Reply to “Comment on ‘Negative Deviations from the Debye–Hückel Limiting Law for High-Charge Polyvalent Electrolytes: Are They Real?’”

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ABSTRACT: In their “Comment on ‘Negative Deviations from the Debye–Hückel Limiting Law for High-Charge Polyvalent Electrolytes: Are They Real?’” (hereinafter referred to as “Comment”), Biver and Malatesta challenge my article2 (cited by them as ref 1), arguing that my analysis of experimental data of Malatesta and co-workers reported during the years 1992–2000 (see refs 2, 3, 18, 23, 24, and 26 in Comment) is wrong and so is my conclusion that negative deviations observed by them are not physically real. Here I rebut their arguments and explain why their rejection of my work is unjustified, and why those authors do not in any way prove me wrong. The core of my study and conclusion remains intact: Negative deviations in the case of high-charge electrolytes with $|z| > 3$ do not always happen, and so far, such observed deviations are not convincingly supported by theory.

INTRODUCTION

In a work3 entitled “Comment on ‘Negative Deviations from the Debye–Hückel Limiting Law for High-Charge Polyvalent Electrolytes: Are They Real?’” (hereinafter referred to as “Comment”), Biver and Malatesta challenge my article2 (cited by them as ref 1), arguing that my analysis of experimental data of Malatesta and co-workers reported during the years 1992–2000 (see refs 2, 3, 18, 23, 24, and 26 in Comment) is wrong and so is my conclusion that the negative deviations observed are not physically real. The purpose of this article is to rebut arguments in the Comment and explain why the rejection of my article by Biver and Malatesta is not justified, and why my analysis and conclusion stand on a quite solid physical ground.

Claims of negative deviations from the Debye–Hückel (DH) limiting law (DHL) have been made in the literature occasionally (see, e.g., ref 3, p 472), and they were proven by me to be physically baseless in the case of hydrochloric acid in nonaqueous solvents4 and in the case of sulfuric acid in water.5 The DH theory is based on the Boltzmann (PB) equation in its linearized form (L-PB equation). Furthermore, the lack of fit of theory with experiment in the case of high charge electrolytes has been given special attention (see ref 3, p 548), and again, researchers suggested that theory–experiment fitting problems should be associated with the linearization of the PB equation. However, I have recently demonstrated8 that the difference between the full PB equation and the L-PB equation is very small even with high-charge ions and at practically any ion strength, provided that the activity coefficients are computed with the DH–SiS equations with the appropriate ion-size parameters (ISPs) and that the average mean-field potential of electrostatic ionic interaction is defined as that at $\frac{1}{2}$ charge of the ion atmosphere.

In 1992, Malatesta and co-workers developed an emf measurement method employing a liquid membrane cell that allows measurements at very dilute aqueous solutions, down to concentration of $10^{-6} \text{ m (mol/(kg of solvent))}$.7 For electrolytes with $|z| > 3$, $z_i (i=+,-)$ being the ion charge, they have later reported activity coefficients $\gamma_i$ data that fall below the DHL line,8−11 and they thus have claimed that those electrolytes, due to their highly charged ions, exhibit an unusual behavior—a negative deviation from the DHL. Using standard literature methods based on the Nernst equation12 to evaluate the “standard potential”, $E^0$, and employing the DH–SiS equations, I have recently reported2 that a few 2−3 electrolytes and the 3−3 electrolyte LaFe(CN)$_6$ in the studies of Malatesta et al. appear to, in fact, not deviate negatively from the DHL, and therefore the general conclusion that electrolytes with $|z| > 3$ should deviate negatively is not correct. I also cast doubt on the physical validity of “negative deviations” short of presenting convincing theoretical arguments according to which the electrostatic attractions at very dilute solutions of highly charged ions could be stronger than the conventional coulomb attractions. Biver and Malatesta have now challenged my analysis and conclusions, claiming...
that my analysis is less accurate than theirs and that my conclusions are wrong and based on errors, misunderstandings, and misconceptions. The purpose of this work (“Reply”) is to address the main arguments of Biver and Malatesta and show that those arguments are not justified or, at least, are not proving that my analysis and conclusion are in any way wrong.

