Thermodynamics of the Ternary Water-Salt Systems

Allakhverdov GR* and Zhdanovich OA
State Scientific-Research Institute of Chemical Reagents and High Purity Chemical Substances–National Research Centre, Kurchatov’s Institute, Russia

Abstract

The article present methods for calculation the thermodynamics characteristics of ternary water-salt solutions based on data for binary solutions of the components that form a mixed solution.

Keywords: Osmotic coefficient; Isopiestic solution; Activity of component

Introduction

The calculation of the characteristics of mixed solution based on the properties of binary solutions is one of the central problems of the theory of solutions. The McKay-Perring equation [1] shows that the calculation of the activity coefficient of the components of mixed electrolyte solutions can be carried out by comparing the experimental data for mixed solutions with the data for binary solutions under the condition of isopiestic equilibrium of all solutions. This condition opens a window for other methods for calculation the properties of mixed solutions based on data for binary solutions of the individual components of ternary system.

Theory

Suppose that two binary solutions of different electrolytes having the equal vapor pressure over a solution, when mixed, form a solution with the same vapor pressure. If in a mixed solution the concentration of one electrolyte \( x_1 \) and another \( x_2 \), then the following relation should hold

\[
\frac{dx_1}{dx_2} = \frac{C}{x_2}
\]

where \( C = \) constant, since the solvent activity remain unchanged.

Here \( x \) is the comparative concentration

\[
x = \frac{vn}{W}
\]

where \( v \) is the stoichiometric coefficient of the electrolyte, \( m \) is molality, \( W \) is the number of moles solvent per 1kg (for water \( W = 55.51 \)). The molar fraction of the components of the mixed solution can be defined as

\[
f_1 = \frac{x_1}{X_1}; f_2 = \frac{x_2}{X_2}
\]

where \( x_{1,2} \) and further determine \( C \) as

\[
c = \frac{f_1}{f_2} = \frac{\frac{C}{X_1}}{\frac{C}{X_2}} = \frac{X_2}{X_1}
\]

Separating variables and integrating Eq. (3), we obtain

\[
\frac{X_2}{X_1} = \int \frac{1+C}{f_1(f_1+C)-C} df_1
\]

Hence, we have

\[
\frac{dx_1}{dx_2} = \frac{x_1}{x_2}
\]

where \( X_1 \) and \( X_2 \) are the concentrations of isopiestic binary solutions. Integrating Eq. (5) taking into account the boundary conditions, we obtain [2]

\[
\frac{x_1}{x_1} + \frac{x_2}{x_2} = 1
\]
or, using Eq. (2)

\[
\frac{f_i}{x_i} + \frac{f_j}{x_j} = \frac{1}{x}
\]  

(7)

Eq. (6), using Eq. (1), can be represented as

\[
\frac{m_i}{m} = \frac{m_i}{m'}
\]  

(8)

where \(m_i\) is the molality of the components in mixed solution and \(m'\) is the molality of the components in binary isopiestic solutions. In this form Eq. (8) reflects the empirical rule by Zdanovsky [2], which shows a linear dependence of the inverse molality on the composition of the solution (Figure 1).

**Figure 1:** The composition of a mixed solution in the system NaCl-KCl-H2O at \(a_w=0.851\) (T=298K). The dotted line according to Eq. (8).

At constant pressure and temperature, the Gibbs-Duhem equation for a ternary water-salt system can be represented as

\[
v_i m_i \ln a_i + v_j m_j \ln a_j + W d \ln a_w = 0
\]  

(9)

where \(a_w\) is the solvent activity and \(a_i\) is the activity of the component in the mixed solution, for example,

\[
a_i = \gamma_i (a_1 + a_2 + a_3) \gamma_i
\]  

(10)

where \(\gamma_i\) is activity coefficient in ternary solution. Substitution Eq. (10) into (9) and using Eq. (1), we have

\[
v_i m_i \ln a_i + v_j m_j \ln a_j + d \ln a_w = 0
\]  

(11)

where \(a_1 = a_2 + a_3\). Combining Eq. (7) and (11) we obtain

\[
\left(\frac{a_1}{\gamma_i} \right) \frac{1}{a_1} \frac{\partial f_i}{a_1} = \frac{1}{x} \frac{\partial a_i}{x} + d \ln a_w = 0
\]  

(12)

On the other hand, for each binary solution it is possible to write

\[
\frac{d \ln a_i}{a_i} + \frac{1}{\gamma_i} \frac{\partial a_i}{\gamma_i} = 0
\]  

