

Equation for the solvent activity correlation in ternary electrolyte solutions

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ABSTRACT

An analytical equation is proposed for the dependence on composition of the solvent activity of aqueous ternary electrolyte solutions. This equation was derived taking into account the limiting behaviour that must obey the solvent activity in order to be thermodynamically consistent. The correlation of experimental data corresponding to 23 ternary systems was successfully carried out. The results obtained demonstrate an excellent fitting capability of the proposed equation.

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1. Introduction

A common way for the evaluation of the solvent activity (a_1) and the mean ionic coefficient ($\gamma_{\pm k}$) of the electrolyte (k) in a multicomponent electrolytic solution is based in the experimental determination of the osmotic coefficient (ϕ) as a function of the solution molality (m) and the internal molal fraction (y) through the isopiestic method. Then, the solvent activity is evaluated starting from its relationship with the osmotic coefficient ($a_1 = \exp(-\phi \sum m_i/n_i^0)$, being i the ionic species). Moreover, the mean ionic coefficients of the electrolytes are calculated through the Pitzer equation [1] or by the use of the Mc Kay-Perrin expression [2] or variants of it [3–5]. In the last case, the integration of both, $\phi(m,y)$ and its derivative $\partial\phi/\partial y$, from $m=0$ to $m=m$ must be carried out. It is also required that the analytical expression used for the description of $\phi(m,y)$ must be compatible with the limiting behaviour determined by the thermodynamics of solutions, in order to obtain accurate values of $\ln \gamma_{\pm k}$.

On the other hand, taking into account that the solvent activity can be evaluated directly from experimental determinations of the vapour pressure of a nonvolatile electrolyte solution, it is not necessary to use the osmotic coefficient for the evaluation of the activity coefficients of the electrolytes. This evaluation can be made more accurately, avoiding the error propagation resulting from the calculation of the osmotic coefficient, by the determination of the solvent activity. However, an accurate description of the dependence $a_1(m,y)$ is required for the later evaluation of the

activity coefficients. The simpler way to describe the monotonically decreasing function $a_1(m,y)$ is the use of polynomial expansions, which were already employed [6–8] but without any analysis of their thermodynamic consistency.

In this context, the aim of the present work is to develop a thermodynamically self-consistent expression that accurately describes the experimental dependence $a_1(m,y)$ for ternary electrolytic solutions, in order to have an analytical equation suitable for the application of the Mc Kay-Perrin method or for any other requirement of thermodynamic calculations.

2. Theoretical considerations

It is considered a ternary solution constituted by a solvent (1) and two electrolytes (2,3), characterized by the formula unit $A_{\nu_{A_k}} C_{\nu_{C_k}}$,

$$A_{\nu_{A_k}} C_{\nu_{C_k}} \rightarrow \nu_{A_k} A_k^{z_{A_k}} + \nu_{C_k} C_k^{z_{C_k}}, \quad k : 2, 3 \quad (1)$$

being ν_{A_k} (ν_{C_k}) the stoichiometric coefficient of the anion (cation) corresponding to the dissociation of the electrolyte k ($k: 2,3$), which concentration (m_k) is given by,

$$m_2 = ym \quad (2)$$

$$m_3 = (1 - y)m \quad (3)$$

where y the internal molal fraction and $m = m_1 + m_2$ the total molality of the electrolyte solution.

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2.1. Equation proposal

In order to develop the multiparametric equation of the solvent activity $a_1(m, y)$, the independent variables y and $z = m^{0.5}$ are adopted. The first one is chosen in order to describe easily the binary systems ($y=0$ or 1). Moreover, the definition of z is originated in order to make compatible the behaviour of the solution at infinite dilution ($m \rightarrow 0, y \rightarrow 0$) with the way in which the correlation equation is set. In this context, the dependence $a_1(z, y)$ can be described by a McLaurin series expansion as follows,

