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The Activity Coefficients of High-Charge Electrolytes in Aqueous Dilute Solutions

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Abstract

We examine in detail the activity coefficient of higher-charge electrolytes, which, in dilute solutions, can display negative deviations from the Debye–Hückel limiting law instead of the usual positive deviations typical of lower-charge electrolytes. This fact is of considerable relevance for scientists concerned with extrapolation to infinite dilution of thermodynamic and kinetic quantities. It is shown that this "strange" behavior originates merely from the electrostatic interactions between each ion and all other ions, with no necessity of hypothesizing the presence of chemical association; these negative deviations, indeed, are predicted even at the level of the "primitive model" (ions assumed as charged, unpolarizable, rigid spheres inside an unstructured, isotropic, dielectric fluid). Three different approximations for the behavior of the primitive model of low-charge and high-charge electrolytes are tested, in addition to the Debye–Hückel theory; i.e. IPBE (a numerical accurate integration of the Poisson–Boltzmann equation), the Mayer theory of the electrolytes in the so-called DHLL + B2 approximation, and the Bjerrum theory. In the Supporting Information, the fundamentals of the respective algorithms are reported, and the effects produced by the differences of size between cations and anions, are also examined.

Keywords Activity coefficient · Electrolyte solutions · Debye–Hückel theory · Bjerrum theory · Mayer theory

1 Introduction

In 2018, Fraenkel published a paper [1] that reexamined the activity coefficients of several high-charge electrolytes using his DH-SiS theory [2]. He reached the conclusion that the negative deviations from the Debye–Hückel limiting slope (LL), which have been observed for many years in dilute solutions (ionic strengths, $I < 10^{-2}$ mol·kg^{-1}) of

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2–2 [3–7], 2–3 [8, 9] or 3–2 [10, 11], and 3–3 electrolytes [12], were presumably not real. DH-SiS, like the Debye–Hückel theory (DH), is based on the primitive model (PM: rigid unpolarizable charged spheres inside a continuum, isotropic dielectric medium); the principal difference consists in the fact that while DH adopts the restricted primitive model (RPM), where all spheres have an identical size a, the DH-SiS theory is able to account for the different sizes of the cation and anion. Both DH and DH-SiS adopt a mathematical-statistical approach based on the Poisson–Boltzmann equation (PB) in its linear approximation (L-PB), and by consequence neither DH nor DH-SiS are able to predict activity coefficients that deviate negatively from the LL in the dilute regions. Fraenkel disputes that it is possible for the RPM and PM to predict the negative deviation of the high charge electrolytes since the L-PB always predicts positive deviations. He argues that at extreme dilution levels the only solute–solute interactions that do not vanish are the electrostatic ones, thus PM necessarily becomes a correct representation of any electrolyte solution; *ergo*, negative deviations should not exist.

Biver and Malatesta proved that Fraenkel's reexaminations of past experimental data on high-charge electrolytes were affected by basic errors [13]. Fraenkel rejected their conclusions in a reply paper [14] in which he provides a plot based on incorrect data. In their turn, the arguments of [14] are rejected in Sect. 7 of the electronic supplementary information (S.I.) of the present paper. The definitive conclusion is that the negative deviations in the dilute region are a non-questionable experimental reality for a number of highly charged electrolytes, MSO_4 (M = Mg, Ca, Sr, Zn, Cd, Co, Ni, Mn), $M_3[Fe(CN)_6]_2$ (M = Mg, Ca, Sr, Ba), $M_3[Co(CN)_6]_2$ (M = Mg, Ca), $[Co(en)_3]_2(SO_4)_3$ (where "en" denotes ethylenediamine), $La_2(SO_4)_3$, $La[Fe(CN)_6]$, $La[Co(CN)_6]$, $[Co(en)_3][Fe(CN)_6]$, and $[Co(en)_3][Co(CN)_6]$ [3–12]; the only question that possibly can be raised concerns the reasons why these negative deviations occur, i.e. whether these are a sign of chemical associations—i.e. for weak electrolytes—or originate in the intrinsic properties of the PM for the corresponding ionic charges.

Yet, the debate about the negative deviations reveals that the theoretical and experimental behavior of the electrolytes (in particular, high-charge electrolytes) in dilute solutions is even today a non-definitely settled subject for many scientists.

Knowledge of the behavior of the different kinds of electrolytes in the dilute and hyper-dilute regions is a necessity that cannot be given up for researchers concerned with equilibrium and kinetic measurements in electrolyte solutions, since the problem of extrapolation to infinite dilution is involved in manifold experimental situations (determination of standard potentials of cells, equilibrium constants, kinetic constants, activity coefficients from relative activity coefficients, etc.). There exists the incorrect diffused idea that, once dilution levels of the order of 10^{-2}–10^{-3} $mol \cdot kg^{-1}$ or so are reached, one can rely on the certainty that the system will behave subsequently in a DH-like manner. This thought can lead to incorrect extrapolations. Theories that go beyond the DH approximation may be of help to predict the kind of behavior to really be expected. Therefore, we will provide here an overview of what, in the regions that are important for extrapolation to zero concentration of experimental results, is to be expected for the activity coefficients of different kinds of electrolytes. Calculations are performed on the basis of the simple primitive model, i.e. rigid spheres and electrostatic interactions, with only the radii of the spheres as parameters. We will see that the striking differences experimentally noticed between higher charge (2–2, 2–3 and 3–3) and lower charge (1–1, 1–2, 1–3, and also 1–4) electrolytes, are already present in the primitive model.