**DISCUSSION**

**Meaning of “Negative Deviation”**. Biver and Malatesta declare that my thought derives “from a misunderstanding of what negative deviations really are.” They then explain that the “negative deviations exist only at finite (even though low) concentrations and do not imply a violation of the LL in the limit of infinite dilution; simply, in these cases the LL is attained at dilution levels beyond those accessible to experiments.” Yet, why nondeviations start to become deviations at some concentration, and why those deviations “turn back” (see, e.g., Figure 1 of Comment1) to become nondeviations, is unexplained. It definitely looks like an unphysical behavior. In mathematical terms, it means that starting from zero concentration, the derivative \( \frac{d(\ln \gamma_c)}{d(t^{1/2})} \) is first constant, reflecting the slope of the DHL, then becoming more negative, then less negative than that of the DHL. In fact, adherence to the DHL is not following the straight line of the limiting law but, at decreasing concentration, continuously approaching that line asymptotically, so in the conventional case, the derivative is gradually becoming more negative at lower concentration until approaching the slope of the DHL (i.e., the tangent of the line of the DH “extended equation”, DHEE, at zero concentration), which has the largest negative value of the derivative. If a negative deviation occurs (instead of the expected positive deviation), then one would expect it to occur all the way to infinite dilution and the qualitative trend of the \( \frac{d(\ln \gamma_c)}{d(t^{1/2})} \) derivative would be expected to be the same as that of the positive deviation except that it would carry the opposite sign. In the other direction, going to more concentrated solutions, the deviation—positive or negative—should be gradually stronger, thus, more diverting from the limiting law, positively or negatively. So, if the deviations shown by Malatesta are physically real, there has to be a totally different explanation to that rather than “improving” the treatment of the primitive model by considering the full PB equation, or a parallel treatment, or resorting to advanced integral equations thereby including high-concentration core effects. The observation by Biver and Malatesta that the negative deviation in their studies is such that occurs only at finite concentration should have been made clear in the publications of Malatesta et al. in 1992–2000. Despite this, it still is a violation of the DHL, though. In the “pure” case of the DH theory, data cannot fall below the DHL.

The above is such an important issue in the current dispute that it demands more elaboration. Figures such as Figure 1 of Comment1 shown for LaFe(CN)\(_6\) have been given in other cases in the reports of Malatesta and co-workers (see refs 2, 18, 23, and 26 in Comment1). Such a presentation is quite misleading; it is done to emphasize data at very low concentration and (relatively) deemphasize those at higher concentration, but the limiting law is conventionally presented as a straight line of the function \( \ln \gamma_c vs m^{1/2} \) or \( I^{1/2} \), not \( \ln \gamma_c \) against m on a logarithmic scale (as in Figure 1 of Comment1). I have, therefore, taken the liberty to reconstruct Figure 1 of Comment1 to present the data and the DHL as \( \ln \gamma_c vs m^{1/2} \). This is done in Figure 1 of this Reply. It is very clear from Figure 1 that the above statement of Biver and Malatesta on the meaning of negative deviation is not supported by their data. In fact, there is no sign that initially the experiment follows the limiting law and then it starts deviating negatively. From “point zero,” the experiment appears to deviate strongly from the DHL. It is inconceivable that the difference between the two curves of Figure 1 could be reconciled by employing for the theoretical calculation the full PB equation instead of the L-PB equation.

As related to the above, the argument that \( d^2(\ln \gamma_c)/d(I^{1/2})^2 \) does not have to necessarily be positive is strange and unconvincing, at least unsubstantiated at any level of physical reality. Biver and Malatesta argue that the second derivative is always positive in the DH extended equation (eq 1 in Comment1), but it could be negative in “the complete solution (by numerical methods) of the PB equation (IPBE)...at \( I^{1/2} = 0 \).” I challenge Biver and Malatesta to prove that from a pure physics standpoint (not as a mathematical artifact) this is a viable case, i.e., that the second derivative is negative in IPBE at \( I \to 0 \). Even if they do, IPBE will remain inadequate for “correcting” for the deficiency of the L-PB equation (see below, and especially Appendix A).

**Use of DH–SIS for the Analysis: Why?** Biver and Malatesta do not recognize the advantage of DH–SIS in addressing not only the ionic behavior at very dilute solution but also the overall ionic behavior, its agreement with theory, and its compatibility with data from other sources [for example, of \( \text{LaCl}_3 \) (Figure 3 in ref 2) and \( \text{K}_3\text{Co(CN)}_6 \) (Figure 4 in ref 2)]. In all cases, DH–SIS fits with experiment with very reasonable ISPs—the co-ion \( b \) diameters, \( b_+ \) and \( b_- \), and the counterion’s contact distance \( a \). Instead, theories used by Malatesta and co-workers are less accurate than DH–SIS because of using only one ISP (“\( a_1 \)”), e.g., Bjerrum ion pairing theory, or—even worse—are empirical and use multiple adjustable parameters, e.g., Pitzer’s equation (with six adjustable parameters). The fit obtained using the former theories is by adjusting \( a \) (see, e.g., Figure 1 of Comment1 with \( a = 0.65 \) nm; thus, not a true ISP), and it is inferior to the DH–SIS fit where \( a, b_+ \), and \( b_- \) are more realistic ISPs, so, more correctly representing ion–ion contact distances in solution. Also, no
information is provided by Biver and Malatesta on the theoretical functions used for the fit in the figures of Comment,1 so there is no way to check and analyze the theory, or theories, used by Malatesta and co-workers to fit their data.