$$\begin{aligned} a_1(z, y) = & 1 + \\ & + A_1 z + A_2 y + \\ & + B_1 z^2 + B_2 z y + B_3 y^2 + \\ & + C_1 z^3 + C_2 z^2 y + C_3 z y^2 + C_4 y^3 + \\ & + D_1 z^4 + D_2 z^3 y + D_3 z^2 y^2 + D_4 z y^3 + D_5 y^4 + \\ & + E_1 z^5 + E_2 z^4 y + E_3 z^3 y^2 + E_4 z^2 y^3 + E_5 z y^4 + E_6 y^5 + \\ & + F_1 z^6 + F_2 z^5 y + F_3 z^4 y^2 + F_4 z^3 y^3 + F_5 z^2 y^4 + F_6 z y^5 + F_7 y^6 + \\ & + G_1 z^7 + G_2 z^6 y + G_3 z^5 y^2 + G_4 z^4 y^3 + G_5 z^3 y^4 + G_6 z^2 y^5 + G_7 z y^6 + G_8 y^7 \end{aligned} \quad (4)$$

This initial expression contains 35 coefficients, which should be analysed in the context of the well known limiting behaviour of the electrolyte solutions.

2.2. Limiting behaviour of $a_1(z, y)$

The electrolyte solution must satisfy the limiting behaviour ($m \rightarrow 0$ and $y \rightarrow 0$) established by the Debye-Hückel theory, which fixes the value of many of the coefficients of Eq. (4). For multicomponent systems, the limiting behaviour of the solvent is governed by the following expression, which established the dependence of the osmotic coefficient with the ionic strength [1],

$$\phi = - \frac{n_1^0}{\sum m_i} \ln a_1 = 1 - \frac{2A^\phi I^{3/2}}{\sum m_i} \quad (5)$$

where A^ϕ is the osmotic coefficient Debye-Hückel constant, which is a function of temperature [1] and I is the ionic strength defined as,

$$\begin{aligned} I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} [y (v_{A_2} z_{A_2}^2 + v_{C_2} z_{C_2}^2) \\ + (1-y) (v_{A_3} z_{A_3}^2 + v_{C_3} z_{C_3}^2)] m \end{aligned} \quad (6)$$

and besides,

$$\sum m_i = [y (v_{A_2} + v_{C_2}) + (1-y) (v_{A_3} + v_{C_3})] m \quad (7)$$

where $v_{A_k} + v_{C_k} = v_k, k: 2,3$. Thus, Eq. (5) can be written as,

$$\phi = 1 - \frac{A^\phi g(y)}{\sqrt{2} f(y)} \sqrt{m} \quad (8)$$

Being the functions $f(y)$ and $g(y)$ defined as,

$$f(y) = [v_2 y + v_3 (1-y)] \quad (9)$$

$$g(y) = [y (v_{A_2} z_{A_2}^2 + v_{C_2} z_{C_2}^2) + (1-y) (v_{A_3} z_{A_3}^2 + v_{C_3} z_{C_3}^2)]^{3/2} \quad (10)$$

The corresponding expression for a_1 is,

$$\ln a_1 = - \frac{1}{n_1^0} \left[f(y) z^2 - \frac{A^\phi}{\sqrt{2}} g(y) z^3 \right] \quad (11)$$

It can be appreciated that the effect of the type of electrolyte on the solvent activity is given through the stoichiometric coefficients

(v_{A_k}, v_{C_k}) and the ionic charges (z_{A_k}, z_{C_k}). Moreover, the limiting behaviour that must satisfy the function $a_1(z, y)$ proposed for a ternary electrolyte solution can be established from Eq. (11). Such limiting behaviour is determined by the values of the derivatives with respect to z and to y at the origin.