2 The RPM and PM in the Dilute Regions

"Experimental" results (Monte Carlo simulations) about the behavior of the PM have generally been limited to situations that mimic 1–1 and other low charge electrolytes, although computations exist for 2–2 electrolytes that cover the low concentration regime and support the negative deviations [15–17]. Yet, systematic identification of the general behavior of RPM or PM via Monte Carlo calculations for the different kinds of electrolytes in situations comparable to very dilute solutions (10^{-5} to 10^{-2} $\mathrm{mol{\cdot}L^{-1}}$) to study the direction and extent of the deviations from the LL, seems a prohibitive task (the same considerations apply also to Molecular Dynamics computations).

Useful information can be obtained more easily by the coordinated use of radically dissimilar approximations to RPM. IPBE (numerically accurate integration of the Poisson–Boltzmann equation, PB) [18–22], and Mayer's cluster theory in its basic approximation, usually named DHLL + B2 [23–30], are a possibility.[1] The mechanical-statistical frameworks of such treatments, whose cumbersome underlying equations are reported in the S.I. are completely different and independent, since Mayer's theory (unlike IPBE, DH, and DH-SiS) does not rely at all on the Poisson–Boltzmann equation or the Güntelberg or Debye charging processes, but adopts a peculiar development of the PM,[2] based on an infinite series of clusters of ion–ion interactions. The combinatorial complexity of this development is extreme; only the more important kinds of clusters were considered and collected (the simpler ones generate the LL), neglecting those that become important only at higher concentrations, thus causing DHLL + B2 to be suitable only for very dilute solutions. In addition, the main terms of the DHLL + B2 equations present serious computational problems, as they incorporate slowly convergent infinite series of exponential integrals that, in the original Mayer paper [23] and subsequent developments [24–27], were in their turn approximated quite drastically. Appreciable improvements were attained in the 1970′s with a method used by Indelli and De Santis [28, 29] and by Indelli and Malatesta [20], allowing the sums of integrals to be extended to hundreds rather than tens of terms as previously and later by Malatesta who, developing a Meeron idea [27], inverted the order between integrations and sums inside the different infinite series of integrals, thus transforming these infinite series into numeric integrals of single functions [30]. With modern computers, the DHLL + B2 computations are now easy, but the relevant predictions are usually considered of little utility since the theory, by its intrinsic limitations, applies only to very dilute solutions (and in addition, the situation worsens in cases of higher charges, spheres of smaller size, and solvents with low dielectric constant). However, an interesting result of Mayer's theory is the fact that it converges to the LL in the limit of infinite dilution, thus confirming the soundness of the LL by a method that is completely independent

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[1] DHLL + B2, unlike IPBE and DH, applies consistently also to unrestricted PM (as many distances of closest approach a_{ij} between the centers of two ions i and j, as the possible combinations of i and j). The special emphasis on the RPM restriction is to permit comparison with DH and IPBE, which do not admit the use of different a_{ij} values. However, as shown in Sect. 4 of the S.I., for solutions of single electrolytes the postulation of different a_{ij} values rather than one single a has a negligible effect as long as a is taken equal to a_{+-}, independently of the values of a_{++} and a_{-}. This observation indicates that for single salts in dilute solutions there exists no perceptible difference between PM and RPM.

[2] Mayer's theory is not necessarily limited to PM, it can be extended freely to more realistic descriptions of the short-range interactions. Yet, at the concentrations imposed by the drastic truncation of the cluster series, only suitable in very dilute solutions, any improvement at the level of short range interactions is as effective, as lightening the buttons of the shirt for a man of over 100 kg to make easier his walking.

of the adoption of the PB mechanical-statistical approach and Güntelberg or Debye charging processes. Since IPBE and DHLL + B2 are two completely independent ways to estimate the behavior of diluted RPM, where their results coincide, this necessarily suggests the true behavior of RPM and PM.

In addition to IPBE and DHLL + B2, the approximate Bjerrum theory (BT) [31] is considered. Bjerrum used his fictitious "ion pairs" as a simplification to avoid the complex problem of the ion distribution in the nearer neighborhoods of each ion, i.e. at distances too low for the linear approximation of PB to hold. A critical distance, d, from the ion on which the coordinates are centered, is selected to separate approximately the zone where the L-PB is expected not to hold, from the surroundings where the L-PB is expected to hold.[3] We skate over the details and discussions, available in several past papers and textbooks [32–37], regarding the rationale of the original Bjerrum choice for d, calculation of the association constant, arbitrariness of the conception of ion pairs, etc. The Bjerrum artifice of ion pairs does not necessarily imply any real existence of associated species, and can be considered rightly as a simplified, approximate development of the RPM, a sort of poor substitute for IPBE. However, it provides also an example of the effects that real chemical association would have in an incompletely dissociated electrolyte, thus proving that effects of chemical association and effects of strong electrostatic diffuse interactions are virtually equivalent. Activity coefficients of high-charge electrolytes which deviate negatively from the LL can nearly always be interpreted as the cumulative consequence of the electrostatic long range interactions intrinsically involved in the PM, and additional possible effect of weak chemical bonds (short range interactions). Unusually low values of a required by the RPM to fit particularly large negative deviations of some electrolytes (typically, sulfate salts) may be a symptom of chemical association that adds to the long-range interactions. In the absence of independent experimental determinations, the trend of the activity coefficients alone does not provide sufficient information to separate such effects.

