

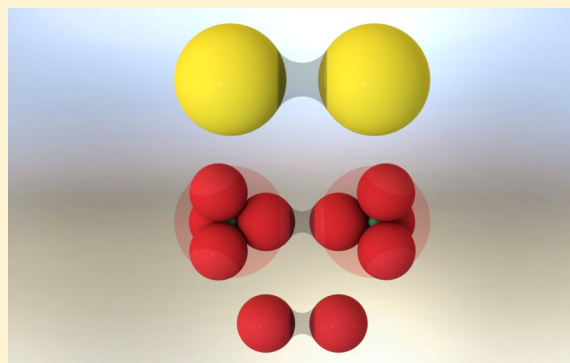
Computing Excess Functions of Ionic Solutions: The Smaller-Ion Shell Model *versus* the Primitive Model. 2. Ion-Size Parameters

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ABSTRACT: A recent Monte Carlo (MC) simulation study of the primitive model (PM) of ionic solutions (Abbas, Z. et al. *J. Phys. Chem. B* **2009**, *113*, 5905) has resulted in an extensive “mapping” of real aqueous solutions of 1–1, 2–1, and 3–1 binary electrolytes and a list of “recommended ionic radii” for many ions. For the smaller cations, the model–experiment fitting process gave much larger radii than the respective crystallographic radii, and those cations were therefore claimed to be hydrated. In Part 1 (DOI 10.1021/ct5006938) of the present work, the above study for the unrestricted PM – dubbed MC–UPM – has been confronted with the Smaller-ion Shell (SiS) treatment (Fraenkel, D. *Mol. Phys.* **2010**, *108*, 1435), or “DH–SiS”, by comparing the range and quality of model–experiment fits of the *mean ionic activity coefficient* as a function of ionic concentration.

Here I compare the ion-size parameters (ISPs) of “best fit” of the two models and argue that since ISPs derived from DH–SiS are identical with (or close to) crystallographic or thermochemical ionic diameters for both cations and anions, and they do not depend on the counterion – they are more reliable, as physicochemical entities, than the PM-derived “recommended ionic radii”.



1. INTRODUCTION

In Part 1 of the present study,¹ I compared results of Monte Carlo (MC) simulations of the unrestricted primitive model (UPM) for activity coefficients, as reported by Abbas et al.,² with computations for the same electrolytes, under parallel conditions, using the Smaller-ion Shell treatment³ that extends the Debye–Hückel (DH) model for size-dissimilar counterions. The two models, dubbed MC–UPM and DH–SiS, respectively, are both *ab initio* fundamental models of ionic solutions, and therefore their adjustable factors are only ion-size parameters (ISPs), that is, the “contact distances” of positive and negative co-ions and of counterions. Throughout the long history of ionic solution theories (over a century), there has been a constant yearning for ISPs of sound physicochemical meaning; in parallel, there has been a considerable effort to explain the disagreement of fit-optimized ISPs with realistic ionic sizes.

The frustration over the inability to employ physicochemically acceptable ISPs in correlating theoretical excess functions with those derived experimentally has urged researchers to develop practical models and mathematical treatments that can avoid the ISP altogether.⁴ Thus, “thermodynamic” models (such as that of Pitzer) have replaced ISPs by virial coefficients and their “constants” in assumed mathematical functionalities. Such models have become especially popular during the past four decades, particularly in studies of multicomponent ionic systems. Thus, ternary and higher-level electrolyte mixtures could be treated with mathematical expressions in which ion sizes are not explicitly considered. Obviously, dealing with all the different ion–ion distances of closest approach in even a ternary system is almost impossible as a general approach to electrolyte theories of mixed ionic systems. However, I have recently demonstrated⁵

that, through judicious approximations, DH–SiS can be modified to effectively treat ternary systems while still employing ISPs that reasonably represent ion–ion contact distances. Nonetheless, confidence has to be restored in the effective use of ISPs as fitted factors bearing physicochemical validity. The work of Abbas et al.² has produced a large list of “best-fit” ISPs for many ions, positive and negative, as obtained for solutions of many different electrolytes. The list constitutes what the authors called “recommended ionic radii”. DH–SiS is based on a very different theoretical approach to electrolyte solutions than that of the UPM (see Part 1¹). Therefore, comparing MC–UPM with DH–SiS is valuable for assessing the physicochemical validity of ISPs of the model–experiment best fit. This ISP examination is the aim of the current article that follows a comparison of fit quality and fit range of the two models, in Part 1.¹

