# Calculation of the activity coefficients of uni-uni-valent electrolytes without common ions in mixed solutions

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Correlations were derived for calculating the activity coefficients of solutes in a solution prepared by mixing two binary solutions of uni-uni-valent electrolytes without common ions.

The problem of calculating the activity coefficients of solutes in mixed solutions has attracted considerable attention.[1–5] For example, McKay and Perring suggested an equation for calculating the activity coefficients $\gamma_\mathrm{i}$ of solutes in a solution containing two uni-uni-valent electrolytes with a common ion or two nonelectrolytes.[1] The derivation of this equation and the equation that describes solutions containing an arbitrary number of electrolytes, generally speaking, of different valence types, with a common ion[2] are based on the possibility to change the concentration of a solute without changes in the concentrations of the other solutes. A solution obtained by mixing binary solutions of the uni-uni-valent electrolytes without common ions AM and BN, where A and B are cations and M and N are anions, is known to contain the four electrolytes AM, AN, BM and BN.[3,6] The concentration of any of them cannot be changed without changing the concentrations of the others. Thus, the conditions for the derivation of the McKay–Perring equation, as well as the equations from ref. 2 are not fulfilled. Previously, equations for the activity coefficients of solutes in a solution containing AM, AN, BM and BN were obtained for the case when the $x$ value, which is equal to the fraction of the cation A among the cations, can vary at any $y$ value, which is equal to the fraction of the anion M among the anions.[7] Seemingly, it is not difficult to go from the previously obtained equations[7] to the equations describing the test system, *i.e.*, a solution containing AM, AN, BM and BN on condition that the fraction of the cation A among the cations is equal to the fraction of the anion M among the anions accepting that $x = y$. However, equations for the activity coefficients of AM, AN, BM and BN in mixed solutions contain the derivatives

$$\left(\frac{\partial m^{-1}}{\partial x}\right)_{y,\mu_\mathrm{s}}\left(\frac{\partial m^{-1}}{\partial y}\right)_{x,\mu_\mathrm{s}},$$

where $m$ is the total molality, and $\mu_\mathrm{s}$ is the chemical potential of the solvent, which lose their meaning at $x = y$. According to refs. 1, 2 and 7, let us begin from the Gibbs–Duhem equation for a mixed solution

$$10^3 M_\mathrm{s}^{-1}\mathrm{d}\mu_\mathrm{s} + m_1\mathrm{d}\mu_1 + m_2\mathrm{d}\mu_2 + m_3\mathrm{d}\mu_3 + m_4\mathrm{d}\mu_4 = 0 \qquad (1)$$

where subscripts 1, 2, 3 and 4 correspond to the electrolytes AM, AN, BM and BN, respectively; $m_i$ and $\mu_i$ are the molality and the chemical potential of the $i$th component in the mixed solution, respectively. Now, let us consider the correlation for the chemical potentials of solutes[1]

$$\left(\frac{\partial \mu_i}{\partial m_j}\right)_{m_{k,k\neq j}} = \left(\frac{\partial \mu_j}{\partial m_i}\right)_{m_{l,l\neq i}}. \qquad (2)$$

To apply equation (2) to the test system, we should assume[7] at the initial stage of the derivation that the concentrations of all solutes can vary independently of one another. Next, taking into account relation (2), we have the system of four differential equations

$$\sum_{i=1}^{4} m_i\left(\frac{\partial \mu_j}{\partial m_i}\right)_{(3)} + \frac{10^3}{M_\mathrm{s}}\left(\frac{\partial \mu_s}{\partial m_j}\right)_{(3)} = 0 \quad (j = 1\text{–}4), \qquad (3)$$

where $M_\mathrm{s}$ is the molar mass of the solvent, and the subscripts in parentheses indicate the number of variables, which do not vary upon differentiation with respect to $m_j$; for example, $(\partial\mu_i/\partial m_1)_{(3)}$ means $(\partial\mu_i/\partial m_1)_{m_2,m_3,m_4}$. Taking into account the equations

$$m_1 = mx^2,\;\; m_2 = m_3 = mx(1 - x),\;\; m_4 = m(1 - x)^2, \qquad (4)$$

which follow from the exchange reaction AM + BN $\longleftrightarrow$ AN + + BM, one can see that the concentrations of the two solutes $m_3$ and $m_4$ depend on the concentrations of the other two solutes