**Full PB Equation vs L-PB Equation.** Biver and Malatesta argue that there is advantage in replacing the L-PB equation by the full PB equation, to get more accurate representation of the real behavior of electrolytes in solution at very high dilution, because—they claim—at such high dilution, the use of the L-PB equation is not justified. However, the major literature on electrolyte solutions claims that, at very high dilution, the L-PB equation is physically correct; that is, the L-PB equation is as good as the nonlinearized PB equation when ion strength is very small.3,12,13 Deviations between the two equations, when advocated, are related almost always to effects existing, or assumed to exist, at high concentration. There, the truncation of the series expansion of the exponential part of the PB equation after the second expansion term is believed by scholars to result in missing the contribution of higher terms.3,12,13 (But as I have recently shown, including higher terms does not contribute much even at relatively high concentration.) The DH theory becomes gradually more accurate as dilution increases, up to a point at which the DHLL is a very effective representation of the physics of the system. Even then, being a linear function of ln γa vs 1/2, DHLL is unphysical and therefore, in principle, incorrect no matter how high the dilution.

Likewise, the argument of Biver and Malatesta that even where one expects the DHLL to be effective, a negative deviation is theoretically possible, is false. Their views on this matter are not supported by reality. I challenge Biver and Malatesta to show how IPBE or Bjerrum, or any other theory mentioned by them, gives a negative deviation while being only based on coulomb forces. This process of fitting data with theory has to be fully exposed to allow a legitimate scrutiny by peers. The theories based on which Biver and Malatesta arrived at their fit (as in the figures of Comment1) are not described and discussed in Comment1, so it is impossible to check (and perhaps challenge) the computation. The “explanation” as if the ionic atmosphere is different for the nonlinearized PB equation and for the L-PB equation at very high dilution, is not based on any serious scientific rationale or physical evidence. The ionic atmosphere is not a “hypothetical ionic atmosphere” when using the L-PB equation more than it is “hypothetical” when using the full PB equation (in fact, it is far more hypothetical in the latter case; see Appendix A). At least, this is the case at very high dilution. As to the reference to Guggenheim, his numerical integration of the PB equation is not clear and transparent to accept it as a gospel. (See more on this in Appendix A.)

**Evaluation of the “Standard Potential”.** Biver and Malatesta do not agree that at least some of the measurements of Malatesta and co-workers with high-charge electrolytes could be interpreted, through better extrapolation of E to E°, as adhering to the DHLL. They dismiss my extrapolation as being based on "empiric methods". However, use of the Nernst equation26,27 is a common way in the literature to evaluate E°, as done, for example, by Harned, Hamer, and others during the 1930s (see, e.g., references in refs 4 and 5, and, more generally, ref 3, pp 430–433, 457–461, and 568–573). Biver and Malatesta claim that E should not be directly extrapolated to E° (in their notation, E*) because of the instability of E values and the existence (?) of many values for E° (or E*). Therefore, they argue, one should better extrapolate γa to 1 (or ln γa to 0); this is a very strange argument in view of the need to have E° (E*) for calculating γa. See more on this below. Biver and Malatesta also get into petty issues such as the slight drift of the slope of 3–3 and 2–3 electrolytes in Method 2 (Figure 1b in ref 2), not recognizing that nonetheless the two methods (1 and 2) mutually agree nicely (so if one dismisses 2, one may use 1).

Furthermore, Malatesta has derived E° (E*) by using “theories” that are “empirical” through being based on numerical mathematical solutions of inadequate equations (see Appendix A) and/or including a as the sole ISP and achieving fit with experiment by adjusting a without any physical guidance. Biver and Malatesta mention many theories that they supposedly have used (DHT, IPBE, DHLL+B2, Bjerrum, Gronwall–La Mer–Sandved, and even theories based on advanced integral equations, such as HNC).1 All those theories have various pitfalls and deficiencies of their own, which cause them to not fit with experiment at an adequate degree of accuracy (see discussion in ref 14, pp 407–420, on IPBE, Bjerrum, and Gronwall–La Mer–Sandved). For example, as I have mentioned previously,15–17 and as is well-known in the literature (see cited references in ref 15), the primitive model (PM) based HNC (and similarly, Outhwaite’s MPB and SPB, MSA, and other advanced integral equation theories) fails at low ionic strength and cannot be used for extrapolation to infinite dilution. HNC has been mostly shown to fit not with real electrolytes but with Monte Carlo (or molecular dynamics) simulations of electrolyte solutions, which become more inaccurate at lower ion density. Moreover, the fit has been almost always examined for electrolyte systems of only univalent anions, usually, of the 1–1 and 2–1 valence families. (The fit with 3–1 and 2–2 electrolytes was poor, or poorer.23,25). Therefore, HNC, MPB, MSA, etc., should be avoided in extrapolating data to zero concentration, especially for high-charge electrolytes such as those of the 2–2, 2–3, and 3–3 valence families. Advanced integral equation theories are primarily meant to fit with activity coefficient and osmotic coefficient data at high ionic concentration, through including the contribution of the core potential (of non-electrostatic, London-type dispersive forces), and they are notoriously less effective at dilute solutions, let alone highly dilute solutions. In this context, one should mention the very recent analysis of electrolyte solutions using MPB and SPB, and its comparison with MC simulations and with some experimental data of single-ion activities;18 the authors admit that the PM is missing some important physical features and, therefore, its fit with experiment is limited and is only qualitative in nature.