Figure 1 displays IPBE, DHLL + B2, and BT approximations for the RPM of a 2–2 electrolyte with $a = 0.4$ nm, at 298.15 K in a dielectric fluid equivalent to water. Points calculated with the MPB and SPB equations [38, 39] are also reported (data kindly supplied by Outhwaite and Bhuiyan). We see that for $I^{1/2} < 0.1\ \mathrm{mol}^{1/2}\cdot\mathrm{L}^{-1/2}$ IPBE, DHLL + B2, the Bjerrum theory and MPB agree perfectly, supporting the premise that the negative deviations *are an intrinsic property of the RPM*. SPB also displays the same type of negative deviations, with values only slightly higher for $I^{1/2} > 0.07\ \mathrm{mol}^{1/2}\cdot\mathrm{L}^{-1/2}$. The reason why IPBE and SPB are *not perfectly equivalent* is because IPBE neglects the uncharged hard sphere contribution. It is not so clear instead why IPBE graphically coincides with MPB because the latter includes the uncharged hard sphere contribution like SPB. The MPB also accounts for the fluctuation effect, and the latter probably balances in part the uncharged hard sphere involvement, thus providing (in dilute solutions) results very similar to IPBE that neither considers fluctuation nor uncharged hard sphere contributions. DH fails in accounting for the negative deviations, because of the L-PB approximation that does not interpret the RPM correctly in the case of 2–2 electrolytes; the radial distribution of the ionic atmosphere in the nearer neighborhoods of the ions differs appreciably from the distribution deduced via L-PB (see Chap. 4 of [36]).

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[3] In the Bjerrum theory, d is a univocal function of charges of ions, temperature, and dielectric constant of the solvent. In water at 298.15 K, Bjerrum values of d are: 0.358 nm for 1–1, 0.715 nm for 1–2, 1.073 nm for 1–3, 1.431 nm for 1–4 and 2–2, 2.146 nm for 2–3, 2.861 nm for 2–4, and 3.219 nm for 3–3 electrolytes. When $d < a$, no *ion pairs* exist and Bjerrum's theory exactly coincides with the DH theory.

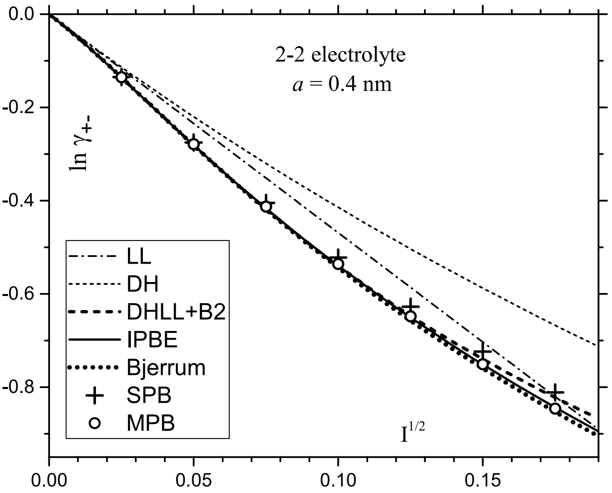

Fig. 1 RPM of a 2–2 electrolyte in water, $a = 0.4$ nm, according to approximations DH, IPBE, DHLL + B2, BT, MPB, and SPB. For comparison, Debye Hückel limiting law LL

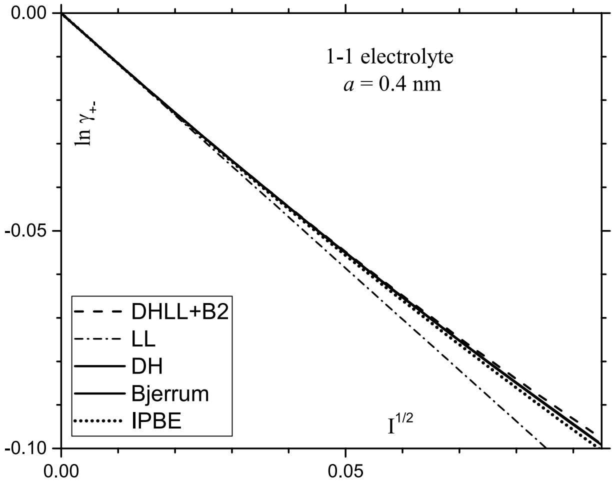

Fig. 2 RPM of a 1–1 electrolyte in water, $a = 0.4$ nm, in the DH, IPBE, DHLL + B2 and Bjerrum theory approximations (note that in this case the DH and Bjerrum curves coincide since $d < a$). For comparison, Debye Hückel limiting law LL

The situation is profoundly different when we deal with 1–1 electrolytes, where the L-PB is instead sufficient to reproduce correctly the behavior of the RPM. In this case, DH agrees with other theories, and all predict positive deviations from the LL (Fig. 2).

Spheres of smaller size enhance the negative deviations in the RPM of 2–2 electrolytes; negative deviations become possible even in the RPM of 1–1 electrolytes, though only for improbable a values lower than 0.15 nm. Conversely, larger spheres cause the opposite effect; for instance, the RPM of a 2–2 electrolyte with $a > 0.7$ nm only yields positive deviations; the inversion occurs for a between 0.6 and 0.7 nm. The RPM of non-aqueous

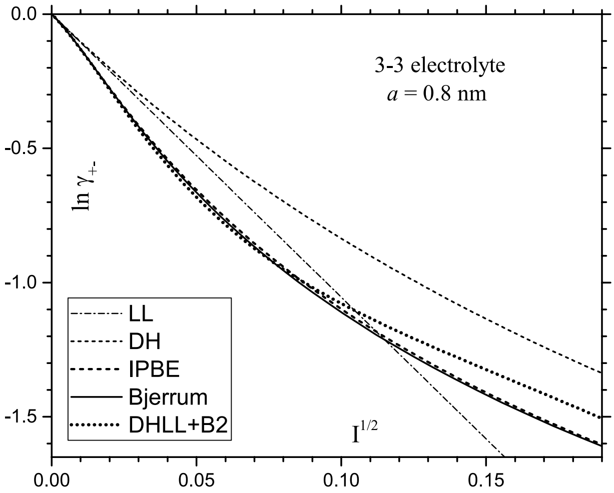

Fig. 3 RPM of a 3–3 electrolyte in water, $a=0.8$ nm, in the DH, IPBE, DHLL + B2 and BT approximations. For comparison, Debye Hückel limiting law LL

solutions proves that lower dielectric constants favor, as expected, negative deviations. For instance, a dielectric constant of one quarter than of water causes the 1–1 electrolytes to behave like the equivalent 2–2 electrolyte in water, which is logical since the electrostatic interactions are equal [20].

