Comment on "Factorizing of a concentration function for the mean activity coefficients of aqueous strong electrolytes into individual functions for the ionic species" by A. Ferse and H.O. Müller

Francesco Malatesta

Abstract A. Ferse and H.O. Müller have recently presented a mathematical method aimed at subdividing the activity coefficients of electrolytes into functions of individual ionic species; these functions are suggested to be the ionic activity coefficients. By examining the method, it is possible to verify that the peculiar mathematical structure of the functions in question really guarantees a unique result, unlike the usual subdivisions of electrolyte activity coefficients, which admit infinite possibilities for the ionic activity coefficients. But the subsequent step of the reasoning, i.e., that these functions have to be the activity coefficients of the ionic species, is an illation. And indeed, another kind of subdivision in individual functions can be exemplified, whose mathematical structure also guarantees results that are unique and perfectly compatible with all theoretical properties of the ionic activity coefficients. It is concluded that it is impossible to rely on mathematical method to pull the activity coefficients of ions out of the mean activity coefficients of the electrolytes. And hence, the individual functions for the ionic species determined by Ferse and Müller do not represent the ionic activity coefficients and do not have any particular utility.

On November 2010, A. Ferse contacted me about a paper that he and H.O. Müller were writing, regarding a mathematical method able to subdivide univocally the activity coefficients of the electrolytes into their ionic constituents. As I was not convinced by their reasoning, and Ferse was not convinced by my opposite arguments, we continued to have friendly contacts by mail for months, until April 2011, when we finally agreed that persisting in our exchange of ideas further on, was of no utility. I realized lately that Ferse and Müller succeeded in publishing the abovementioned paper in J Solid State Electrochem [1]. However, I persist in my belief that such arguments are ill-founded, for reasons exposed in the discussion that follows.

We will consider for simplicity only 1:1 electrolytes, where dimensionless ionic strength (J) and dimensionless molality (m) coincide. We indicate as x the quantity $x = J^{1/2} = m^{1/2}$. The mean activity coefficient $\gamma_\pm$ can always be expressed as a series of powers of x,

$$\ln \gamma_\pm(x) = \sum_{i \geq 1} s_i x^i \qquad (1)$$

in which $s_{i=1}$ ($= -A_{DH}$) is the Debye-Hückel limiting slope, and all other s_i ($i > 1$) are empirical coefficients. It is generally admitted that $\gamma_\pm^2(x)$ can be expressed formally as the product $\gamma_+(x)\, \gamma_-(x)$, although $\gamma_+(x)$ and $\gamma_-(x)$, the individual activity coefficients of the cation and anion, cannot be defined in thermodynamic terms and remain a rather undefined conception. There exist, however, infinite possible couples of other functions $\xi_1(x)$ and $\xi_2(x)$ of the kind

$$\ln \xi_1(x) = -A_{DH}x + \sum_{i \geq 2} s_i' x^i, \ \text{i.e., } \xi_1(x)$$

$$= \exp\left(-A_{DH}x + \sum_{i \geq 2} s_i' x^i \right) \qquad (2)$$

F. Malatesta (✉)
Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
Via Risorgimento 35,
56126 Pisa, Italy
e-mail: franco@dcci.unipi.it

$$\ln \xi_2(x) = -A_{DH}x + \sum_{i \geq 2} s_i'' x^i, \quad \text{i.e., } \xi_2(x)$$

$$= \exp\left(-A_{DH}x + \sum_{i \geq 2} s_i'' x^i\right) \tag{3}$$

with $(s_i' + s_i'') = 2s_i$ (s_i, the corresponding coefficient of Eq. 1), which fulfill all properties that theoretically characterize γ_+ and γ_-, i.e., $\xi_1 \xi_2 = \gamma_\pm^2$; $\lim_{(x \to 0)} [d(\ln \xi_1)/dx] = \lim_{(x \to 0)} [d(\ln \xi_2)/dx] = \lim_{(x \to 0)} [d(\ln \gamma_\pm)/dx] = -A_{DH}$; and $\lim_{(x \to 0)} \xi_1 = \lim_{(x \to 0)} \xi_2 = 1$. Thus, even assuming that we are able to provide a univocal definition of the rather indefinite conceptions of γ_+ and γ_-, all these infinite couples of ξ_1 and ξ_2 could be considered as equally ranked for the title of the *legitimate* γ_+ and γ_-.