(13)

where \(a_i^*\) is the activity of the components in isopiestic binary solution. Combining Eq. (12) and (13) we obtain

\[
f_i \left(\frac{d \ln a_i}{a_i} - d \ln a_i^* \right) + f_j \left(\frac{d \ln a_j}{a_j} - d \ln a_j^* \right) = 0
\]  

(14)

The solution of Eq. (12) can be represented as

\[
a_i^* = f_i a_i
\]  

(15)

Revealing the activity of the components in the binary isopiestic solutions: \(a_i^* = x_i a_i^*\), Eq. (15) can be transformed to the form

\[
r_i = \gamma_i \frac{a_i^*}{a_i}
\]  

(16)

or, moving on to molality

\[
r_i = \gamma_i \frac{m_i}{\sum m_i}
\]  

(17)

where \(\gamma_i^*\) are activity coefficients in the binary isopiestic solution.

The McKay-Perring equation can be expressed in integral form as

\[
\ln \frac{a_i^*}{f a_i} = \frac{1}{X_i} - \frac{1}{X} - (1 - f_i) \left(\frac{\gamma_i}{\gamma_i^*} \right) d \ln a_i
\]  

(18)

Substitution here Eq. (7) turns the integral expression into zero and Eq. (18) turns into Eq. (15). Thus, Eq. (15) is an approximate solution to Eq. (18). A more rigorous solution can be obtained using equation

\[
\frac{1}{X} = \frac{f_1}{X_1} + \frac{f_2}{X_2} + b f f_2
\]  

(19)

where \(k\) is a constant coefficient. Then, according to [2], integrating Eq. (18) we have

\[
\frac{\ln \gamma_i}{\gamma_i} = \ln \frac{X_i}{X} + k \left(1 - f_i\right)^2 \ln \frac{X_i \gamma_i^*}{X_2 \gamma_2}
\]  

(20)

**Discussion**

Eq. (20) described very well the properties of ternary systems, but the coefficient \(k\) can only be determined experimentally. However, for most systems this coefficient is quite small, therefore, below we will consider the practical application of Eq. (7) and the associated Eq. (15-17), which allow us to calculate the activity of the components without involving experimental data for ternary systems. For two binary isopiestic solutions, the equality must be satisfied

\[
X_1 \phi(x_1) = X_2 \phi(x_2)
\]  

(21)

where \(\phi\) is the osmotic coefficient. If form of function \(\phi(x)\) is known, then for a given concentration of one of the solutions, the concentration of other solution can be calculated. Function \(\phi(x)\), according to [3], can be represented as

\[
\phi = 1 + \phi_a + \phi_b + \phi_h
\]  

(22)

where \(\phi_a, \phi_b, \phi_h\) are bound up with electrostatic interaction, association and hydration ions, respectively. Further, using the known ratio

\[
\ln \gamma = \phi - 1 + \frac{1}{\theta} (\phi - 1) d \ln x
\]  

(23)
the electrolyte activity coefficient can be defined as

$$\gamma = \gamma_e \gamma_a \gamma_h$$  \hspace{1cm} (24)

where $$\gamma_e, \gamma_a, \gamma_h$$ are corresponding constituents:

$$\ln \gamma_e = -\frac{1}{6} L Q_{0e} \sqrt{\frac{\rho}{\rho}} - \frac{L}{3\delta_e} \left(1 - \sqrt{\frac{\rho}{\rho}}\right)$$  \hspace{1cm} (25)

$$\ln \gamma_a = -\frac{2L}{1 + \delta_a \gamma_a} - \frac{4\xi_a}{\gamma_a} \ln \left(1 + \gamma_a\right)$$  \hspace{1cm} (26)

$$\ln \gamma_h = (h + 2h^2x) + \frac{1}{B}(h_0 - h^2x) - \frac{1}{2B}(h_0^2 - h^2)$$  \hspace{1cm} (27)

where the first term of each equation is corresponding to $$\varphi_i$$; Here $$r_0$$ is ionic radius, $$k_a$$ is ion association constant, $$h = h_0 \exp(-Bx)$$, where $$h_0$$ is hydration number in infinitely dilute solution and $$B$$ is the decrement, $$L = k_c \cdot 7.156 \times 10^{-8} \text{ cm}, \quad Q = k_c \cdot 7.135 \times 10^{-8} \text{ cm}^{-1}, \quad \text{where} \quad z_+ \quad \text{and} \quad z_- \quad \text{are the charges of ions}, \quad \xi = \frac{v_i}{v_i^*} 