As expected, at a parity of *a*, the negative deviations of 3–3 electrolytes are much larger than those of 2–2 electrolytes. Unfortunately, also the discrepancies between IPBE and DHLL + B2 become much larger, making the identification of the exact behavior of RPM problematic (Fig. S7 in the S.I.), except for spheres of rather large size like those considered in Fig. 3 ($a=0.8$ nm). Extremely large, improbable values of *a* (from 1.5 nm onwards) are required for the negative deviations of the RPM in the hyper dilute regions to disappear and convert into positive deviations. Therefore, we must conclude that 3–3 electrolytes are affected *always* by negative deviations.[4]

Considering spheres of 0.4 nm, the RPM of 1–2 and 1–3 aqueous electrolytes does not yield negative deviations. The agreement between IPBE and DHLL+ B2 is excellent, and the DH, too, is not so different. The Bjerrum theory approximation worsens with unsymmetrical electrolytes, where the ion pairs also have a net charge. It is hard to think that BT may still represent an accurate approximation to the RPM in such situations; and in fact, compared to IPBE and DHLL+ B2 whose nearly indistinguishable curves draw the correct behavior of the RPM, BT tends to overestimate the negative deviations. This situation is even more evident for 1–4 electrolytes, where for $I<5\times10^{-3}$ mol·L^{-1} we find again very good agreement between IPBE and DHLL+ B2, which in this region do not deviate appreciably from the LL, whereas BT predicts moderate negative deviations. DH, of course, always predicts positive deviations. Figures for 1–2, 1–3 and 1–4 electrolytes are reported only in S.I., Sect. 5, where the different colors are an aid to distinguish the different curves.

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[4] The opposite opinion of Fraenkel, based on those he presented as the *correct* experimental data for La[Fe(CN)$_6$] (Fig. 2 of ref.[14]), arises from an incorrect interpretation of the real experimental data of Ref. [40]. See S.I., Sect. 7.

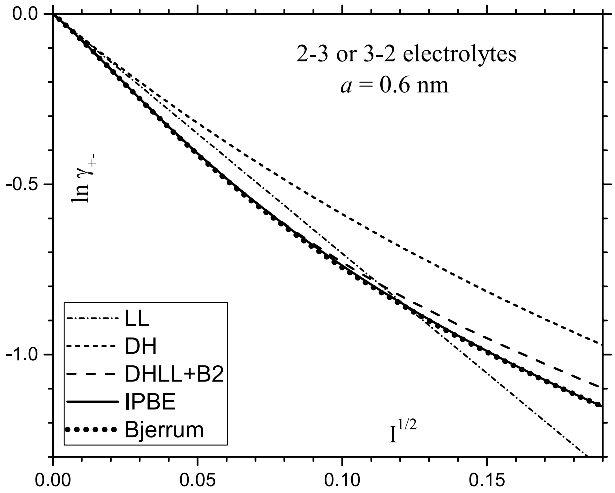

Fig. 4 RPM of a 2–3 electrolyte in water, $a = 0.6$ nm, in the DH, IPBE, DHLL + B2 and Bjerrum theory approximations. Truncation of cluster series causes DHLL + B2 predictions be intrinsically unreliable for $I > 0.01$ mol·L^{-1}

As for 2–3 electrolytes, the RPM yields as expected considerable negative deviations for $a = 0.4$ nm; yet in this case the exact behavior can be identified only for $I < 10^{-4}$ mol·L^{-1} since at higher ionic strengths the trends of IPBE and DHLL + B2 are progressively divergent (Fig. S5 in the S.I.). Satisfactory results are obtained for larger *a*, such as 0.6 nm (Fig. 4), where for $I < 0.01$ mol·L^{-1} IPBE, DHLL+B2, and to a slightly lesser degree Bjerrum theory, predict for the RPM the same behavior. Spheres with size larger than ca. 1.0 nm no longer yield negative deviations in the initial zone.

The predicted behavior of 2–4 electrolytes is intermediate between 2–3 and 3–3. Yet, there exist no 2–4 electrolytes whose experimental activity coefficients are known. The apparent molar volumes of $Mg_2[Fe(CN)_6]$ and $Sr_2[Fe(CN)_6]$ have been determined using dilatometric methods down to concentrations of ca. 2×10^{-4} mol·L^{-1} [41], and deviations from the corresponding LL were found occur in the direction opposite to predicted by DH (i.e. positive deviations, where DH predicts negative deviations; the signs are inverted with respect to activity coefficients). Inverted deviations have been observed also in the relative apparent molal enthalpies [42, 43].

No calculations for 3–4, 4–4, etc. electrolytes have been performed since no corresponding real salts exist whose experimental activity coefficients have been determined, making the respective theoretical calculations a vain exercise.

3 The Reason Why the Dilute Regions are Important

Determinations of activity coefficients are usually intended as determinations of In $\gamma_\pm$.[5] Yet, experiments never provide directly such quantities, but other quantities ln $\gamma'_\pm$ biased by an unknown additional constant, ln $\gamma'_\pm = const + \ln \gamma_\pm$ ($\gamma'_\pm$ being denoted as *relative mean activity coefficient*). The nature and origin of the *const* depends on the method with which the values of ln $\gamma'_\pm$ are obtained. Potentiometric methods typically provide quantities ln $\gamma'_\pm = \ln \gamma_\pm - \ln \gamma_\pm (r)$, where $\gamma_\pm (r)$ is the unknown value of $\gamma_\pm$ in a solution (r) used as reference; here, *const* means –[ln $\gamma_\pm (r)$]. Conversely, with methods based on integration of the osmotic coefficients (ϕ, obtained via cryoscopy or isopiestic methods), *const* represents the integration error generated by the unknown trend of the integrand $(\phi - 1)/m^{1/2}$ between the lower m accessible to experimental determination of ϕ, and $m = 0$ (see discussion in Ref [5].).