The derivative with respect to z at constant y is,

$$\left. \frac{\partial a_1}{\partial z} \right|_y = - \frac{a_1}{n_1^0} \left\{ 2f(y)z - \frac{3A^\phi}{\sqrt{2}} g(y)z^2 \right\} \quad (12)$$

Deriving Eq. (4) and applying the condition $z=0$, it is verified for a given value of y that,

$$\left. \frac{\partial a_1}{\partial z} \right|_{z=0} = 0 = A_1 \quad (13)$$

Moreover, the derivative of a_1 with respect to y at constant z is,

$$\left. \frac{\partial a_1}{\partial y} \right|_z = - \frac{a_1}{n_1^0} \left\{ \left(\frac{\partial f(y)}{\partial y} \right) z^2 - \frac{A^\phi}{\sqrt{2}} \left(\frac{\partial g(y)}{\partial y} \right) z^3 \right\} \quad (14)$$

Comparing with the corresponding derivative of Eq. (4) and applying the condition $y=0$, it is verified for a given value of z that,

$$\left. \frac{\partial a_1}{\partial y} \right|_{y=0} = 0 = A_2 \quad (15)$$

The second order derivative of Eq. (12) with respect to z is,

$$\begin{aligned} \left. \frac{\partial^2 a_1}{\partial z^2} \right|_y = - \frac{1}{n_1^0} \left\{ \frac{\partial a_1}{\partial z} \left(2f(y)z - \frac{3A^\phi}{\sqrt{2}} g(y)z^2 \right) \right. \\ \left. + a_1 \left(2f(y) - \frac{6A^\phi}{\sqrt{2}} g(y)z \right) \right\} \end{aligned} \quad (16)$$

and thus, applying the condition $z=y=0$ it is obtained,

$$\left. \frac{\partial^2 a_1}{\partial z^2} \right|_{z=0, y=0} = - \frac{2v_3}{n_1^0} = 2B_1 \quad (17)$$

Following the same procedure, it can be demonstrated the identities,

$$\left. \frac{\partial^2 a_1}{\partial z \partial y} \right|_{z=0, y=0} = 0 = B_2 \quad (18)$$

$$\left. \frac{\partial^2 a_1}{\partial y^2} \right|_{z=0, y=0} = 0 = 2B_3 \quad (19)$$

$$\left. \frac{\partial^3 a_1}{\partial z^3} \right|_{z=0, y=0} = \frac{6A^\phi}{\sqrt{2} n_1^0} (v_{A_3} z_{A_3}^2 + v_{C_3} z_{C_3}^2)^{3/2} = 6C_1 \quad (20)$$

$$\left. \frac{\partial^3 a_1}{\partial z^2 \partial y} \right|_{z=0, y=0} = - \frac{2}{n_1^0} (v_2 - v_3) = 2C_2 \quad (21)$$

$$\left. \frac{\partial^3 a_1}{\partial z \partial y^2} \right|_{z=0, y=0} = 0 = 6C_3 \quad (22)$$

Eqs. (20) and (21) show that the type of electrolyte influences even the third order derivatives. It can be also appreciated that the derivatives involved in Eqs. (13), (15) and (17–22) correspond to the first 8 coefficients of Eq. (4).

2.3. Analysis of the coefficients of the order $n > 3$

The application of the conditions of self-consistency corresponding to the limiting behaviour of the electrolyte solutions to Eq. (4) allowed to established the values of the coefficients up to order $n = 3$. Thus, it can be concluded that coefficients A_1, A_2, B_3 and C_3 are equal to 0. In this sense, there are other conditions that must be accomplished by Eq. (4) in order to be thermodynamically consistent, which will be analysed here. First, as the permutation of the electrolytes 2 and 3 should not introduce any change, the third order derivative must satisfy the following condition,

$$\left. \frac{\partial^3 a_1}{\partial z^3} \right)_{z=0} = \frac{6A^\phi}{\sqrt{2}n_1^0} (v_{A_2}z_{A_2}^2 + v_{C_2}z_{C_2}^2)^{3/2} = 6D_2 \quad (23)$$

$$y = 1$$

Deriving the third order derivative of Eq. (4) and evaluating it at $z = 0$ and $y = 1$, the following relationship is obtained,

$$\left. \frac{\partial^3 a_1}{\partial z^3} \right)_{z=0} = \left. \frac{\partial^3 a_1}{\partial z^3} \right)_{z=0} + 6D_2 \quad (24)$$

$$y = 1 \quad y = 0$$

Thus, the following expression for coefficient D_2 is obtained from Eq. (24),

$$D_2 = \frac{A^\phi}{\sqrt{2}n_1^0} \left[(v_{A_2}z_{A_2}^2 + v_{C_2}z_{C_2}^2)^{3/2} - (v_{A_3}z_{A_3}^2 + v_{C_3}z_{C_3}^2)^{3/2} \right] \quad (25)$$