To solve the impasse, Ferse and Müller [1] observe that it is possible to split $\gamma_\pm^2(x)$ into the product of two functions having a completely different mathematical structure, which they indicate as a γ with an over bar; we will use here a different symbol, $\widetilde{\xi}$, better avoiding any subliminal suggestion that these functions have just to be the activity coefficients $\gamma_+(x)$ and $\gamma_-(x)$. These $\widetilde{\xi}$ are defined by:

$$\gamma_\pm^2(x) = \widetilde{\xi}_1(x)\widetilde{\xi}_2(x) = \left[\sum_{i=1}^{3} b_i \exp(\beta_i x^i)\right]$$

$$\times \left[\sum_{i=1}^{3} d_i \exp(\delta_i x^i)\right] \tag{4}$$

$$\widetilde{\xi}_1(x) = \sum_{i=1}^{3} b_i \exp(\beta_i x^i) \tag{5}$$

$$\widetilde{\xi}_2(x) = \sum_{i=1}^{3} d_i \exp(\delta_i x^i) \tag{6}$$

and, in this case, there exists only one set of the adjustable parameters b_i, β_i, d_i, and δ_i which is compatible with all conditions that $\gamma_+(x)$ and $\gamma_-(x)$ have to fulfill, and whose values are such as to minimize the sum of the squared differences $\left[\gamma_{\pm \text{exper.}}^2 - \widetilde{\xi}_1 \widetilde{\xi}_2\right]^2$. Thus, Ferse and Müller are undoubtedly right, as for the conclusion that the mathematical subdivision of $\gamma_\pm^2(x)$ according to (4) is univocal, unlike the usual subdivisions according to (2) and (3), which admit an infinite number of valid solutions.

However, it is impossible to agree with the subsequent step of their reasoning, which is mere illation, as they come to suggest that, since the subdivision $\gamma_\pm^2(x) = \widetilde{\xi}_1(x)\widetilde{\xi}_2(x)$ is unique, then $\widetilde{\xi}_1(x)$ and $\widetilde{\xi}_2(x)$ have to be $\gamma_+(x)$ and $\gamma_-(x)$. No logical reasons exist for such a conclusion.

Indeed, also $\ln \widetilde{\xi}_1(x)$ and $\ln \widetilde{\xi}_2(x)$ can be developed in terms of powers of x like those of Eqs. 2 and 3, using appropriate values, $\widetilde{s}_i'$ and $\widetilde{s}_i''$, for s_i' and s_i'',

$$\ln \widetilde{\xi}_1(x) = -A_{DH}x + \sum_{i \geq 2} \widetilde{s}_i' x^i, \quad \text{i.e., } \widetilde{\xi}_1(x)$$

$$= \exp\left(-A_{DH}x + \sum_{i \geq 2} \widetilde{s}_i' x^i\right) \tag{7}$$

$$\ln \widetilde{\xi}_2(x) = -A_{DH}x + \sum_{i \geq 2} \widetilde{s}_i'' x^i, \quad \text{i.e., } \widetilde{\xi}_2(x)$$

$$= \exp\left(-A_{DH}x + \sum_{i \geq 2} \widetilde{s}_i'' x^i\right) \tag{8}$$

With respect to all other ξ_1 and ξ_2 functions that also fulfill all conditions theoretically required by γ_+ and γ_-, the peculiarity of $\widetilde{\xi}_1$ and $\widetilde{\xi}_2$ consists of the fact that these are the only ones that obey *also* (5) and (6). Yet, this fact has no relevance, since (5) and (6) are not required properties of γ_+ and γ_-, but only, by their own definition, of $\widetilde{\xi}_1$ and $\widetilde{\xi}_2$. An artificial constraint has been imposed to the ξ functions, and the unique ones that get through this constraint are taken for γ_+ and γ_-. That is completely arbitrary.

