



Equation for solvent activity correlation in ternary solutions with electrolyte and molecular components



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ABSTRACT

An analytical thermodynamically self-consistent equation is proposed for the dependence on composition of the solvent activity of ternary solutions with electrolytic and molecular components (polyols, sugars, etc.). This equation was derived on the basis of the sum of contributions from short and long range interactions to the excess Gibbs free energy of solution. The correlation of experimental data corresponding to 20 aqueous ternary systems was successfully carried out. The results obtained demonstrate an excellent fitting capability of the proposed equation.

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1. Introduction

Thermodynamics of solution is characterized by its ability to describe the mixing effects through the use of partial molar properties. For example, the chemical potential of a given component in solution is evaluated from the partial molar excess Gibbs free energy ($RT \ln \gamma_i$), which dependence on composition can be described by one of the many correlation equations available. The parameters of such equations are calculated starting from the correlation of the experimental dependence of the excess Gibbs free energy on composition.

A different situation arises when only one component, the solvent (1), is volatile, while the solutes (2, 3) can be considered non volatile (electrolytes, polysaccharides, amino acids, etc.). In these cases, the activity of the solvent can be evaluated directly from the corresponding solution vapor pressure and thus the experimental dependence of the solvent activity on composition $a_1(m_2, m_3)$ is obtained. To describe these systems, binary or ternary, it is usual to employ polynomial expressions [1–11], which are used independently of the nature of the solution. The problem is that the first terms of the polynomial are strongly dependent on the nature of the system and consequently, in most cases these expressions are not thermodynamically consistent, as they do not satisfy the limiting behavior required by the thermodynamics of solutions. Therefore, the subsequent use of the equation $a_1(m_2, m_3)$

for the evaluation of other thermodynamic properties (activity coefficients of the solutes, etc.) will lead to erroneous results.

In this context and due to the lack of reliable analytical expressions to describe the dependence $a_1(m_2, m_3)$, the aim of the present work is to develop a thermodynamically consistent simple multiparametric equation that can represent the experimental dependence of the solvent activity on composition with high accuracy for ternary solutions constituted by one electrolytic compound and one molecular compound in the whole range of composition. Moreover, the resulting expression will be suitable for the application of the McKay-Perrin [12,13], Canagaratna [14] or de Pablo [15] methods for the calculation of the activity coefficients of the other components of the solution, as well as for any other calculations of thermodynamic properties.

2. Theoretical considerations

2.1. Multiparametric equation

It is considered a ternary solution constituted by a solvent (1) an electrolyte (2) and a molecular component (3). The electrolyte its characterized by the formula unit $A_{\nu_A}C_{\nu_C}$,

$$A_{\nu_A}C_{\nu_C} \rightarrow \nu_A A^{Z_A} + \nu_C C^{Z_C} \quad (1)$$

Being ν_A (ν_C) the stoichiometric coefficient of the anion (cation) corresponding to the dissociation of the electrolyte (2). The molality (m_i) is the concentration used for both components, however in order to develop the multiparametric equation of the solvent activity $a_1(m_2, m_3)$, the independent variables $z = m_2^{1/2}$ and

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m_3 are adopted. The first one is chosen in order to make compatible the behavior of the solution at infinite dilution ($m_i \rightarrow 0$) with the way in which the correlation equation is set. In this context, the dependence $a_1(z, m_3)$ can be described by a McLaurin series expansion as follows,

$$a_1(z, m_3) = 1 + A_{11}z + A_{12}m_3 + A_{21}z^2 + A_{22}zm_3 + A_{23}m_3^2 + A_{31}z^3 + A_{32}z^2m_3 + A_{33}zm_3^2 + A_{34}m_3^3 + A_{41}z^4 + A_{42}z^3m_3 + A_{43}z^2m_3^2 + A_{44}zm_3^3 + A_{45}m_3^4 + A_{51}z^5 + \dots \tag{2}$$

This expression contains 15 coefficients, being many of them determined by the limiting behavior of this type of solutions, which is developed in the following item.

2.2. Analytical description of the behavior of dilute solutions

The coefficients A_{ij} of the expression $a_1(z, m_3)$ given by Eq. (2) must be consistent with the constrains imposed by the Thermodynamics of solutions. In order to ensure this consistency, a condition of third order contact with the limiting behavior is applied to the proposed expression. Consequently, an exact dependence of $a_1(z, m_3)$ for diluted solutions is required. This can be obtained from the integration of the Gibbs–Dühem equation on terms of activity coefficients. The equation at constant temperature and neglecting the effect of pressure change with composition can be written as,

$$n_1^0 d\ln\gamma_1 + \nu m_2 d\ln\gamma_{\pm}^0 + m_3 d\ln\gamma_3^0 = 0 \tag{3}$$

The corresponding reference states for the activity coefficients are perfect solution for the solvent (γ_1) and ideal dilute solution for components 2 (γ_{\pm}^0) and 3 (γ_3^0). From the integration of Eq. (3) along constant $x_3^0 = m_3/(\nu m_2 + m_3)$, the following expression for the logarithm of the activity coefficient of solvent is obtained (see derivation in Appendix),

$$\ln\gamma_1 = \frac{A^{\nu}}{3\sqrt{2}n_1^0}(\nu_A z_A^2 + \nu_C z_C^2)^{3/2} m_2^{3/2} + \frac{Bm_3^2 + 0.5(B - C)\nu m_2 m_3}{(n_1^0 + \nu m_2 + m_3)^2} \tag{4}$$