$$m_3 = m_2,\;\; m_4 = m_2^2 m_1^{-1}. \qquad (5)$$

The derivatives of a function $f$ at constant values of one variable $(\partial f/\partial m)_{(1)}$ and three variables $(\partial f/\partial m)_{(3)}$ are related by the equation[8]

$$\left(\frac{\partial f}{\partial m_j}\right)_{(1)} = \left(\frac{\partial f}{\partial m_j}\right)_{(3)} + \left(\frac{\partial f}{\partial m_3}\right)_{(3)}\left(\frac{\partial m_3}{\partial m_j}\right)_{(1)} + \left(\frac{\partial f}{\partial m_4}\right)_{(3)}\left(\frac{\partial m_4}{\partial m_j}\right)_{(1)}. \qquad (6)$$

Inserting $\mu_i$ ($i$ = 1–4) and $\mu_\mathrm{s}$ instead of $f$, we transform the first two equations of system (3) to the form

$$\sum_{i=1}^{2} m_i\left[\left(\frac{\partial \mu_j}{\partial m_i}\right)_{(1)} - \sum_{k=3}^{4}\left(\frac{\partial \mu_j}{\partial m_k}\right)_{(3)}\left(\frac{\partial m_k}{\partial m_i}\right)_{(1)}\right] +$$

$$+ \frac{10^3}{M_\mathrm{s}}\left[\left(\frac{\partial \mu_\mathrm{s}}{\partial m_j}\right)_{(1)} - \sum_{l=3}^{4}\left(\frac{\partial \mu_\mathrm{s}}{\partial m_l}\right)_{(3)}\left(\frac{\partial m_l}{\partial m_i}\right)_{(1)}\right] = 0. \qquad (7)$$

According to relations (5), which connect the molalities of solutes, only two of them are independent. Thus, the derivatives $(\partial\mu_i/\partial m_j)_{(3)}$ included in relation (3) may be considered meaningless. However, textbooks in mathematics, for example, consider complex functions depending on several variables, which could be functions of a single variable $t$, for example $z = f(x,y)$, where $x = x(t)$, $y = y(t)$. Obviously, if $x$ varies, $t$ could not be constant. Thus, $y$ varies too. Fikhtengol'ts[8] took into account the derivatives $\partial f/\partial x$ and $\partial f/\partial y$. The second example belongs to chemical thermodynamics. If a component takes part in a chemical reaction, the number of its moles cannot be considered to be independent of the other components of the test system. Thus, the chemical potential of such a component cannot be determined, and the chemical affinity, which is equal to the difference between the chemical potentials of the reaction products and sums of the reactants cannot also be determined.

Taking into account correlations following from equation (5), we have

$$\left(\frac{\partial m_3}{\partial m_1}\right)_{(1)} = 0, \quad \left(\frac{\partial m_3}{\partial m_2}\right)_{(1)} = 1,$$

$$\left(\frac{\partial m_4}{\partial m_i}\right)_{m_j,\, j\neq i} = \mathrm{i}(-1)^i\left(\frac{m_2}{m_1}\right)^{3-i} \; (i = 1, 2). \qquad (8)$$

Equation (7) can be easily presented in the form

$$\sum_{i=1}^{2} m_i\left(\frac{\partial \mu_j}{\partial m_i}\right)_{(1)} = -\frac{10^3}{M_\mathrm{s}}\left[\left(\frac{\partial \mu_\mathrm{s}}{\partial m_j}\right)_{(1)} - \left(\frac{\partial \mu_\mathrm{s}}{\partial m_3}\right)_{(3)}\left(\frac{\partial m_3}{\partial m_j}\right)_{(1)} -\right.$$

$$\left. - \left(\frac{\partial \mu_\mathrm{s}}{\partial m_4}\right)_{(3)}\left(\frac{\partial m_4}{\partial m_j}\right)_{(1)}\right] \quad (j = 1, 2). \qquad (9)$$