In the example of Comment’s Figure 1,1 the fit is with IPBE with a = 6.5 Å. This arbitrary value means that (a) the radius of La3+ (crystallographic value, 1.06 Å) and that of Fe(CN)63− are the same, and (b) this same radius is 3.25 Å. But another “theory” may give a good fit with experiment, with a = 5 Å, a = 7 Å, or any other a value. Would ion size, therefore, vary with the theory applied? Obviously, a in the fits of Malatesta and co-workers is only an arbitrary fitting factor, not an ion-size parameter of physical validity.

**Pitzer Equation: Was It Used or Not Used by Malatesta et al. for Extrapolating E to E°?** Biver and Malatesta state1 that “Fraenkel supposes that...our extrapolation to infinite dilution relies on the semiempirical Pitzer equation.... Yet, he was mistaken...the extrapolation to infinite dilution of the
relative activity coefficient did not rely on the Pitzer equation. The latter was used instead for interpolation purposes...reported only for the reader’s utility”. However, the Malatesta works teach otherwise. Thus, in ref 8, we find (the underlining is mine, for emphasis): “Tables I, II, and III give the original data as cell potentials vs. molal concentrations for the different runs, together with our direct estimates (based on Pitzer’s equation, ion interaction theories and additivity relationships) for E*...” And then, in footnote d of Table II: “Best fit value of E* relevant to the specific run...“ found by least-squares with Pitzer’s equation.” In ref 26 of Comment,1 footnote a in Table 1 states that (underlining is mine again) “The activity coefficients and E* labeled as A and B refer, respectively, to the extrapolation to infinite dilution suggested by Pitzer’s equation (A) and by IPBE (B).” In other publications of Malatesta et al. (see refs 3, 18, 22, and 23 in Comment;1 e.g., Table IV in ref 22), the Pitzer equation was used to generate (and smooth) the “relative ln γζ” curves that later were adjusted to fit the “absolute reference points” (see below) as a part of the (indirect) extrapolation process.

I rest my case.

Effect of the Number of Electrolytes Exhibiting “Negative Deviation”. Biver and Malatesta claim that the negative deviation is a solid behavior and has physical meaning, based on the fact that their group conducted many experiments with a large number of different electrolytes that show such a behavior. They blame me for ignoring all the other cases that they have reported. However, the fact that so many electrolytes exhibit an apparent deviation that is negative, and they do so “without violating the limiting law” (1), is not a proof of the physical validity of such a deviation. I could not analyze all Malatesta’s experiments because of a variety of reasons: (a) the analysis is very time-consuming, (b) some systems do not seem to follow the DH—SiS condition of bζ < a < bζ, (c) many systems do not have clear ISP values that one can rely on (e.g., what is the size of the [Co(en)]3+ ion?), and (d) many data series, for whatever reason, are not “cooperating” with my analysis (but see Appendix B for a plausible explanation!). My approach was, instead, to examine only a few systems with shared ions, some claimed by Malatesta to not deviate, others to clearly deviate negatively from the DHLL; I chose some 2–3 and 3–3 systems that exhibit deviation, along with 1–1 and 3–1 systems that do not exhibit deviation. For the electrolytes examined, fixed ISP values were used for the same ion regardless of the counterion. I thought—and still think—that suffice it to show that all those chosen systems (save LaCo(CN)6 but see Appendix B) do not in fact deviate negatively, in order to cast doubt on the sweeping conclusion of Malatesta and co-workers that all systems with \( |z_{ζ}\>1 > 3 \) deviate negatively from DHLL.

Case of LaFe(CN)6. Struggling with the difficulties of directly extrapolating E to E0 in the case of LaFe(CN)6 (difficulties typical to the high-charge electrolytes of the 2–2, 2–3, 3–2, 2–4, and 3–3 valence families), Malatesta and co-workers used a complicated and cumbersome approach to derive E0 (E*) indirectly, by, as mentioned above, extrapolating ln γζ to zero concentration. They obtained “relative values” of the activity coefficient as ln γζ = Δ + ln γζ* and they used a “theory-assisted extrapolation” to determine Δ as Δ = ln γζ − ln γζ* (theory), where Δ = lim Δ′ at m = 0. Δ was determined by shifting the curves of ln γζ vs m to fit with two “absolute reference points”. The latter were obtained by using the principle of thermodynamic additivity of cells with common ions, allowing one to indirectly derive E* from the more easily derived E’s of the parallel KCl, LaCl3, and KFe(CN)6 cells.

Two problems are associated with the above approach. First, if one can avoid the troublesome direct measurement of LaFe(CN)6 (see ref 8) by obtaining the behavior of this salt as a sum of behaviors of the La3+ and Fe(CN)3− ions, from their respective E’s in other salts, why bother at all with the direct measurement of the 3–3 salt? Instead of two “absolute reference points”, derive 10 or 100 such points while covering the entire range of concentration of 10−6−10−2 mol. Second, the “absolute reference point” of LaFe(CN)6 at m = −3.35 is well inside the range of “negative deviation” (see Figure 4 in ref 8, and Figure 3 in ref 9). How could this happen when the additive thermodynamic process of deriving E* is based on salts that do not exhibit negative deviation? Maybe if Biver and Malatesta correct their data of KCl, LaCl3, and KFe(CN)6 using my analysis (see it for the latter two salts in ref 2), they will find that the negative deviation of LaFe(CN)6 in fact, does not happen.