If the mixed solution is in equilibrium with the solid phase of one of the components, then in this scope the activity of the component of the solution remain constant and equal to its activity in a binary saturated solution. For example, in system NaCl-KCl-H$_2$O (I-I valente electrolytes) we have

$$a_2 = \gamma_2^m \left( m_1 + m_2 \right) \gamma_2^0 m_2 \gamma_2^0$$  \hspace{1cm} (28)

where $$\gamma_2^0$$ and $$m_2^0$$ activity coefficient and molality, respectively, in saturated solution. On the other hand, comparing the mixed solution with binary isopiestic solutions of pure components and using Eq. (8), we obtain

$$m_1 = m_1^* - m_2 \frac{m_2^*}{m_2}$$  \hspace{1cm} (29)

where $$m_1^*$$ is an arbitrarily chosen concentration. Substituting Eq. (29) and (17) into Eq. (28), we can determine the concentration of the component in the mixed solution $$m_1$$ by the equation

$$m_1 \left[ 1 - \left( \frac{m_2^*}{m_2} \right) \left( \frac{\gamma_2^0 m_2^*}{\gamma_2^0 m_2} \right)^2 \right] = m_1 \left( \frac{\gamma_2^0 m_2^*}{\gamma_2^0 m_2} \right)^2$$  \hspace{1cm} (30)

when $$m_2^*$$ can be defined, using Eq. (21) and functions $$\varphi_i(x)$$ for binary solutions of components. Further, using Eq. (24)-(27), we can define $$\gamma_2^m$$. After that, we can determine $$m_1$$ according to Eq. (29). Similarly, calculation can be made when another component there is in the solid phase. Figure 2 shows the calculated and experimental data on the composition of saturated solutions in the ternary system. The component activity was calculated using Eq. (24-27); experimental data for osmotic coefficients in binary solutions were used as initial data to determine the parameters of equations [4]. These parameters were also using when the calculated concentrations were in the scope of oversaturated solutions, since the transition in this scope is not accompanied by a sudden change in the properties of the solution. Considering the ternary water-salt systems in another aspect, it is possible to evaluate the efficiency of the separation of inorganic substances during crystallization from solutions. For inorganic compounds that do not form solid solution, according Ref. [5], the co-crystallization coefficient can be defined as

$$D_2 = \frac{\gamma_2/m_2}{x_2} = a_2^*/a_2$$  \hspace{1cm} (31)

where $$y_i$$ is the molar fraction of the component in solid phase. In the limiting case when $$x_2 \rightarrow 0$$ also $$a_2^* \rightarrow a_2$$ and co-crystallization coefficient of impurity component can be expressed as

$$D_2 = \lim_{x_2 \rightarrow 0} \frac{x_2 y_2}{x_2} = a_2^* \frac{a_2^*}{a_2}$$  \hspace{1cm} (32)

Table 1: Cocrystallization coefficients in ternary systems at 298K.

<table>
<thead>
<tr>
<th>System</th>
<th>$D_2$ (calc.)</th>
<th>$D_2$ (meas.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO$_3$-KCl-H$_2$O</td>
<td>0.444</td>
<td>0.454</td>
</tr>
<tr>
<td>KNO$_2$-Mg(N0$_3$)$_2$-H$_2$O</td>
<td>0.032</td>
<td>0.035</td>
</tr>
<tr>
<td>KNO$_2$-Co(NO$_3$)$_2$-H$_2$O</td>
<td>0.028</td>
<td>0.030</td>
</tr>
<tr>
<td>KNO$_2$-Cu(NO$_3$)$_2$-H$_2$O</td>
<td>0.016</td>
<td>0.018</td>
</tr>
<tr>
<td>KNO$_2$-Al(NO$_3$)$_2$-H$_2$O</td>
<td>0.035</td>
<td>0.036</td>
</tr>
</tbody>
</table>
where $a_i = m_i \gamma_i$ is the activity of impurity component in its binary solution, which isopiestic to the saturated of the main component. Using Eq. (21) and functions $\phi(x)$ for binary solutions of components, we can define $m_i^*$ and further $\gamma_i^*$, using Eq. (24). The calculated and experimental data [6] of co-crystallization coefficient for some systems, where the main component is potassium nitrate, are given in Table 1.

### Conclusion

Thus, using the example of solubility and co-crystallization of components in ternary water-salt systems, the possibility of calculating the properties of ternary systems using properties of binary solution of individual components has been shown, which is of theoretical and practical interest for the technology of processing mineral raw materials.

### References