Thus, the solvent activity of dilute solutions constituted by an electrolyte and a molecular solute can be described,

$$\ln a_1 = \ln\left(\frac{n_1^0}{n_1^0 + \nu m_2 + m_3}\right) + \frac{A^{\nu}}{3\sqrt{2}n_1^0}(\nu_A z_A^2 + \nu_C z_C^2)^{3/2} m_2^{3/2} + \frac{Bm_3^2 + 0.5(B - C)\nu m_2 m_3}{(n_1^0 + \nu m_2 + m_3)^2} \tag{5}$$

where the first term on the right is the logarithm of the solvent molar fraction. Eq. (5) describes the asymptotic behavior that must follow $a_1(m_2, m_3)$.

Coefficients A_{ij} can be related to the limiting experimental behavior starting from Eq. (5). Differentiating Eq. (5) with respect to z ,

$$\left(\frac{1}{a_1} \frac{\partial a_1}{\partial z}\right) = -\frac{2\nu_2 z}{(n_1^0 + \nu_2 z^2 + m_3)} + 4A^{\nu} \nu_2 z n_1^0 \frac{(\nu_2 z^2 + m_3)}{(n_1^0 + \nu_2 z^2 + m_3)^3} \tag{7}$$

and taking the limit for the solvent molar fraction $x_1 \rightarrow 1$, the coefficient A_{11} is evaluated,

$$A_{11} = \left(\lim_{x_1 \rightarrow 1} \frac{\partial a_1}{\partial z}\right) = 0 \tag{8}$$

Then the differentiation with respect to m_3 ,

$$\left(\frac{1}{a_1} \frac{\partial a_1}{\partial m}\right) = -\frac{1}{(n_1^0 + \nu_2 z^2 + m_3)} + 2A^{\nu} n_1^0 \frac{(\nu_2 z^2 + m_3)}{(n_1^0 + \nu_2 z^2 + m_3)^3} \tag{11}$$

leads to coefficient A_{12} ,

$$A_{12} = \left(\lim_{x_1 \rightarrow 1} \frac{\partial a_1}{\partial m_3}\right) = -\frac{1}{n_1^0} \tag{12}$$

Applying the same procedure with the derivatives of higher order of Eq. (5) and taking into account the relationship between the derivatives of $\ln a_1$ and those of a_1 , it can be demonstrated the following identities,

$$A_{21} = \left(\frac{1}{2} \lim_{x_1 \rightarrow 1} \frac{\partial^2 a_1}{\partial z^2}\right) = -\frac{\nu}{n_1^0} \tag{13}$$

$$A_{22} = \left(\lim_{x_1 \rightarrow 1} \frac{\partial^2 a_1}{\partial m_3 \partial z}\right) = 0 \tag{14}$$

$$A_{23} = \left(\frac{1}{2} \lim_{x_1 \rightarrow 1} \frac{\partial^2 a_1}{\partial m_3^2}\right) = \frac{(1 + 2B)}{2n_1^0 2} \tag{15}$$

$$A_{31} = \left(\frac{1}{6} \lim_{x_1 \rightarrow 1} \frac{\partial^3 a_1}{\partial z^3}\right) = \frac{A^{\nu}}{3\sqrt{2}n_1^0}(\nu_A z_A^2 + \nu_C z_C^2)^{3/2} \tag{16}$$

$$A_{32} = \left(\frac{1}{2} \lim_{x_1 \rightarrow 1} \frac{\partial^3 a_1}{\partial z^2 \partial m_3}\right) = \frac{\nu(4 + B - C)}{2n_1^0 2} \tag{17}$$

$$A_{33} = \left(\frac{1}{2} \lim_{x_1 \rightarrow 1} \frac{\partial^3 a_1}{\partial z m_3^2}\right) = 0 \tag{18}$$

$$A_{34} = \left(\frac{1}{6} \lim_{x_1 \rightarrow 1} \frac{\partial^3 a_1}{\partial m_3^3}\right) = -\frac{(3 + 18B)}{6n_1^0 3} \tag{19}$$

Substituting the coefficients given in Eqs. (8,12–19) into Eq. (2), the following expression of the dependence $a_1(z, m_3)$ is obtained,

$$a_1(z, m_3) = 1 - \frac{1}{n_1^0} m_3 - \frac{\nu}{n_1^0} z^2 + \frac{(1 + 2B)}{2n_1^0 2} m_3^2 + \frac{A^{\nu}}{3\sqrt{2}n_1^0}[(\nu_A z_A^2 + \nu_C z_C^2)^{3/2}] z^3 + \frac{\nu(4 + B - C)}{2n_1^0 2} z^2 m_3 - \frac{(3 + 18B)}{6n_1^0 3} m_3^3 + A_{41} z^4 + A_{42} z^3 m_3 + A_{43} z^2 m_3^2 + A_{44} z^4 m_3^3 + A_{45} m_3^4 + A_{51} z^5 + \dots \tag{20}$$

From the comparison of Eqs. (20) and (2), it can be observed that the number of coefficients is decreased from 15 to 8. Renaming the coefficients and expressing Eq. (20) on terms of total molality m_2 , the final expression is,

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