Considering all of the above, the apparent discrepancy of data below 10−4 mol/kg in Figure 4 of ref 8 is not convincing as a real problem even though it is “corrected” in ref 9 (see Figure 3 there) by a set of “improvements” of the measuring method (see more on this in Appendix B). It is not clear what the “improvements” of ref 9 indeed do. However, applying the analysis of my method2 to the “improved” data did not yield a ln γζ−m line that agrees with DHLL. Yet, the results of ref 8 are almost perfectly adhering to my method, they fit well with the DH−SiS equations, and they thus exhibit the classical behavior expected from a 3–3 system, with no negative deviation from the limiting law. For ease of the comparison of my analysis with that of Malatesta et al.,3 I provide in this Reply Figure 2 that presents the result of my analysis on a scale of log γζ against log m. The data are those used in Figure 7a of ref 2. Figure 2 exhibits the same quality of theory—experiment fit as that of Figure 1 of Comment,1 but using data...
of ref 8, not ref 9, and the theoretical curve of DH−SiS, not that of Malatesta’s IPBE. Also, as in Figure 1 of Comment, Figure 2 includes the DHLL line. I invite Biver and Malatesta to inspect Figure 2. Then, perhaps rather than claiming that the results of ref 8 are less accurate than those of ref 9, or inaccurate (and they are, in fact, due to incorrect extrapolation!), they could reexamine the results of ref 9 and try to explain (perhaps while considering my arguments in Appendix B) why those results do not agree with DHLL.

"Negative Deviations": Physically Real or Unreal? In my opinion, the only way out from this issue of the apparent negative deviations is to look for the reason(s) why experiment does not obey theory at low concentration when ions are highly charged, and not a priori accept the concept of “negative deviation” as a physical must. There are many directions one may pursue, from experimental inaccuracies and artifacts (just compare ref 9 with ref 8 to learn how sensitive the experimental method and setup of the Malatesta group are; also, see Appendix B), through details of the materials used (again compare the two above references), to even slight deviations of the ion charge from solid integer number (see Appendix C). The participation of H+ and OH− ions at very low electrolyte concentration, where the contribution of water dissociation to the ionic composition in solution becomes significant, may also affect the measurements. Furthermore, issues relating to the membrane electrode and its affinity to high-charge ions and ion pairs, should also be inspected. During the measurement, contamination and blockage of the membrane may be a serious issue causing diffusional and osmotic pressure variations, and other effects, perhaps even variations of the membrane’s electronic and electric properties. The varying standard potential from point to point (or at least between consecutive experiment series) should also be scrutinized, and that may be a problem especially at low concentration and with high-charge ions. In Appendix C I show a freshly conducted analysis of the 2−2 MgSO4 system, with data reported by Malatesta and co-

Figure 3. log \( \gamma_\pm \) vs \( I^{1/2} \) for MgSO4 in H2O at 25 °C. (a) Entire behavior. Empty diamond symbols (excluding the one at \( I = 0 \)) represent experimental data: Upper seven data points, corrected values from ref 23 of Comment; lower data points, literature values at \( m \geq 0.1 \). Full line, theoretical behavior computed by DH−SiS; dashed and dashed-dotted lines, computed single-ion behaviors of Mg2+ and SO42−, respectively. (b) Behavior at moderate ion strength. Full diamond symbols are the same as empty diamonds in panel a, full line is as in panel a, and dashed line is the limiting law. (c) Same as panel b at very low I. (d) Same as panel c but with \( \Delta^* = 0.10 \). See text.
workers (ref 23 in Comment¹), from which one may learn more on the possible nature of the observed negative deviation.

■ CONCLUSION

Biver and Malatesta strongly argue that the negative deviations from the limiting law, which they have observed in many experiments of emf measurements of high-charge electrolytes, are physically valid. But there are other ways of explaining why their data for high-charge electrolytes do not adhere to the DHLL. At least with some of those electrolytes, the negative deviations appear false, and, instead, the electrolytes are shown² to fit nicely with the simple and fully transparent DH–SiS theory, using adequate ISPs. One only needs to perform the extrapolation of $E$ to $E'$ more effectively, and it would also be valuable to try to improve as much as possible the quality of the experiment. If the negative deviations from the DHLL are explainable by reasonable arguments, and those deviations vanish through simple treatments (e.g., better extrapolation of $E$ to $E'$), one should avoid concluding that the deviations occur due to real physical factors and/or due to theory inadequacies. Especially, one should not claim that such apparent deviations prove that the L-PB equation is less accurate than the full PB equation at very dilute electrolyte solutions.