Another aspect is related to the coefficients involved in the terms that contain y^n , which must be zero in order to accomplish the condition that the solvent activity must be equal to 1 when $m \rightarrow 0$ for any y value. Consequently, the coefficients C_4, D_5, E_6, F_7 and G_8 must be null.

The coefficients corresponding to the terms that contain zy^{n-1} with $n > 3$ must also be null, as it was demonstrated through Eq. (13) that the first derivative with respect to z applied to $z = 0$ must be equal to 0 for any value of y . Consequently, the coefficients D_4, E_5, F_6 and G_7 must be null. Moreover, the coefficients corresponding to the terms that contain z^2y^{n-2} with $n > 3$ must also be null, as the second order derivative with respect to z leads to y^{n-2} , which generates a dependence of y different to that required by Eq. (17). Therefore, the coefficients D_3, E_4, F_5 and G_6 must be null. Finally and for the same reasons the coefficients corresponding to the terms that contain z^3y^{n-2} with $n > 4$ must also be null and therefore E_3, F_4 and G_5 are zero.

Substituting the expressions found for B_1 (Eq. (17)), C_1 (Eq. (20)), C_2 (Eq. (21)) and D_2 (Eq. (25)), the expression for function $a_1(z, y)$ is obtained,

$$a_1(z, y) = 1 - \frac{[yv_2 + (1-y)v_3]}{n_1^0} z^2$$

$$+ \frac{A^\phi}{\sqrt{2}n_1^0} \left[y(v_{A_2}z_{A_2}^2 + v_{C_2}z_{C_2}^2)^{3/2} + (1-y)(v_{A_3}z_{A_3}^2 + v_{C_3}z_{C_3}^2)^{3/2} \right] z^3 \quad (26)$$

$$+ D_1 z^4 + E_1 z^5 + E_2 z^4 y + F_1 z^6 + F_2 z^5 y + F_3 z^4 y^2$$

$$+ G_1 z^7 + G_2 z^6 y + G_3 z^5 y^2 + G_4 z^4 y^3$$

From the comparison of Eqs. (26) and (4), it can be observed that the number of coefficients is reduced from 35 to 10. Renaming the coefficients and expressing Eq. (26) on terms of total molality m , the final equation is,

$$a_1(m, y) = 1 - \frac{[yv_2 + (1-y)v_3]}{n_1^0} m$$

$$+ \frac{A^\phi}{\sqrt{2}n_1^0} \left[y(v_{A_2}z_{A_2}^2 + v_{C_2}z_{C_2}^2)^{3/2} + (1-y)(v_{A_3}z_{A_3}^2 + v_{C_3}z_{C_3}^2)^{3/2} \right] m^{3/2} \quad (27)$$

$$+ am^2 + bm^{5/2} + cm^2 y + dm^3 + em^{5/2} y + fm^2 y^2 + gm^{7/2} + hm^3 y + im^{5/2} y^2 + jm^2 y^3$$

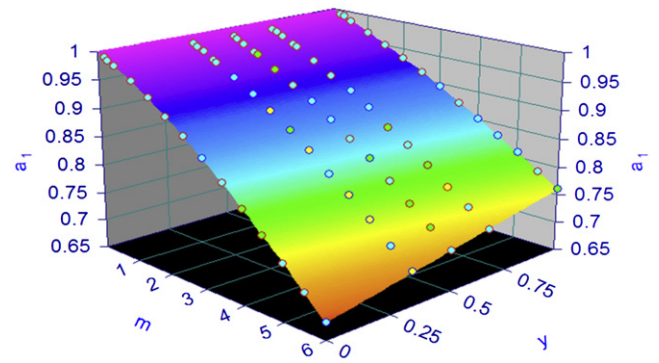


Fig. 1. Dependence of solvent activity (a_1) on total molality (m) and NaCl internal molal fraction (y) for the system NaCl–LiCl–H₂O at 298.15 K. Dots: experimental data [9,10]; surface: correlation with Eq. (27).

