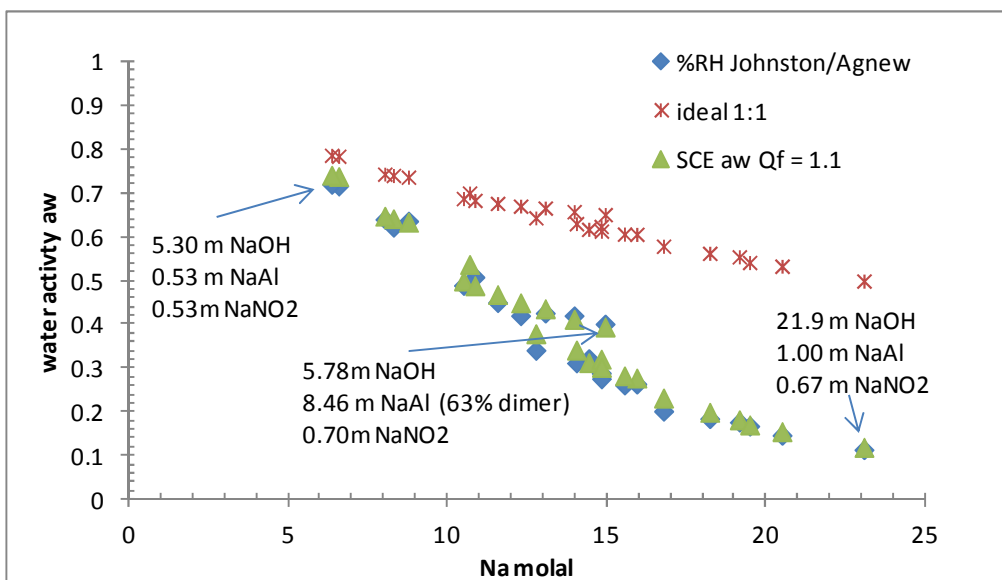


Fig. 5. Plot showing reported a<sub>w</sub> [4,5] and SCE a<sub>w</sub>. The SCE NaOH and NaNO<sub>2</sub> were those of pure electrolytes while aluminate monomer and dimer SCE parameters were regressed to this and other data.

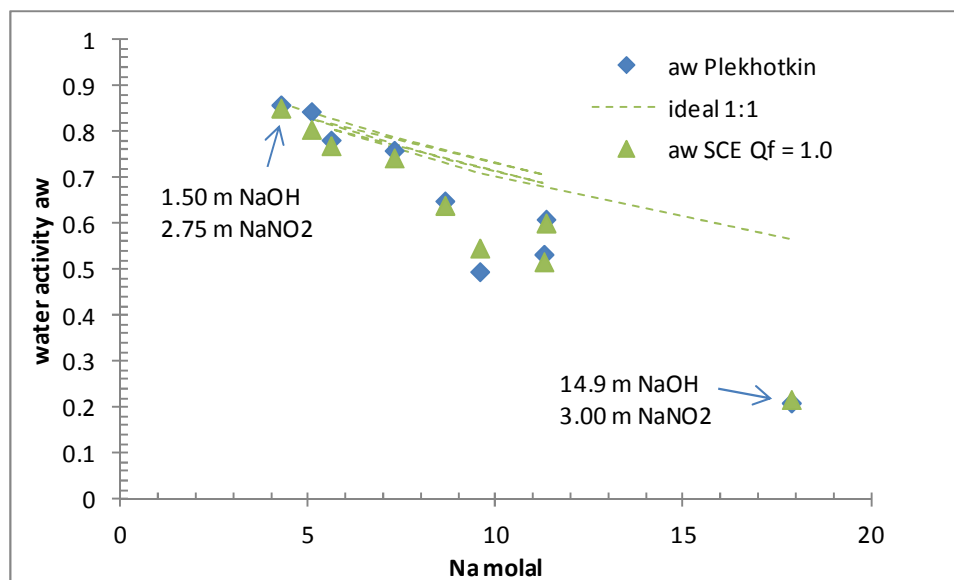


Fig. 6. Plot showing results of comparing reported  $a_w$  [6] versus SCE predictions for mixtures of NaOH and NaNO<sub>2</sub>. The SCE parameters were those for the pure electrolytes with multinary  $Q_f = 1.0$  for the mixture.