■ APPENDIX A

Peculiar Behavior of 2−2 Sulfates—1: Difference between Full PB and Linearized PB Equation

Biver and Malatesta mention¹ two articles by Guggenheim, from 1959 and 1960, on numerical integration of the PB equation (the respective refs 4 and 28 in Comment¹) and raise the question, why is my analysis⁶ of the full PB equation not coherent with that of Guggenheim (and those of others cited by him)? A few comments are in order on Guggenheim’s computations:

(1) Guggenheim’s method of computation of the full PB equation is not quite easy to follow, hence scientifically judge; for one thing, it is based on assumptions outside the mere solution of the PB equation, such as using a continuous charging process in the integration rather than applying the conventional method of including the charging process (of Güntelberg or Debye) in the theoretical development. It is not clear how Guggenheim’s integration process is affected by his charging assumption, but one may reasonably guess that Guggenheim would have not made that assumption if it was not important for his computations.

(2) In his 1960 paper, Guggenheim devoted his effort toward the 2−2 electrolyte system, stating that the “procedure here used for 2−2 electrolytes is not applicable without modification to 3−3 electrolytes...” (ref 28 of Comment¹). (This could read better, as Guggenheim most probably intended, as the “procedure here used for 2−2 electrolytes is not applicable to 3−3 electrolytes without modification”—D.F.). Malatesta and co-worker claimed that they were able to apply their IPBE numerical method to the 3−3 electrolyte LaFe(CN)$_6$ (e.g., Figure 1 in Comment¹), but their method and results have so far remained unpublished (see Comment¹).

(3) Since Guggenheim’s analysis was done with a constant $a$ of 4.0 Å, as a sole ISP, a legitimate question is how the choice of $a$ affects the outcome of the analysis; according to Biver and Malatesta (Figure 2 in Comment¹), there is some a value between 4 and 8 Å (perhaps, 7 Å) at which the numerical computation for 2−2 electrolytes merges with the DHLL. This casts doubt on the entire merit of the effort to solve the PB equation in its entirety in attempt to improve over the L-PB equation, based on $a$ as a sole adjustable parameter, due to the high sensitivity of the solution to the choice of $a$. At least the vulnerability of the computation to the value of $a$ has to be acknowledged as a serious problem, let alone using a single ISP ($a$). I have advocated⁶,¹³ that using only one ISP ($a$) instead of all three ($b_s$, $b_n$, and $a$) is a very serious drawback in the analysis of activity coefficients based on the PB equation, in general, and specifically in the DH theory (i.e., DHEE).

(4) I have difficulty understanding why the potential applied by Guggenheim (following Müller) is $\Phi = A \exp(-kr)/r$, whereas in the standard DH development¹⁰ it is $\Phi = A \exp(-kr)/r$. At $I = 10^{-4}$, in water at 25 °C, the former potential is 300 larger than the latter, and at $I = 10^{-6}$ it is 3,000 larger; is that potential still within the $\Phi \ll 1$ restriction? At least, there appears to be some inconsistency here, if not a real discrepancy.

(5) Even more difficult for me to understand is why Guggenheim of 1959 and 1960 ignored and contradicted Guggenheim of 1949 who clearly stated (in his 1949 book¹⁴ and then late Sir Ralph Fowler, on page 409) that “We shall, however, not go further into the details of these solutions [i.e., of Müller and of Gronwall–La Mer–Sandved—D.F.] of the Poisson–Boltzmann equation because they are not self-consistent...the integrability conditions...are not satisfied.” And later, on page 409, Guggenheim stated that “...in the more general case of ions of differing numerical valencies...the conditions of self-consistency...inevitably fail far more completely than in the symmetrical case. It must be regretfully admitted that this most promising method [of solving the full PB equation—D.F.] cannot be carried logically beyond the first approximation of Debye.” How this well-known reality has changed in Guggenheim’s mind during the 10 years between 1949 and 1959, is not clear. If his 1959 and 1960 calculations were not indeed “carried logically,” one would expect a comment on this in his publications. But such a comment is absent.

Anyway, the analysis of Guggenheim and others is very complex, cumbersome, tedious, and electrolyte-type-dependent; and eventually, it is not clear where the results are taking us. In contrast with the development of Guggenheim and others cited by him, I have taken the simple and straightforward approach of analyzing the full PB equation by presenting it as an expansion series of the exponent (Boltzmann’s probability function), and examining the contribution of the expansion terms beyond the linear form of the equation; this was done to quantitatively assess how much we lose by dropping those extra terms. My analysis⁶,¹¹ unlike that of Guggenheim and that of Malatesta, is fully transparent and relatively simple; it has two major assumptions:

(1) The L-PB-equation-based DH–SiS development is a good approximation for the theoretical $\gamma_{\gamma}$-vs-$I$ behavior, extending beyond the old DH theory, but the analysis must apply ISPs that are typical to each electrolyte valence family.

(2) The average mean-field potential of electrostatic interaction has to be chosen as that at $r_{1/2}$, the distance from the origin (chosen-ion center) “cutting” the ion atmosphere into two spherical parts of equal charge.

My analysis has resulted in the conclusions that (a) the applicability of the L-PB equation is not ion-charge-dependent, and (b) the L-PB equation is a good approximation of the full
PB equation practically at any ion strength within the limitation of the ion atmosphere model.