Eq. (27) is a thermodynamically consistent expression that can accurately correlate the experimental dependence $a_1(m, y)$ for ternary electrolyte solutions. Moreover, using $y = 0$ or $y = 1$ and reordering, a correlation equation for the binary system is obtained, which is also thermodynamically self-consistent.

The proposed equation will be verified through its application to several systems, which will be described in the next section.

3. Evaluation of the proposed equation

The proposed equation ensures that the description of the dependence $a_1(z, y)$ has at the origin a third order contact with the limiting behaviour established for electrolyte solutions. Thus, the effect of the type of electrolyte is taking into account and it is possible to describe the transition between two different types of electrolytes ($v_2 \neq v_3$) at constant m through the variation of y . This effect is contained in second and third terms of Eq. (27), with non adjustable coefficients that involve the stoichiometric coefficients (v_{A_k}, v_{C_k}) and the ionic charges (z_{A_k}, z_{C_k}), characteristic of a given electrolyte, and the constant A^ϕ . Meanwhile, the remaining terms describe the deviation to such behaviour.

In order to verify the applicability of Eqs. (27) and (23) aqueous ternary systems were evaluated, constituted by electrolytes of the type 1:1, 1:2, 2:2 and a combination of them [9–29]. Six adjustable parameters were used, as it was realized that they were enough for the appropriate correlation of the experimental dependence $a_1(m, y)$. All the systems were evaluated at 298.15 K, thus $A^\phi = 0.39765$ [1], being the solvent molality $n_1^0 = 55.5084$.

The results obtained are summarized in Table 1, where it is reported for each system the values of the six coefficients of Eq. (27), the number of experimental data (N) involved in the correlation, the maximum concentration (m_{\max}), the standard deviation $S = \left(\sum (a_1^{\text{corr}} - a_1^{\text{exp}})^2 / N \right)^{1/2}$ and the references from where the experimental data were obtained. The correlation capability of the proposed equation is illustrated for four cases that can be considered representative of all the systems analysed. Figs. 1–4 show the dependencies $a_1(m, y)$ for different systems, involving unsymmetrical electrolytes, through which the capability of Eq. (27) to describe the effect of the variation of the ionic charges is verified. It can be quickly concluded that if $v_2 = v_3$ the second and third coefficient do

Table 1
Values of the parameters (*a–f*) of equation (27) evaluated from the correlation of *N* experimental points of ternary electrolyte solutions (salt 2–salt 3–water) of maximum total molality (m_{\max}), standard deviation (*S*).