No matter its specific meaning, for the experimental sets of ln $\gamma'_\pm$ to be transformed into sets of ln $\gamma_\pm$, the value of *const* needs be determined. The function ln $\gamma'_\pm$ has to be extrapolated to infinite dilution, where it becomes equal to *const*. Extrapolation to infinite dilution, however, requires knowledge of the law the activity coefficients obey in the dilute regions. Preliminary knowledge of the dilute solutions is, therefore, of vital importance; *otherwise, the activity coefficients of concentrated electrolytes remain biased by an unidentified error in their turn.*

For low charge electrolytes, in particular 1–1, extrapolation to infinite dilution usually relies on the empiric equation:

$$\ln \gamma'_\pm = const + S_1 I^{1/2} + S_2 I + \sum\nolimits_{i>2} S_i I^{i/2} \tag{1}$$

where S_1 is the LL slope; S_2 and the other S_i are empirical coefficients. Subtracting the LL from experimental ln $\gamma'_\pm$, we have therefore:

$$1n\,\gamma'_\pm - \mathrm{LL} = const + S_2 I + \sum\nolimits_{i>2} S_i I^{i/2} \tag{2}$$

Supposing that the concentrations are sufficiently low for $\sum_{i>2} S_i\ I^{i/2}$ to be negligible, one expects a quasi-linear trend of ln $\gamma'_\pm$ – LL plotted vs. I, with intercept *const* (of course, this supposition is suspect in the case of negative deviations from the LL). In reality, the method is problematic also in absence of negative deviations, since the omitted residual terms often generate trends whose slope varies continuously and does not permit linear extrapolation of *const*. Figure 5 shows the situation observed with $Mn(ClO_4)_2$, whose relative activity coefficients have been measured with high precision down to $m = 5.739 \times 10^{-5}$ mol·kg^{-1} using a cell with permselective liquid membranes [7]. The reference solution was 9.183×10^{-4} mol·kg^{-1}; therefore, in this case *const* means the value

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[5] In the present paper the mean activity coefficients are always denoted as $\gamma_\pm$. Indeed, the differences between activity coefficients $\gamma_\pm$ (molal scale), $\gamma'_\pm$ (molar scale), and $f_\pm$ (rational scale = mole fraction scale) vanish at the dilution levels required for DH, IPBE, DHLL + B2 and BT to agree with the RPM. We selected $\gamma_\pm$ for better consistence with the experimental determinations of activity coefficients, usually performed in solutions of know molality m, rather than molarity C. Furthermore, C and m are nearly proportional at high dilutions ($C \approx m\ d^\circ$ with d° = solvent density), and nearly equal when the solvent is water. Therefore, although the natural variable of ionic interaction theories is C rather than m, at high dilution the results obtained in function of molar concentrationsor molar ionic strengths apply also to the molal concentrations, or molal ionic strengths. For C and m we intend generally the dimensionless quantities $C/(C^\circ = 1)$ and $m/(m^\circ = 1)$.

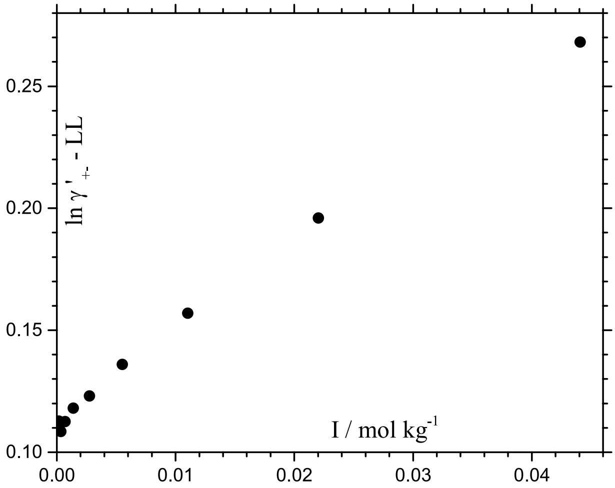

Fig. 5 Values of ln $\gamma^{'}_{\pm}-$ LL in function of I for $Mn(ClO_4)_2$. In spite of the high dilution levels, no linear trend is observed, and the plot is of no particular aid to extrapolate the intercept *const* at $I=0$. Experimental data from Ref [7]

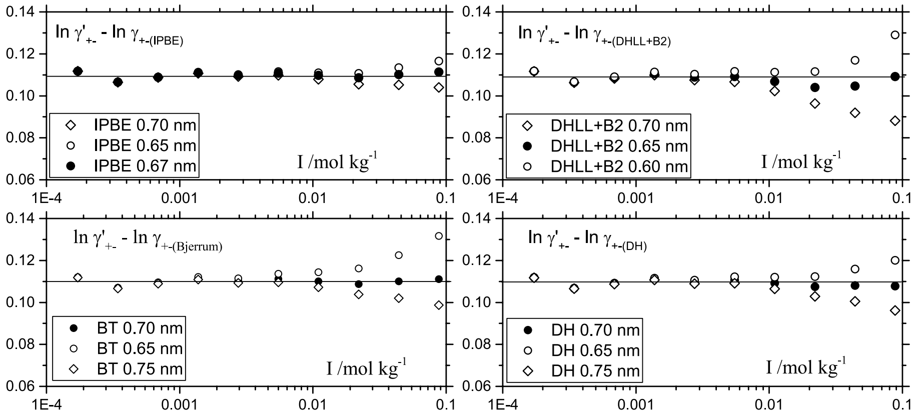

Fig. 6 IPBE, DHLL + B2, Bjerrum theory, and DH used as extrapolation tools for the relative activity coefficients of $Mn(ClO_4)_2$; horizontal trends individuate $const = -\ln \gamma_{\pm}$ (r), where (r) is 9.183×10^{-4} mol kg^{-1} $Mn(ClO_4)_2$. Experimental data are from Ref [7]

of –ln $\gamma_{\pm}$ at $m=9.183\times10^{-4}$ mol·kg^{-1}. It is evident that, although $Mn(ClO_4)_2$ is a perfectly normal 1–2 salt, ln $\gamma^{'}_{\pm}-$ LL does not obey any linear law, and no linear extrapolation as a function of I is feasible. Even worse: when (as is rather usual) no data are available at so high dilution as for $Mn(ClO_4)_2$, pseudo-linear trends observed at higher concentrations may suggest biased extrapolations.