These conclusions are corroborated by the good-to-excellent fit of the DH–SIS expressions with numerous electrolytes of practically all the known valence families at broad concentration ranges and, in select cases for which data are available, at broad ranges of temperature and of the (solvent’s) dielectric constant. In contrast, the analysis of Malatesta (and Guggenheim and others) seems to take us backwards in terms of our ability to theoretically comprehend and explain the behavior of strong electrolytes in solution.

### APPENDIX B

**Difference between Malatesta’s Investigations of LaFe(CN)₆ in 1994 and 1995**

In this Appendix, I attempt to address a reviewer’s concern regarding the decision of Malatesta in 1995 to change his experimental system of 1994. To this end, I provide here a more thorough discussion (and critique) of the comparison between the older and newer measurements of LaFe(CN)₆ by Malatesta and his co-workers.

In 1995, Malatesta “revised” the activity coefficients of LaFe(CN)₆ obtained by his group in 1994. In the 1995 investigation, Malatesta employed a new electromotive cell “entirely made of PTFE with the electrodes assembled in a different way which does not require the use of any gel in the inner section; the membrane composition has also been improved.” And further, “In the previous investigation, the solvent was 2-nitrophenyl acetyl ether (NPOE). However, (TDA)₃Fe(CN)₆ does not actually require any solvent, since it is a viscous liquid at ordinary temperatures. Therefore, in the present study [of 1995—D.F.], the (TDA)₃Fe(CN)₆ membrane was composed of pure (TDA)₃Fe(CN)₆ without any solvent. Moreover...the cell section...the ferricyanide electrode was assembled inside a machined PTFE shaft without the presence of the agar jelly...”

Thus, the main “improvements” of the newer (1995) investigation were as follows:

1. cell entirely made of PTFE;
2. no agar jelly in the inner section;
3. improved membrane composition;
4. no solvent.

With regard to (2), the 1992 work of Malatesta and Carrara clearly stated that there “are several indications that the AgIAgCl electrode slowly reacts with the agar gel so that steady-state rather than equilibrium potentials are obtained. To avoid the inelegance, a slightly different design of membrane electrode was tested...with no use of gelled solutions... The results we obtained were practically the same.” This tends to eliminate (2) as an “improvement”. While it is not clear how (1) improved the experiment, it is even less clear what the improvement of (3) was. This leaves us with “improvement” (4)—No use of a solvent. But why is avoiding the solvent an improvement?

In all fairness, one remains puzzled by all the “improvements” Malatesta introduced in his 1995 investigation. Those “improvements” were carried over to the subsequent studies of ferricyanides and cobalt cyanides as performed by the Malatesta group thereafter. Were they real improvements? Judging by the experimental results of LaFe(CN)₆, one arrives at two major conclusions:

(a) Apart from some differences in the very dilute region, as compared to the older results (of 1994), the experimental data of 1995 appear to be almost identical to the older ones (see Figure 3 in the 1995 work).

(b) While in both cases (1994 and 1995 investigations) Malatesta has shown negative deviations from the DHL, the fit of experiment with theory was done using empirical methods; for example, Bjerrum’s theory (BT line in Figure 3 mentioned above), with $a = 0.667$ nm. In this regard, Malatesta’s own words (in the 1995 work) are of special importance: “As Fig. 3 shows, the new values of the activity coefficients do not present unreasonable bending below $10^{-4}$ mol·kg$^{-1}$ found in the earlier study. On the contrary, to a good approximation, they recall the behavior expected for a population of hard charged spheres in either IPBE and Bjerrum’s views. This is very interesting finding, since it would mean that LaFe(CN)$_6$ behaves in dilute solution like a non-associated electrolyte or like an electrolyte “associated in Bjerrum’s sense,” which is the same thing (since Bjerrum’s ion pair is in practice a mathematical trick to shunt off the complicated distribution functions in the primitive model, and is expectedly unfit if true association occurs).”

In view of the above Malatesta’s reflections, what is the theoretical value of fitting Bjerrum’s theory to the experimental data? In what way is Bjerrum’s “mathematical trick” helping explain theoretically the observed negative deviations from the limiting law?

One is thus forced to conclude that the “improved” experimental data of the activity coefficient in the LaFe(CN)$_6$ case have not advanced the overall argument of Malatesta with regard to the negative deviations; those deviations were observed by him in the 1995 investigation but also in his 1994 investigation. However, the fact that the 1994 results lent themselves to the analysis of ref 2 (“my analysis”), whereas the 1995 results did not, is prompting me to interpret Malatesta’s investigations differently than the way he did, as discussed next.