Transforming the left members of the third and fourth equations of system (3) according to equation (9) and taking into account the equation

$$\mu_1 + \mu_4 = \mu_2 + \mu_3, \qquad (10)$$

system of equations (9) can be presented in the form

$$\sum_{i=1}^{2} m_i\left(\frac{\partial\mu_1}{\partial m_i}\right)_{(1)} = -\frac{10^3}{M_\mathrm{s}}\left(\frac{\partial\mu_\mathrm{s}}{\partial m_1}\right)_{(1)} + \frac{m_2^2}{m_1^2}\sum_{j=1}^{2} m_j\left(\frac{\partial\mu_4}{\partial m_j}\right)_{(1)}; \qquad (11)$$

$$\sum_{i=1}^{2} m_i\left(\frac{\partial\mu_2}{\partial m_i}\right)_{(1)} = -\frac{10^3}{M_\mathrm{s}}\left(\frac{\partial\mu_\mathrm{s}}{\partial m_2}\right)_{(1)} - $$

$$-\sum_{k=1}^{2} m_k\left(\frac{\partial\mu_3}{\partial m_k}\right)_{(1)} - \frac{2m_2}{m_1}\sum_{j=1}^{2} m_j\left(\frac{\partial\mu_4}{\partial m_j}\right)_{(1)}. \qquad (12)$$

Using equation (10) we have

$$\sum_{i=1}^{2} m_i\left(\frac{\partial\mu_1}{\partial m_i}\right)_{(1)} - \frac{m_2^2}{m_1^2}\sum_{l=1}^{2} m_l\left(\frac{\partial\mu_4}{\partial m_l}\right)_{(1)} = -\frac{10^3}{M_\mathrm{s}}\left(\frac{\partial\mu_\mathrm{s}}{\partial m_1}\right)_{m_2}; \qquad (13)$$

$$\sum_{i=1}^{2} m_i\left(\frac{\partial\mu_1}{\partial m_i}\right)_{(1)} + \left(1 + \frac{2m_2}{m_1}\right)\sum_{k=1}^{2} m_k\left(\frac{\partial\mu_4}{\partial m_k}\right)_{(1)} = -\frac{10^3}{M_\mathrm{s}}\left(\frac{\partial\mu_\mathrm{s}}{\partial m_2}\right)_{m_1}. \qquad (14)$$

According to ref. 3, let us go from the variables $m_1$ and $m_2$ to the variables $x$ and $\mu_\mathrm{s}$. Considering the correlations for the differentials d$m_1$, d$m_2$

$$\mathrm{d}m_t = \left(\frac{\partial m_t}{\partial x}\right)_{\mu_\mathrm{s}}\mathrm{d}x + \left(\frac{\partial m_t}{\partial \mu_\mathrm{s}}\right)_x\mathrm{d}\mu_\mathrm{s} \quad (t = 1, 2) \qquad (15)$$

as a system of linear equations with respect to d$x$ and d$\mu_\mathrm{s}$ and taking into account equations (4), one can find the solution

$$\mathrm{d}x = \frac{1-x}{x}\frac{\mathrm{d}m_1}{m} - \frac{\mathrm{d}m_2}{m}; \qquad (16)$$

$$\mathrm{d}\mu_\mathrm{s} = \left\{-\left[\frac{1-2x}{x} + \frac{1-x}{mx}\left(\frac{\partial m}{\partial x}\right)_{\mu_\mathrm{s}}\right]\mathrm{d}m_1 + \right.$$

$$\left. + \left[\frac{2}{x} + \frac{1}{m}\left(\frac{\partial m}{\partial x}\right)_{\mu_\mathrm{s}}\right]\mathrm{d}m_2\right\}\left(\frac{\partial m}{\partial \mu_\mathrm{s}}\right)_x^{-1}. \qquad (17)$$

Taking into account the equations, which follow from relations (16) and (17),

$$\left(\frac{\partial\mu_k}{\partial m_1}\right)_{m_2} = \left(\frac{\partial\,\mu_k}{\partial x}\right)_{\mu_\mathrm{s}}\frac{1-x}{mx} - $$

$$-\left(\frac{\partial\mu_k}{\partial\mu_\mathrm{s}}\right)_x\left[\frac{1-2x}{x^2} + \frac{1-x}{mx}\left(\frac{\partial m}{\partial x}\right)_{\mu_\mathrm{s}}\right]\left(\frac{\partial m}{\partial\mu_\mathrm{s}}\right)_x^{-1}; \qquad (18)$$