It is strongly advisable to proceed in a different manner. As shown in the previous section (see also the S.I. for 1–2, 1–3 and 1–4 electrolytes) IPBE, DHLL + B2 and BT (and also DH, if we deal with a low-charge electrolyte) are able to mimic to a good approximation the RPM in the dilute regions, where the RPM in its turn mimics the limiting behavior of the real electrolytes; the only problem is to identify the appropriate diameter of the spheres, a.[6] We proceed by attempts, for any different theory, calculating $\gamma_{\pm\,(\mathrm{theory},\,a)}$ for each theory with different values of a. The differences $\ln \gamma'_{\pm\,(\mathrm{exp})} - \ln \gamma_{\pm\,(\mathrm{theory},\,a)}$ are plotted in function of I using a logarithmic abscissa. The correct value of a yields points that, in the dilute regions, group around a horizontal line that identifies *const*; other values of a provide trends that in their turn converge towards the same horizontal line. Figure 6 shows the application of this method to $Mn(ClO_4)_2$ using IPBE, DHLL + B2, BT, and DH, in the concentration range 0.02937 to 5.739×10^{-5} mol·kg^{-1}. All trends converge to a value of *const* of 0.11_0, i.e. to $\ln \gamma'_{\pm}(r) = -0.11_0$, which is indeed the value reported in Ref [7] for 9.183×10^{-4} mol·kg^{-1} $Mn(ClO_4)_2$.

The method described above (*theory assisted extrapolation to zero concentration*) can be used reliably also for electrolytes with negative deviations like those of Figs. 1, 3 and 4, provided the dilution levels are sufficient for the theories used to agree with each other on the behavior of the RPM. The method has been used for bivalent metal sulfates [5–7] (a plot similar to Fig. 6 is shown in Ref [5] for $ZnSO_4$), bivalent metal hexacyanoferrates(III) and hexacyanocobaltates(III) [8, 9], and 3–2 electrolytes that presented moderate negative deviations [44]. The DH is obviously failing in these cases, as are other linear theories such as DH-SiS [1, 2]. Even the integral equation approach of the mean spherical approximation MSA [45] fails, being incapable of reproducing the intrinsic negative deviations of the RPM of high-charge electrolytes (negative deviations within the MSA can only be achieved by adopting the hybrid approach of using ion pairing, such as in the MSA-MAL approach of Ebeling and Grigo for the osmotic coefficients of 2:2 salts [46] and similar, more recent, applications [47, 48]). It is expected, instead, that the integral equation approach of the hypernetted chain equation (HNC), which predicts the negative deviations of the PM of high charge electrolytes [49–52], and the SPB and MPB theories [38, 39, 53–56] as well, are better than DHLL + B2, IPBE, and Bjerrum theory for theory-assisted extrapolation to zero concentration.

With trivial modifications, the theory-assisted extrapolation method is directly extended to extrapolation of standard potentials ($E°$) of cells without transference from their electromotive forces (emf, E) experimentally determined. Similar E^* quantities, that substitute for $E°$ standard potentials in the liquid-membrane cells (thermodynamically equivalent to cells without transference)[7] are determined in the same way.

Problems, however, arise with electrolytes whose negative deviations are strongly increased, which is the case of 3–3 electrolytes [12] and, among 3–2 electrolytes, of $La_2(SO_4)_3$ [11] and $[Co(en)_3]_2(SO_4)_3$ [10]. As is visible in Figs. S5 and S7 (S.I.), IPBE, DHLL + B2, and BT no longer agree well with each other (except at extreme dilutions, out of the experimental range) about the actual behavior of the RPM of 2–3 electrolytes for $a = 0.4$ nm or lower, or of 3–3 electrolytes for $a = 0.6$ nm or lower. Theory assisted extrapolation to zero concentration in similar situations leads IPBE, DHLL + B2 and BT not to agree about the value of *const* (or of $E°$ or E^*) making this method unusable. Fortunately, there exists an alternative method to transform the relative activity coefficients of 2–2, 2–3 or 3–2, and 3–3 electrolytes into corresponding activity coefficients, thanks to an indirect

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[6] The single value of a of the RPM is equivalent to the distance of closest approach of cation-to-anion in the PM. Computations applied to PM prove, indeed, that in dilute solutions the effects of the distances of closest approach cation–cation and anion–anion are practically unimportant (see S.I., Sect. 4).

[7] Concerning the rationale of cells based on perfectly permselective liquid membranes, see Ref.[57] or the SI of Ref.[13]. Diagrams of membrane electrodes and cell assemblage are reported in the S.I. of Ref.[22].

thermodynamic cycle that we will designate for brevity as the "*absolute reference point*" method.

