

Comment on "Single-Ion Activity: Experiment versus Theory"

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In his recent paper^{1a} in this journal, Fraenkel compared theoretical ionic activity coefficients, γ_i , derived from his extension of the Debye–Hückel theory, called the smaller-ion shell model^{1b} (the DH–SiS), with γ_i calculated from potentiometric measurements on cells with liquid junctions. In doing so, he dismissed the phenomenological interpretation^{2–4} according to which measured γ_i are functionals of mean activity coefficients and transport numbers of ions in the liquid junction. It could be thought that agreement between theory and experiment refutes that interpretation. It should be noted, however, that γ_i of cations and anions (γ_+ and γ_-) in the DH–SiS differ by virtue of ion sizes, apart from charges. These may be related to ionic mobilities and, therefore, may correlate with transport numbers. In fact, one can ascertain, for the six electrolytes chosen for the comparison,^{1a} that transport numbers of cations, as calculated from limiting conductivities of ions,⁵ correlate with the b_+ parameters of the DH–SiS with correlation coefficient 0.98.

Relevance of transport numbers to features of γ_i functions can be learned from the following crude formulas for γ_- and γ_+ of 1:1 chlorides, MCl, measured in cells with KCl in the liquid junction ($M^+ \neq K^+$)

$$\gamma_- \propto \gamma_{\text{MCl}}^{2t_{\text{M}}} \gamma_{(0)\text{KCl}}^{2t_{\text{K}}} \quad (1)$$

$$\gamma_+ \propto \gamma_{\text{MCl}}^2 \gamma_-^{-1} = \gamma_{\text{MCl}}^{2(1-t_{\text{M}})} \gamma_{(0)\text{KCl}}^{-2t_{\text{K}}} \quad (2)$$

which are extracted from the exact γ_- functional⁴ appropriate to the case (eq 76 in ref 4). Here γ_{MCl} is the mean activity coefficient of MCl in the MCl solution, $\gamma_{(0)\text{KCl}}$ is the trace coefficient of KCl in the same solution, and t_{M} and t_{K} are some average, effective transport numbers of ions M^+ and K^+ found in the MCl + KCl mixtures in the liquid junction. The formulas make sense provided that potentiometric measurements are corrected for the (ideal part of the) liquid junction potential.

One can see from them that, if γ_{MCl} has a minimum and $\gamma_{(0)\text{KCl}}$ decreases with the MCl molality, then the minimum will be mapped to the γ_- subset at a higher molality relative to the minimum in γ_{MCl} , and to the γ_+ subset at lower molality. Transport numbers of cations, especially in such mixtures, are generally lower than 0.5. Therefore, the γ_- minimum will be shallow and the γ_+ minimum deep.

Now, the DH–SiS predicts a minimum in γ_+ , usually in harmony with eq 2 and with measured γ_+ , but an unbounded decrease in γ_- . In fact, one can find out from the most extensive γ_i measurements^{6,7} that a pronounced minimum in γ_+ is always accompanied by a broad one in γ_- at higher molality, generally at 0.5–2 mol·kg^{−1}. An example is shown in Figure 1a where the

γ_- minimum occurs at 0.8 mol·kg^{−1}, and deviations between experiment and theory become apparent at 0.5 mol·kg^{−1}.

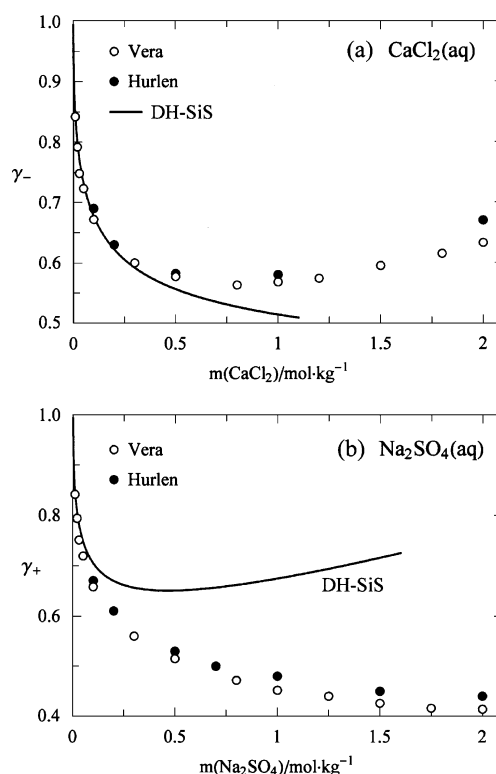


Figure 1. Two types of failures of the DH–SiS to account for experimental γ_i . (Experimental: “Vera” stands for Wilczek-Vera et al.⁶ and “Hurlen” for Hurlen.⁷ Theoretical: calculations with the DH–SiS formulas and parameters found in ref 1.)

Moreover, at least in one case (Figure 1b), the DH–SiS predicts a minimum in γ_+ , whereas there is no minimum in γ_{\pm} and, accordingly, no minima in measured γ_+ and γ_- , as expected from the types of eqs 1 and 2.

These facts together with the results of the previous analysis⁴ clearly show which of the two interpretations of experiment is genuine.

However, the problem broached in Fraenkel’s paper is twofold. While it has been known since the works of Taylor and Guggenheim that measured γ_i are misnomers, the physical meaning of theoretical γ_i has never been highlighted.

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We know that the DH theory is a theory for electrically neutral ionic solutions for it makes use of the electrical neutrality condition twice in deriving the Debye potential: once as a global one and once as a local one. On the other hand, the γ_i definition, being by way of partial Gibbs energy, G , implies that G must be known as a function of molality of the ion under consideration at fixed molalities of other species, in a finite range of molality (because differentiation involves taking limits of the function). Therefore, quantities γ_i in this theory are such that would be if the Debye potential were valid regardless of the electrical neutrality condition. However, this cannot be the case because the key feature of the DH theory—screening of electric field—is a direct consequence of that condition.⁸ It appears therefore that theoretical γ_i are mathematical constructs that are hardly meaningful from the physical point of view.

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Notes

The authors declare no competing financial interest.

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