$$\left(\frac{\partial\mu_k}{\partial m_2}\right)_{m_1} = -\left(\frac{\partial\mu_k}{\partial x}\right)_{\mu_\mathrm{s}}\frac{1}{m} + \left[\frac{2}{x} + \frac{1}{m}\left(\frac{\partial m}{\partial x}\right)_{\mu_\mathrm{s}}\right]\left(\frac{\partial\mu_k}{\partial\mu_\mathrm{s}}\right)_x\left(\frac{\partial m}{\partial\mu_\mathrm{s}}\right)_x^{-1}, \qquad (19)$$

let us transform the system of equations (13) and (14) to the form

$$m\left(\frac{\partial\mu_1}{\partial\mu_\mathrm{s}}\right)_x - \frac{(1-x)^2 m}{x^2}\left(\frac{\partial\mu_4}{\partial\mu_\mathrm{s}}\right)_x = \frac{10^3}{M_\mathrm{s}}\left[\frac{1-2x}{x^2} + \frac{1-x}{mx}\left(\frac{\partial m}{\partial x}\right)_{\mu_\mathrm{s}}\right]; \qquad (20)$$

$$m\left(\frac{\partial\mu_1}{\partial\mu_\mathrm{s}}\right)_x + \left[1 + \frac{2(1-x)}{x}\right]m\left(\frac{\partial\mu_4}{\partial\mu_\mathrm{s}}\right)_x = -\frac{10^3}{M_\mathrm{s}}\left[\frac{2}{x} + \frac{1}{m}\left(\frac{\partial m}{\partial x}\right)_{\mu_\mathrm{s}}\right]. \qquad (21)$$

Let us solve system of equations (20) and (21)

$$\left(\frac{\partial\mu_i}{\partial\mu_\mathrm{s}}\right)_x = -\frac{10^3}{M_\mathrm{s}}\left[\frac{1}{m} + Q_i\left(\frac{\partial m^{-1}}{\partial x}\right)_{\mu_\mathrm{s}}\right], \qquad (22)$$

where $Q_1 = 1 - x$, $Q_4 = -x$.

Considering the Gibbs–Duhem equation for a binary solution of the *i*th electrolyte, whose molality is $m_i^*$ and the chemical potential $\mu_i^*$ corresponds to the $\mu_\mathrm{s}$ value of the mixed solution, we have

$$\left[\frac{\partial(\mu_i - \mu_i^*)}{\partial\mu_\mathrm{s}}\right]_x = -\frac{10^3}{M_\mathrm{s}}\left[\frac{1}{m} - \frac{1}{m_i^*} + Q_i\left(\frac{\partial m^{-1}}{\partial x}\right)_{\mu_\mathrm{s}}\right] \quad (i = 1, 4). \qquad (23)$$

Each of equations (23) contains only the partial derivative $[\partial(\mu_i - \mu_i^*)/\partial\mu_\mathrm{s}]_x$, when this derivative is calculated, the variable $x$ is considered as constant. Each of equations (23) can be considered as a usual differential equation with the desired function $\mu_i - \mu_i^*$ and independent variable $\mu_\mathrm{s}$. These differential equations contain $x$ as a parameter. Then the solution of each of the above equations contains an arbitrary function of $x$. Following the transformations[3,7] it is easy to show that this function is equal to zero. Equation (23) takes the form

$$\ln\frac{m\gamma_i}{m_i^*\gamma_i^*} = -\frac{10^3}{2M_\mathrm{s}}\int_0^{\ln a_\mathrm{s}}\left[\frac{1}{m} - \frac{1}{m_i^*} + Q_i\left(\frac{\partial m^{-1}}{\partial x}\right)_{a_\mathrm{s}}\right]\mathrm{d}\ln a_\mathrm{s} \quad (i = 1, 4). \qquad (24)$$

where $\gamma_i^*$ is the activity coefficient of the *i*th electrolyte in the isopiestic binary solution. Equations (24) have the same form as the McKay–Perring equations;[1] however, unlike the latter, the $x$ value, generally speaking, is not equal to the molar fraction of a solute in the mixed solution. The $x$ value gains this meaning for the test system if it is assumed that AN and BM are absent from the mixed solution.

The results can be treated using the McKay–Perring equation for a solution of two electrolytes with a common ion and for a solution obtained by mixing two electrolyte solutions without a common ion. The quantity $x$ in the former case is the mole fraction of an electrolyte and in the latter, the mole fraction of the cation A among the cations, which is equal to the mole fraction of the anion B among the anions.

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