3.1 The "Absolute Reference Point" Method

The rationale of the "absolute reference point method" is easily understood if we start with the elementary case of four cells without transference, for HCl, HBr, KBr and KCl:

(1). Ag, AgCl | HCl solution | H_2 (Pt)
(2). Ag, AgBr | HBr solution | H_2 (Pt)
(3). Ag, AgBr | KBr solution | K (saturated amalgam in Hg)
(4). Ag, AgCl | KCl solution | K (saturated amalgam in Hg)

Naming E_1^o, E_2^o, E_3^o, and E_4^o for the respective standard potentials, these $E°$ necessarily obey the thermodynamic cyclic relationship $E_1^\text{o} - E_2^\text{o} + E_3^\text{o} - E_4^\text{o} = 0$, and hence it suffices to know three of these four $E°$ to univocally determine also the fourth one.

Similar relationships apply also to the $E°$ of cells planned for high charge electrolytes, and to the equivalent quantities E^* that substitute for $E°$ in the case of liquid membrane cell. The advantage consists in the fact that the $E°$ (E^*) of a cell for an electrolyte where both the cation and anion are multiply charged (2–2, 2–3 or 3–3), whose determination by theory-assisted extrapolation to zero concentration could be problematic or impossible, can be expressed as a linear combination of the $E°$ (E^*) of three auxiliary cells for electrolytes of lower charge, with which the theory-assisted extrapolation has no problem, e.g., the $E°$ (E^*) of a cell without transference (or a cell with perfect permselective membranes) for $La_2(SO_4)_3$, made of an electrode for La^{3+} and another for SO_4^{2-} (*principal cell*) can be calculated by linear combination of the $E°$ (E^*) of three *auxiliary cells*, (i) one for $LaCl_3$ (made of the above electrode for La^{3+}, and another for Cl^-); (ii) another for K_2SO_4 (made of the above electrode for SO_4^{2-}, and another for K^+); and the third, to close the cycle, for KCl using the previous electrodes for K^+ and Cl^-. The $E°$ (E^*) of the auxiliary cells are deduced from the respective electromotive forces (emf, E) measured at known concentrations, via theory-assisted extrapolation to zero concentration. The explicit relationships to be used to calculate the $E°$ (E^*) of the *principal cell* from the $E°$ (E^*) of its *auxiliary cells*, are reported e.g. in the electronic supporting information of Ref.[13]. As soon as the $E°$ (E^*) of the principal cell has been determined, the activity coefficient of the high-charge electrolyte in its reference solution (the "*absolute reference point*") is immediately calculated from the relevant value of E via the Nernst equation. Details are available in the Supporting Information of Ref.[13].[8]

The absolute reference point method applies to all electrolytes where both the cation and anion have a charge greater than 1. Where both theory-assisted extrapolation and an absolute reference point can be used, their independent results (generally in very good agreement) provide a useful estimate of the residual systematic error made in the transformation of the original set of ln $\gamma'_\pm$ into definitive ln $\gamma_\pm$.

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[8] Erratum in the S.I. of [13]: page SI 5, line 7, substitute "Mg^{2+}, ds^{2-}, Na^+ and Cl^-" for "Mg^{2+}, ds^{2-}, K^+ and Cl^-".

4 The Behavior of Real Electrolytes

The real behavior of electrolytes in dilute solutions is much better known than in the past. This is thanks to liquid membrane cells, which are able to determine the relative activity coefficients for nearly all electrolytes down to dilution levels previously unattainable with other methods (even 10^{-5} mol·kg^{-1} and beyond in a few cases), and to the ability to transform the relative activity coefficients into reliable activity coefficients in nearly all cases. In some cases, the experimental advancements overtook the theoretical developments; for instance, the accurate results in mixed solutions of high charge electrolytes (in particular of 3–3 salts in a predominant quantity of 2–2 or 2–3 salts) [22] are still awaiting a theoretical interpretation.

For 1–1 strong electrolytes in aqueous solutions no negative deviations are predicted by the RPM, because these deviations would be possible only for unreasonably low values of a (ca 0.15 nm). For 1–2 or 2–1 electrolytes, negative deviations would occur only for values of a lower than ca 0.3 nm, which is rather unusual. However, K_2SO_4 [6] displays in the dilute regions a trend that, in terms of RPM, means just a similar low value of a (ca 0.3_0 nm according to both IPBE and DHLL-B2, 0.3_4 nm according to BT); we observe occurrence of an initial quasi-linear trend that coincides approximately with the LL up to $I \cong 0.01$ mol·kg^{-1}, before deviating positively. Other 1–2 and 2–1 salts studied by the Malatesta research group using liquid membrane cells [7, 58, 59] display the regular trend that RPM predicts for $a \cong 0.4$ nm or greater.[9]

Also for 1–3 and 3–1 electrolytes no negative deviations are generally expected, excepting particularly low values of a as in the case of $[Co(en)_3](NO_3)_3$ ($a \cong 0.3_0$ nm [58]). Just a hint of negative deviation, or a trend that coincides with the LL up to concentrations higher than expected, are observed for $[Co(en)_3]Cl_3$ ($a \cong 0.3_7$ nm [10]), $[Co(en)_3](ClO_4)_3$ ($a \cong 0.4_0$ nm [58]), $K_3Fe(CN)_6$ ($a \cong 0.4_2$ nm [40, 58]), $K_3Co(CN)_6$ ($a \cong 0.4_2$ nm [9]), $La(NO_3)_3$ ($a \cong 0.4_3$ nm [11]). $LaCl_3$ ($a \cong 0.5_1$) [40, 58] and $La(ClO_4)_3$ ($a \cong 0.6_4$ [11]) exhibit regular positive deviations.

No experimental data of activity coefficients in very dilute solutions of 1–4 electrolytes are available.