System (2–3–1)	$10^2 a$	$10^3 b$	$10^3 c$	$10^3 d$	$10^3 e$	$10^3 f$	<i>N</i>	m_{\max}	<i>S</i>	Ref.
NaCl–LiCl–H ₂ O	–1.785	5.281	3.292	–0.6395	–0.3419	–0.2044	73	6	0.00140	[9,10]
NaCl–KCl–H ₂ O	–1.421	5.379	–0.9646	–0.7257	–0.01000	–0.09999	72	6	0.00102	[9,29]
LiCl–KCl–H ₂ O	–1.506	6.358	–2.783	–0.9818	0.4346	–1.702	70	6	0.00209	[9,12]
NaCl–CsCl–H ₂ O	–1.267	4.479	–2.512	–0.5515	0.3624	0.2244	82	8	0.00227	[9,13]
LiCl–CsCl–H ₂ O	–1.089	2.975	–5.656	–0.2392	0.8005	0.01150	85	9	0.00283	[9,13]
NH ₄ Cl–CsCl–H ₂ O	–1.210	3.972	–0.07438	–0.4407	–0.0466	0.166	116	12.5	0.00221	[9,14]
NH ₄ Cl–NH ₄ NO ₃ –H ₂ O	–1.018	3.826	–2.812	–0.4499	0.3694	0.408	74	9	0.00174	[9,16]
NH ₄ NO ₃ –NaNO ₃ –H ₂ O	–0.9358	2.950	0.9182	–0.291	–0.3193	–0.1168	66	17.5	0.00485	[15]
NaCl–MgCl ₂ –H ₂ O	–9.763	25.96	86.05	–1.032	–19.18	–5.332	58	6	0.00306	[9,17]
LiCl–MgCl ₂ –H ₂ O	–9.276	21.76	78.36	–0.1485	–18.02	–2.412	60	10	0.00336	[9,18]
NH ₄ Cl–MgCl ₂ –H ₂ O	–10.05	30.48	83.58	–2.514	–17.89	–3.957	65	6	0.00384	[9,19]
LiCl–CaCl ₂ –H ₂ O	–8.275	19.87	61.01	–0.7754	–12.29	–0.4044	71	12.5	0.00799	[9,18]
NH ₄ Cl–CaCl ₂ –H ₂ O	–9.642	29.68	79.01	–2.479	–17.80	–2.016	119	6	0.00759	[9,20,21]
NaCl–BaCl ₂ –H ₂ O	–9.315	28.64	75.95	–0.7797	–23.20	2.038	56	6	0.00209	[9,22]
LiCl–BaCl ₂ –H ₂ O	–9.094	26.45	63.04	–0.3177	–22.65	11.68	45	6	0.00249	[9,18]
NH ₄ Cl–BaCl ₂ –H ₂ O	–9.372	29.47	79.01	–0.9722	–23.12	–0.03504	65	6	0.00251	[9,20]
Na ₂ SO ₄ –(NH ₄) ₂ SO ₄ –H ₂ O	–9.488	50.41	2.482	–9.437	–1.589	–0.1110	91	5	0.00160	[23,24,26]
Li ₂ SO ₄ –(NH ₄) ₂ SO ₄ –H ₂ O	–9.559	51.13	–6.166	–9.626	0.2815	0.2928	58	4.75	0.00180	[23,24]
K ₂ SO ₄ –(NH ₄) ₂ SO ₄ –H ₂ O	–9.065	45.83	–7.865	–8.226	5.655	–1.782	54	5	0.00106	[11,23]
MgCl ₂ –CaCl ₂ –H ₂ O	–10.81	39.20	–2.301	–4.380	0.09665	–0.3573	58	6	0.00380	[9,17]
NaCl–Na ₂ SO ₄ –H ₂ O	–7.922	27.73	61.16	–1.487	–19.16	–0.5342	74	6	0.00177	[9,23,25,26]
Na ₂ SO ₄ –MgSO ₄ –H ₂ O	–17.51	100.0	56.62	–20.89	–16.15	–0.2569	85	3.5	0.00127	[23,25,27]
MgSO ₄ –MnSO ₄ –H ₂ O	–18.07	108.8	0.03097	–23.54	–1.128	0.2174	65	4	0.00201	[23,28]

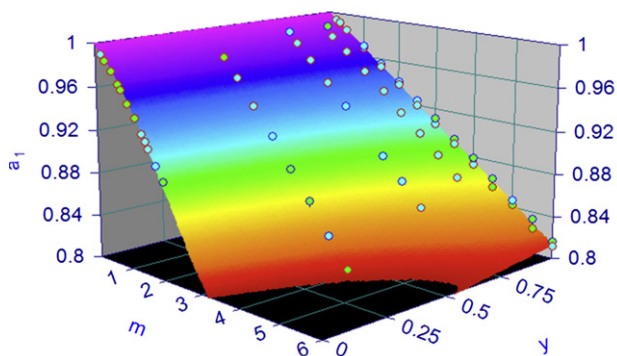


Fig. 2. Dependence of solvent activity (a_1) on total molality (m) and NH₄Cl internal molal fraction (y) for the system NH₄Cl–BaCl₂–H₂O at 298.15 K. Dots: experimental data [9,20]; surface: correlation with Eq. (27).