To better understand the question, let us consider now, as an exercise, an alternative arbitrary subdivision of $\gamma_\pm^2$ into two empirical functions ζ_1 and ζ_2 not too different from the extended Debye–Hückel equation, and expectedly applicable within the same concentration range:

$$2 \ln \gamma_\pm(x) = \ln \zeta_1(x) + \ln \zeta_2(x)$$

$$= \left[(-A_{DH}x + B_1 x^2)/(1 + C_1 x)\right]$$

$$+ \left[(-A_{DH}x + B_2 x^2)/(1 + C_2 x)\right] \tag{9}$$

with four adjustable parameters, B_1, B_2, C_1, and C_2, and the restriction that C_1 and C_2 are positive. By developing (9), it becomes

$$2 \ln \gamma_\pm(x) = \left(-2 A_{DH}x + p_1 x^2 + p_2 x^3\right)/\left(1 + q_1 x + q_2 x^2\right) \tag{10}$$

$$p_1 = [B_1 + B_2 - A_{DH}(C_1 + C_2)] \tag{11}$$

$$p_2 = B_1 C_2 + B_2 C_1 \tag{12}$$

$$q_1 = C_1 + C_2 \tag{13}$$

$$q_2 = C_1 C_2 \tag{14}$$

The best-fit values of p_1, p_2, q_1, and q_2, can be determined by numerical methods, minimizing the sum of the squared

differences $[(-2\,A_{DH}x + p_1 x^2 + p_2 x^3)/(1 + q_1 x + q_2 x^2) - 2\ln \gamma_{\pm exper}]^2$. As for C_1 and C_2, (13) and (14) imply a quadratic relationship, yielding two alternative solutions, either C_{1a} and C_{2a} or C_{1b} and C_{2b}; and by consequence, also alternative solutions B_{1a} and B_{2a}, or B_{1b} and B_{2b}, are obtained for B_1 and B_2. However, selecting B_{1a}, B_{2a}, C_{1a}, C_{2a}, or B_{1b}, B_{2b}, C_{1b}, C_{2b}, corresponds to merely interchanging ζ_1 and ζ_2.[1] i.e., the values of B_1, B_2, C_1, and C_2 are univocal. We have found, therefore, another kind of mathematical subdivision of $\gamma_\pm^2$ which suggests only one couple, rather than infinite couples, of possible γ_+ and γ_-. Are ζ_1 and ζ_2, or $\widetilde{\xi}_1$ and $\widetilde{\xi}_2$, the better candidates for γ_+ and γ_- ?

To conclude, it is perfectly possible to subdivide the activity coefficients of the electrolytes into univocally defined functions compatible with the ionic activity coefficients; but ionic activity coefficients, and functions perfectly compatible with ionic activity coefficients, are two different and non-connected conceptions.

Reference

1. Ferse A, Müller HO (2011) Factorizing of a concentration function for the mean activity coefficients of aqueous strong electrolytes into individual functions for the ionic species. J Solid State Electrochem. doi:10.1007/s10008-011-1413-9

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[1]
$$C_{1a} = \left[q_1 + \left(q_1^2 - 4\,q_2\right)^{1/2}\right]/2 \qquad\qquad C_{1b} = C_{2a}$$

$$C_{2a} = \left[q_1 - \left(q_1{}^2 - 4\,q_2\right)^{1/2}\right]/2 \qquad\qquad C_{2b} = C_{1a}$$

$$B_{1a} = (A_{DH}\,q_1 + p_1)/2 + \left(A_{DH}\,q_1^2 + p_1\,q_1 - 2\,p_2\right)/$$
$$\left[2\left(q_1{}^2 - 4\,q_2\right)^{1/2}\right] \qquad\qquad B_{1b} = B_{2a}$$

$$B_{2a} = (A_{DH}\,q_1 + p_1)/2 - \left(A_{DH}\,q_1{}^2 + p_1\,q1 - 2\,p_2\right)/$$
$$\left[2\left(q_1{}^2 - 4\,q_2\right)^{1/2}\right] \qquad\qquad B_{2b} = B_{1a}$$