Negative deviations have been definitively ascertained for bivalent metal sulfates; accurate activity coefficients are available for magnesium, calcium, strontium, zinc, cadmium, nickel, cobalt, and manganese sulfates [5–7]. These salts behave approximately as predicted by the RPM with spheres sizing between 0.3_4 and 0.4_2 nm (the two extreme values being those of cadmium sulfate and magnesium sulfate): see Fig. 4 of Ref.[6]. The non-sulfate 2–2 salt Mgds (where ds^{2-} stands for 1,5-naphthalenedisulfonate anion) instead does not present negative deviations, behaving like the RPM for $a \cong 0.7_5$ nm [44]. It is apparent that the sulfate anion has a peculiar tendency to generate negative deviations which, in terms of RPM, correspond to rather low values of a (or $a_\pm$ in the PM). Compare for instance the values of a required by sulfate salts with those required by perchlorate salts, quite different despite the equal geometry and similar size of SO_4^{2-} and ClO_4^-; e.g., the RPM requires $a \cong 0.6_8$ nm for $Mn(ClO_4)_2$ and $a \cong 0.3_8$ nm for $MnSO_4$. Other examples are shown in Table V of Ref.[58].

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[9] $Mn(ClO_4)_2$: ca 0.6_7–0.6_8 nm [7]; $Co(ClO_4)_2$ and $Ni(ClO_4)_2$: ca 0.6_6 nm [58]; $CaCl_2$: ca 0.5_1 nm [58]; $K_2C_2O_4$: ca 0.3_8 nm [59]; Na_2ds: ca 0.6_8 nm [59].

All 2–3 salts (M_3X_2) examined (magnesium, calcium, strontium and barium hexacyanoferrate(III) [8]; magnesium and calcium hexacyanocobaltate(III) [9]) display moderate negative deviations, like those of the corresponding RPM for a ranging from ca 0.5_7 nm for barium hexacyanoferrate(III), to ca 0.6_7 nm for magnesium hexacyanocobaltate(III). As for 3–2 salts (R_2Y_3), we observe once again the particular effect of the sulfate ion in $[Co(en)_3]_2(SO_4)_3$ [10, 44, 58] and $La_2(SO_4)_3$ [11], whose impressive negative deviations are like those the RPM predicts for a of ca. 0.3_8 nm [58] and 0.3_5 nm [44], respectively. Conversely, the non-sulfate 3–2 salts $[Co(en)_3]_2ds_3$ and La_2ds_3 display moderate negative deviations like those RPM predicts for a of ca. 0.6_0 and 0.7_5 nm, in that order [44]. The fact that $[Co(en)_3]_2(SO_4)_3$ requires a value of a higher than $La_2(SO_4)_3$ (0.3_8 nm vs. 0.3_5 nm) while on the contrary $[Co(en)_3]_2ds_3$ requires a value of a lower than La_2ds_3 (0.6_0 vs. 0.7_5 nm), is probably an indication that sulfate ion enters the hydration sphere of the cations while ions such as ClO_4^- and ds^{2-} do not (which also would explain the particularly low values of a of all sulfate salts). Bare $[Co(en)_3]^{3+}$ behaves as a "sphere" smaller than hydrated La^{3+}, yet larger than bare La^{3+}.

3–3 salts [12, 40, 60] all display impressive negative deviations, comparable, for $La[Fe(CN)_6]$, to those that IPBE and BT approximations to RPM predict for $a \cong 0.6_5$ nm (IPBE) or 0.6_7 nm (BT); slightly larger values of a are required for $La[Co(CN)_6]$ ($a \cong 0.6_6$ nm, IPBE; 0.6_8 nm, BT). With spheres of ca 0.7–0.6 nm (or less) of cross size, the different approximations to RPM become less accurate for 3–3 electrolytes, and Mayer's DHLL + B2 in particular diverges from IPBE and from BT (which instead remain in a more acceptable agreement with each other: see Fig. S7 of the S.I.). Both the negative deviations and the differences between IPBE, BT and DHLL + B2 increase in the case of $[Co(en)_3][Fe(CN)_6]$ and $[Co(en)_3][Co(CN)_6]$; both salts require $a \cong 0.4_6$ nm in the IPBE approximation and 0.5_1 nm in the BT approximation [12]; DHLL + B2 is of no utility at all in these extreme conditions.

5 Conclusions

All electrolyte theories agree on the fact that electrolytes attain the theoretical limiting slope LL in the limit of infinite dilution and, therefore, that at sufficiently high dilution levels their trends have to approach asymptotically the LL. However, *sufficiently high dilution levels* is a highly undefined term; it means in some cases (1–1 to 1–3 electrolytes) something like 10^{-2}–10^{-3} mol·kg^{-1}; in other cases (3–3 electrolytes and a few 3–2 electrolytes), it can mean 10^{-6}–10^{-8} mol·kg^{-1} and beyond, a range inaccessible to experiments. Furthermore, it is not stated absolutely that the asymptotic approach to LL has to proceed necessarily from above, as DH predicts, rather than from below. Examination of the behavior of the primitive model using independent theoretical approximations, indicates that, while low charge electrolytes in water usually have to display the *positive deviations* from the LL predicted by the DH theory, the combination of higher charges, smaller ions and lower dielectric constants necessarily produce the onset of *negative deviations* from the LL in the dilute regions (by increasing concentration, the covolume effects modify the situation, causing the slope to vary progressively in the positive direction). In water, the negative deviations are predicted (and found) unavoidable for 3–3 salts, very probable with 2–3 or 3–2, often present with 2–2, rare with 1–3 or 3–1, and virtually impossible for 1–2 or 2–1 and 1–1 electrolytes.

Some electrolyte theories, typically the DH theory because of the L-PB approximation, and likewise the DH-SiS theory of Fraenkel [2], are not able to allow for the negative deviations; in its turn, also the integral equation approach of the mean spherical approximation (MSA) [45] is not able to predict negative deviations [61]. Clearly, these theories do not reproduce the correct behavior of the primitive model in situations of stronger interactions between ions, such as those that can occur with high charge electrolytes (or in solvents with low dielectric constant).

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