In view of all the above, I speculate that the main difference between the 1994 and 1995 results was avoiding the solvent in the 1995 measurements. It is plausible, however, that the solvent was actually an absolute necessity in the experimental system. (TDA)$_3$Fe(CN)$_6$ is an ionic liquid (IL)—a liquid salt that is a strong electrolyte (i.e., made of “full” ions, here TDA$^+$ and Fe(CN)$_6^{3−}$). Because of the long hydrophobic alkyl chains of the dodecyl segments of TDA$, the IL rejects water, but it does this incompletely because it is also an ionic medium. The shielding of the IL from water due to the long alkyl chains is not entirely effective, but dissolution of the IL in an organic solvent (such as NPOE), due to those alkyl chains, is complete. When the IL is dissolved in NPOE, a strong electrolyte solution forms, although a solution of an organic nature, so the IL is most probably in the form of molecular ion pair. What the solvent—a non-ionic organic medium—does when surrounding the IL molecules, is preventing the aqueous solution (of LaFe(CN)$_6$) from infiltrating (“invading”) the IL membrane. This is the reason why the experiment employing (TDA)$_3$Fe(CN)$_6$ dissolved in NPOE is successful: NPOE, which is entirely immiscible in water, provides full protection to the (TDA)$_3$Fe(CN)$_6$ membrane, thereby keeping the integrity and selectivity (for Fe(CN)$_6^{3−}$) of the membrane. When the IL is used as “neat” salt, its performance as membrane becomes compromised, and this is especially pronounced in the case of 3–3 ferricyanide electrolytes. There is “invasion” of the aqueous LaFe(CN)$_6$ solution into the organic IL, and the system effectively becomes (as membrane) [(TDA)$_{3−x}$La$_x$] LaFe(CN)$_6$ (x being a fraction), which is a different membrane ±
than \((\text{TDA})_3\text{Fe(CN)}_6\) and has different electronic and electric properties. It is reasonable that the "new" membrane causes the emf values to be higher than the correct ones for the LaFe(CN)_6 system, especially at very dilute solutions, and this may be the reason for the "negative deviations." Furthermore, the same trend of higher apparent emfs and activity coefficients in the dilute region would result from the depletion of LaFe(CN)_6 in the electrolyte solution due to its "invasion" into the membrane. 1–3 ferricyanides may not exhibit a strong deviation because of a mediating effect of the univalent (K+ cation compared to La3+ (perhaps since K+ is on both sides of the ferricyanide membrane or due to the lesser tendency of potassium ferricyanide to form ion pairs in the membrane).

The fact that LaCo(CN)_6 exhibits a behavior similar (in fact, almost identical) to that of LaFe(CN)_6 is hardly surprising since the measurements of LaCo(CN)_6 were done according to the method of 1995, not 1994, i.e., without the NPOE solvent. Like \((\text{TDA})_3\text{Fe(CN)}_6\) \((\text{TDA})_3\text{Co(CN)}_6\) is an IL at ambient conditions, and its membrane behaves almost the same as that of the \((\text{TDA})_3\text{Fe(CN)}_6\) membrane. In conclusion, the fact that LaCo(CN)_6 like LaFe(CN)_6 exhibits negative deviation is not a "corroboration" of the "phenomenon," only an indication of a seemingly defective measurement method used in both cases (i.e., the method of 1995).

Finally, it should be noted that there is no clear and objective reason to prefer the modified method of 1995 over the unmodified method of 1994. According to Malatesta et al, the 1995 method is better only because it eliminated the "unreasonable bending" of the LaFe(CN)_6 curve of 1994. But the perception of "unreasonable bending" is a direct consequence of the theoretical predictions of Malatesta, which I contest as being incorrect. Instead, based on behaviors such as that of Figure 2 of this Reply, the unmodified method of 1994 may be concluded to be the better method. If so, then the quality of the experimental work of Malatesta et al. between 1995 and 2000, when using the method of 1995, may have been compromised.

**APPENDIX C**

### Peculiar Behavior of 2–2 Sulfates—2: MgSO_4 as a Test Case

Here I present—in Figure 3—an analysis of the 2–2 sulfate system MgSO_4 in water at 25 °C. This analysis is very similar to those of the other electrolytes in my work now under dispute. Measured data at \(m < 0.1\) (mol/kg of solvent)) are from ref 23 of Comment, and, for convenience, they are only those of Ser. 4 (but Ser. 5–7 give similar behavior), corrected for better extrapolation of \(E\) to \(E^\circ\) (with \(E^\circ_{\text{ave}} = 0.127873\) V). Experimental \(\gamma_c\) values at \(m \geq 0.1\) are from ref 12 (p S02). In this case, my analysis indeed indicates small apparent negative deviation from DHL, occurring at very high dilution.

Figure 3a depicts the full-scale behavior of \(\gamma_c\) vs \(m^{1/2}\). The fit of data (at \(m < 0.1\), corrected; at \(m \geq 0.1\), as is) with DHL–SiS is very good all over the ion strength range up to \(I = 10(1)\), but the broad scale does not allow a scrutiny of the very low \(I\) data. In Figure 3b, the behavior is shown at low \(I\), up to \(I = 1\), where data generally follow the predicted DH–SiS curve but are a bit lower than expected; the fit with DHLL appears fair. Further focusing on the very low \(I\) below 0.03, Figure 3c, reveals a negative deviation from the DHLL, and also, of course, from DH–SiS. This is in accord with the claims of Biver and Malatesta but is subject to the extent of accuracy of data.
I am indebted to Biver and Malatesta for alerting me to my inattentive wrong use, in ref 2, of the term “electrochemical potential” instead of “electromotive force” (emf); I thank them also for correcting my inattentive wrong statement in ref 2, that $E^\circ$ is $E$ at zero concentration.

**REFERENCES**