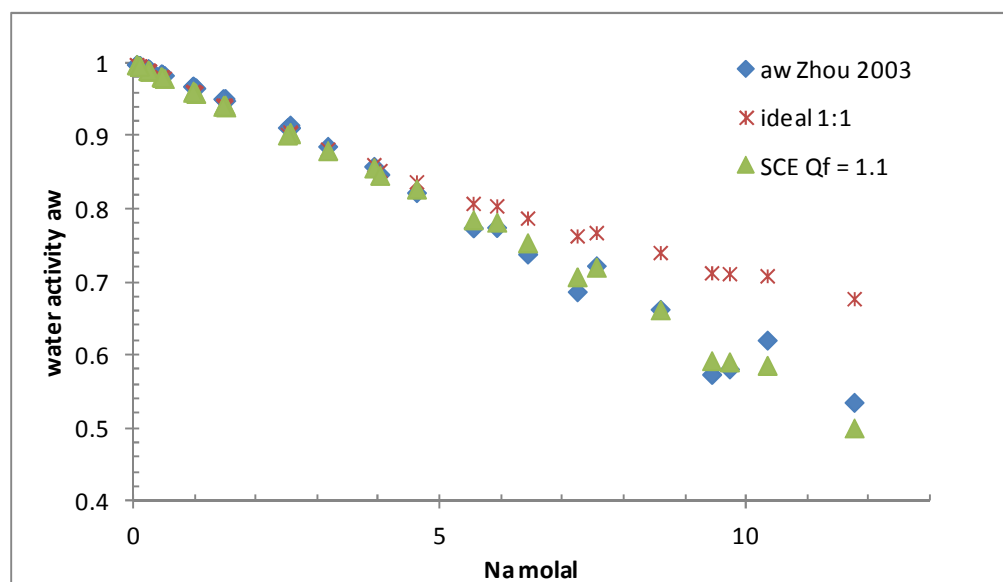


Fig. 7. Plot showing results of comparing reported  $a_w$  [7] versus SCE predictions for NaOH/NaAl(OH)<sub>4</sub> aluminate solutions over a wide range of molal Na. NaOH SCE was for pure NaOH while aluminate monomer and dimer parameters were those reported [5].

Finally Fig. 8 shows a boil-down curve for a very complex electrolyte mixture [8]. This evaporation resulted in solution concentration up to point A, precipitation of small amounts of solids from A to B, and large amounts of solids after point B. The region A to B corresponds to a multinary factor of 0.72 and represents concentration of the solution from 6.2 to 8.4 molal with relatively small amounts of solids. Despite the complexity of this solution, the SCE represents

the water activity in this range. After point B, large amounts of solids precipitate and the slurry water activity changes much more slowly.

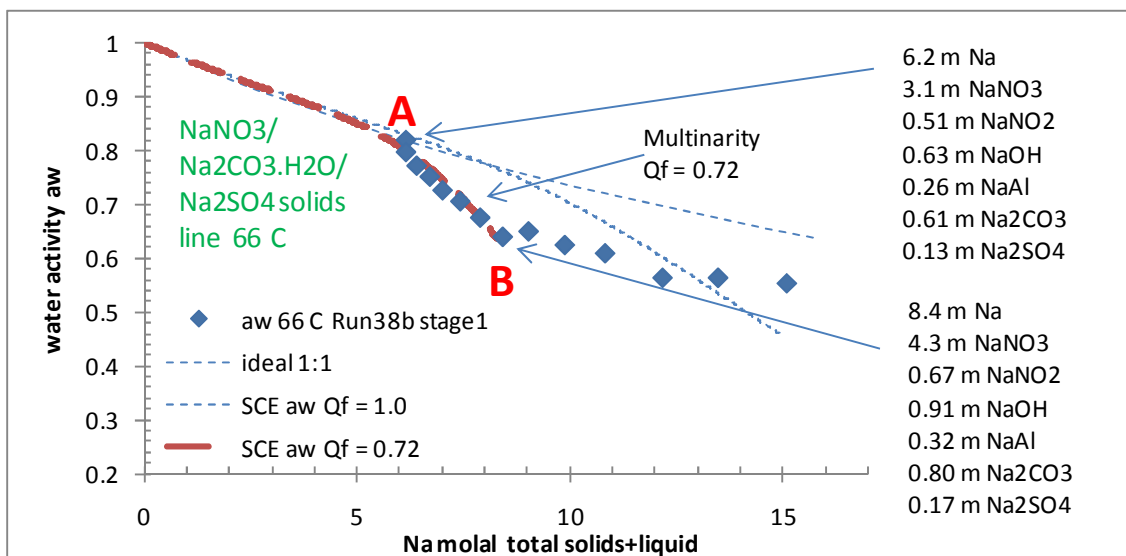


Fig. 8. Plot showing results of water activities for fractional crystallization of waste concentrates [8].