not depend on the internal molal fraction y . These behaviours can be clearly appreciated in Figs. 1–4. Fig. 1 corresponds to a mixture of electrolytes 1:1 where $\nu_2 = \nu_3 = 2$, while Figs. 2–4 correspond to systems involving asymmetric electrolytes, where the stoichiometric coefficients are $\nu_2 \neq \nu_3$. Figs. 2 and 4 correspond to a mixture of an electrolyte of the type 1:1 with a 2:1, while the behaviour

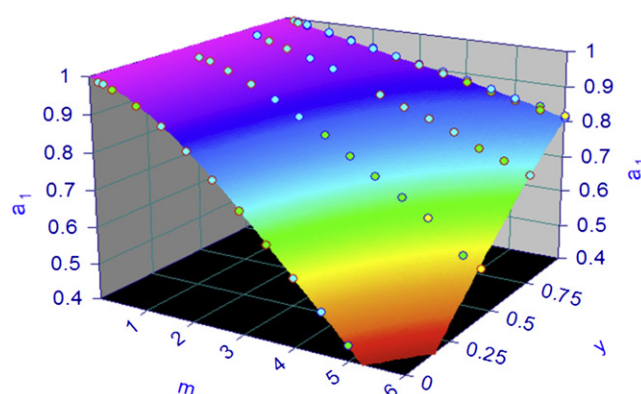


Fig. 4. Dependence of solvent activity (a_1) on total molality (m) and Na₂SO₄ internal molal fraction (y) for the system NH₄Cl–MgCl₂–H₂O at 298.15 K. Dots: experimental data [9,19]; surface: correlation with Eq. (27).

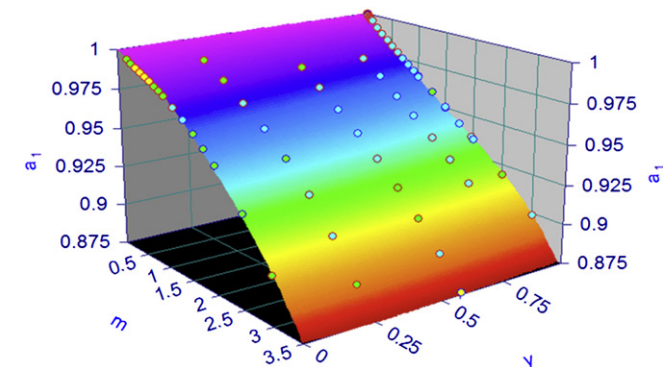


Fig. 3. Dependence of solvent activity (a_1) on total molality (m) and Na₂SO₄ internal molal fraction (y) for the system Na₂SO₄–MgSO₄–H₂O at 298.15 K. Dots: experimental data [23,25,27]; surface: correlation with Eq. (27).

of a mixture of an electrolyte of the type 1:2 and the other 2:2 is illustrated in Fig. 3. It can be observed in all cases that the experimental dependences of $a_1(m, y)$ are accurately fitted. Furthermore, from the analysis of the standard deviation of all the systems studied (Table 1), it can be concluded that the goodness of fit of the proposed equation is high, being the mean value of the standard deviations equal to 0.00281. The maximum standard deviation is 0.00799 and corresponds to the system LiCl–CaCl₂–H₂O, which m_{\max} is 12.5 molal. It should be taken into account that the calculated values of the standard deviation include the errors that could have occurred in the experimental measurements. Thus, from the results obtained it can be concluded that the proposed equation, which is consistent with the limiting behaviours demanded by the thermodynamics of solutions, is an accurate tool for the description of the dependence of the solvent activity on composition of ternary electrolyte solutions.

4. Conclusion

Starting from a McLaurin series expansion of the solvent activity in ternary electrolyte solutions on the variables z and y and taking into account the limiting behaviour that must be accomplished, an

analytical equation was derived that allows the correlation of the dependence of the solvent activity on composition. This equation was applied to 23 ternary systems and the results obtained demonstrate an excellent fitting capability of the experimental data.

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