

Reply to "Comment on 'Single-Ion Activity: Experiment versus Theory'"

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In a Comment¹ on the title's article,² Zarubin accuses me of dismissing "the phenomenological interpretation" of γ_i as a function of γ_{\pm} and t_i (the ionic transport number in the liquid junction). He then goes on explaining the relevance of t_i in γ_i as presented in his eqs 1 and 2,¹ for γ_+ and γ_- , respectively. His interpretation of the γ - t correlation as imposing a correlation between a minimum in γ_{\pm} and minima in both γ_+ and γ_- leads him to examine the DH-SiS theoretical single-ion activity expressions² and show that predicted γ_+ and γ_- are at odds with a few experimental cases in which the predicted γ_- does not have a minimum where it should have (Figure 1a in ref 1) because γ_{\pm} has and the predicted γ_+ does have a minimum where it should not have (Figure 1b, ref 1) because γ_{\pm} does not have. On this basis, Zarubin concludes that the "interpretation of experiment" by DH-SiS is not genuine. The second part of the "twofold" problem of my paper, according to Zarubin, is the lack of physical meaning of the theoretical γ_i when based on the Debye potential that is invalid—so says he—due to the charge neutrality condition.

Zarubin uses here the same type of argumentation that he used in the Zarubin-Wilczek-Vera/Vera debate, as mentioned in my article.² His accusation on the dismissal of the $\gamma_i(\gamma_{\pm}, t_i)$ notion that he has advanced is baseless, since my citation on his work (ref 19 in my article) gives a full access to his views on γ_i . Moreover, there appears to be no incompatibility between Zarubin's interpretation of γ_i and the standard interpretation of γ_i based on the (partial) ionic chemical potential.³ At most, my article indicates once more that different approaches converge over the experimentally measured values of γ_i . The "unsustained statements and inconsistencies"³ in Zarubin's work should not be repeated here, and let me focus now on the specific issues of the Comment.

First, importantly, Zarubin's demonstration⁴ that his $\gamma_i(\gamma_{\pm}, t_i)$ expressions correlate with experimental γ_i data of Vera's group, Hurlen, and others (see relevant references in ref 4) was meant by him to only show that the experimental data are not physically valid γ_i 's, since $\gamma_i(\gamma_{\pm}, t_i)$'s lack physical validity because they depend on t_i . Had Zarubin followed his own logic in the current Comment, he would have praised DH-SiS as perhaps providing "real γ_i 's", since this theory does not agree with experiment! Or, Zarubin could have embraced the cases of experiment-theory agreement² to corroborate his view that γ_i 's predicted by DH-SiS are physically invalid. The "lack of validity" of DH-SiS otherwise remains a possible lack of agreement with $\gamma_i(\gamma_{\pm}, t_i)$; however, again, does this mean validity or lack of validity because $\gamma_i(\gamma_{\pm}, t_i)$ is not a true γ_i ? Note that Vera and Wilczek-Vera³ have suggested a fundamental

correlation equation, $\gamma_i(\gamma_{\pm}, t_i) = \gamma_i(m, T, P) = a_i/[m_i/m^0]$, by which "invalid" and "valid" γ_i 's are equated.

Second, let me analyze the disagreement between DH-SiS and the experiment, as shown by Zarubin and stated¹ as "failures of the DH-SiS" (so, this time, not "failures of the experiment"!). Zarubin's premise is that, in terms of having or not having a minimum, γ_- and γ_+ should both follow the γ_{\pm} trend. This, of course, is at odds with the predictions of DH-SiS according to which, if the cation is the smaller ion, γ_+ shows either a minimum or lack thereof depending on the particular circumstances of the system (e.g., cation size), whereas γ_- never exhibits a minimum. However, this γ_i trend is only that of the electrostatic part of γ_i . DH-SiS neglects the non-electrostatic effects, such as the core potential, that eventually, at some high concentration, should cause γ_- to go through a minimum. The γ_- minimum in CaCl_2 (Figure 1a in ref 1) is beyond the validity limit of DH-SiS (in this case,² $\sim 0.7 m$), and the departure of experiment from the theoretical prediction seems to mirror the missed effects of non-electrostatic factors. Furthermore, the non-electrostatic repulsive effects at higher m are more pronounced for the anion when it is the larger ion, as in the CaCl_2 case. Thus, in fact, Figure 1a of ref 1 serves as an excellent case demonstrating agreement-disagreement between theory (DH-SiS) and experiment subject to the existence or nonexistence of the non-electrostatic contributions to γ_- . Figure 1b of ref 1 is, admittedly, a tougher case: In Na_2SO_4 , DH-SiS predicts a minimum in γ_+ (γ_{Na^+}), whereas experiment does not exhibit a minimum. It is not clear whose fault it is, theory or experiment, but note that DH-SiS is a consistent and quite rigid theoretical treatment and so are its predictions. We cannot change the "rules of the game" when, in one isolated case, fit is not achieved. If DH-SiS fits with experiment in the case of K_2SO_4 ,² why would it not fit in the Na_2SO_4 case? This lack of fit (Figure 1b)¹ should be considered for now as an anomaly.

Third, on the physical meaning of γ_i , Zarubin acknowledges⁴ that scientists are accepting the standard definition of γ_i based on the chemical potential (μ_i) or Gibbs free energy (G_i), as used, e.g., in the Debye-Hückel (DH) theory. However, claims Zarubin, the DH theory is limited to very high dilution even in its extended form "due to its internal inconsistencies". Now that we have perhaps removed those inconsistencies by the DH-SiS extension of the DH theory, maybe it is time to go back to the fundamental γ_i definition.^{3,5} Nonetheless, Zarubin argues that

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DH–SiS, like the DH theory, is unphysical because the Debye potential is not valid due to the requirement of charge neutrality. Indeed, the Debye potential cannot be measured. However, the physical validity point Zarubin raises with respect to theory is a general one. Maybe it is in order here to quote Bockris and Reddy⁶ on the issue of building a theoretical model (with my underlining):

This involves conceiving a model that contains only the essential features of the real situation. All the thinking and mathematical analysis is done on the (relatively simple) model and then the theoretical predictions are compared with the experimental behavior of the real system. A good model simulates nature. If the model yields wrong answers, then one tries again by changing the imagined model until one arrives at a model, the theoretical predictions of which agree well with experimental observation.

Going from the DH model (ions of the same size) to the DH–SiS model (ions of different size), as a model improvement process, precisely follows the above description. Were Zarubin's validity requirement a prerequisite in theoretical modeling, no theory could have ever been devised. In summary, whether the Debye potential is physically valid or not is irrelevant to the physical validity of γ_i as predicted by the DH theory (and DH–SiS).

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Notes

The authors declare no competing financial interest.

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