The term multinarity comes from the materials science of solid solutions and represents mixtures beyond ternary points, i.e. points or regions in a phase diagram where more than three phases coexist. A ternary point is invariant in a two dimensional phase diagram for an electrolyte solution where two solids are in equilibrium with that solution. Phase diagram points or regions where more than two solids coexist with solution are multinarity points and those multinarity points uniquely define a solution vector.

Concentration of a solution vector as in Fig. 8 eventually ends up at its multinarity point, A, where many solids coexist. In this paper each multinarity factor,  $Q_f$ , is simply adjusted to fit the water activity. However, there does appear to be systematic behavior in the  $Q_f$  among solutions and work is progressing to better predict multinarities from first principles.

## SUMMARY

The SCE model predicts water activity for complex electrolyte mixtures based on the water activities of pure electrolytes. Three parameter SCE functions fit the water activities of pure electrolytes and along with a single multinarity parameter for each mixture vector then predict the mixture water activity. Predictions of water activity can in principle predict solution electrolyte activity and this relationship will be explored in the future. Predicting electrolyte activities for complex mixtures provides a means of determining solubilities for each electrolyte.

Although there are a number of reports [9, 10, 11] of water activity models for pure and binary mixtures of electrolytes, none of them compare measured versus calculated water activity for more complex mixtures.



## REFERENCES

1. K. S. Pitzer, in *Activity Coefficients in Electrolyte Solutions*, 2nd. ed., edited by K. S. Pitzer (CRC Press, Boca Raton, FL, 1991).
2. P. Wang, A. Anderko, R.D. Young, R.D. Springer, *A Comprehensive Model for Calculating Phase Equilibria and Thermophysical Properties of Electrolytic Systems*, OLI Systems, Inc., 2008.
3. Glasstone, S., *Textbook of Physical Chemistry*, 2<sup>nd</sup> ed., D. Van Nostrand, New York, NY, 1946.
4. R. Carter, *Water Activity Data Assessment to be Used in Hanford Waste Solubility Calculations*, Hanford Technical Report RPP-RPT-47795, Rev. 2 (2011).
5. Johnston, C. T.; Agnew, S. F.; Schoonover, J. R.; Kenney, III, J. W.; Page, B.; Osborn, J.; Corbin, R., *Raman Study of Aluminum Speciation in Simulated Alkaline Nuclear Waste*, Environ. Sci. Technol., 36 (11), 2451-8, 2002.
6. Plekhotkin, V.F., L.P. Bobrovskaya, *The NaNO<sub>2</sub>-NaOH-H<sub>2</sub>O and NaNO<sub>3</sub>-NaOH-H<sub>2</sub>O Systems*, Zh. Neorgan. Khimii, 15, 1643-7, 1970. Russ. J. Inorg. Chem. 15, 842-4, 1970.
7. Zhou, J., Q.Y. Chen, J. Li, Z.L. Yin, X. Zhou, P.M. Zhang, *Isopiestic measurement for the osmotic and activity coefficients for the NaOH-NaAl(OH)<sub>4</sub>-H<sub>2</sub>O system at 313.2 K*, Geochim. Cosmochem. Acta, 67, 3459-72, 2003.
8. Herting, D.L., *Fractional Crystallization Flowsheet Tests with Actual Tank Waste*, Hanford Technical Report, RPP-RPT-31353, Rev. 1, 2007.
9. Kelly, J.T. et al., *Aerosol thermodynamics of potassium salts, double salts, and water content near the eutectic*, Atmos. Envir. 42, 3717-28, 2008.
10. Metzger, S. and J. Lelieveld, *Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into fog, haze, and clouds*, Atmos. Chem. Phys., 7, 3163-93, 2007.
11. E. Konigsberger, L-C. Konigsberger, G. Hefter, P.M. May, *Zdanovskii's Rule and Isopiestic Measurements Applied to Synthetic Bayer Liquors*, J. Soln. Chem., 36, 1619-34, 2007.

## ACKNOWLEDGEMENTS

We would like to thank Department of Energy Office Environmental Management, Technology Innovation and Development, Washington River Protection Solutions, and Columbia Energy and Environmental Services for support.