Traditionally, the physical validity of modern electrolyte theories, such as advanced integral equations, has been judged by comparing theory-derived values of excess functions, usually osmotic coefficients, with parallel values obtained from simulations of the PM. For this, ISPs were chosen arbitrarily, assuming that they represent some physicochemical reality. In the RPM, $R = 4.2 \text{ \AA}$ ($= 420 \text{ pm}$) has been customarily used as the “standard” size parameter since it is the historic “best fit” value of common aqueous 1–1 solutions (especially of NaCl) when analyzed by the DH extended equation (DHEE).^{6–10} In a number of studies, theories [e.g., the hypernetted chain (HNC) equation,¹¹ the mean spherical approximation (MSA) equation,^{12–14} etc.] were compared with simulations of the

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UPM, in most cases for osmotic coefficients. Outhwaite and co-workers have spent a great deal of effort to compare excess functions, including activity coefficients, as calculated from their Modified Poisson–Boltzmann (MPB) theory and its different variants,^{15,16} with the same functions as calculated by HNC or MSA, or by simulation of the PM, e.g., using MC methods. Comparisons were made using both levels of the primitive model, the RPM and the UPM. However, neither Outhwaite and his group, nor other researchers, have compared theories or MC simulations with *real* electrolyte systems.

As apparent from the foregoing, the mindset in regard to theory verification has usually been that since the PM is the physically most appropriate model, theories should comply with this model, and there is no need to compare theory-derived excess functions with those of *actual* electrolyte solutions. Therefore, no much attention has been devoted to the comparison of theoretical ISPs with known ionic dimensions. However, in one case, Rasaiah examined the HNC equation using ISPs of real electrolytes – the 1–1 alkali metal halides,¹⁷ thereby indirectly comparing MC simulations of the PM with the real world; this is so since for the same sets of arbitrarily chosen ISPs, HNC computations agree very well with MC simulations of the UPM. Rasaiah did not optimize the fit of HNC with experiment because he chose to not adjust ISPs. He compared experimental osmotic coefficients (ϕ^{exp}) with the parallel calculated values (ϕ^{calc}) for various ionic solutions, using Pauling's radii and assuming full ISP additivity. The results were unsatisfactory, and better fits were achieved with elongated ISPs that could represent hydrated ions. With Pauling's radii, the deviation of ϕ^{calc} from ϕ^{exp} was ± 0.2 up to $I = 1$ (I , ionic strength), LiI giving the largest positive deviation (as $\phi^{\text{exp}} - \phi^{\text{calc}}$) and CsI, the largest negative deviation. Even though Rasaiah's study was done with only 1–1 salt solutions and it avoided optimization, the study gave a first hint on the suitability of the PM (both RPM and UPM) for representing electrolytes in nature. In the recent work of Abbas et al.,² MC simulations of the PM have been optimized for “best fit” with experiment through ISP adjustment; this study, therefore, is a step further in importance from the early investigations of Rasaiah and other researchers.

The present article complements the previous one.¹ I again examine the study of Abbas et al.² and its interpretation, restricting this examination to the MC–UPM case. A further restriction, as in Part 1,¹ is to the activity coefficient, as excess function, and its dependence on the solute content. I compare the MC–UPM simulations with DH–SiS computations of parallel ionic systems. More specifically, in the current comparison, I scrutinize the model–experiment fit in both cases in regard to *ISP choice and consistency*. Effects that are assumed without clear physicochemical evidence or rationale, such as ion hydration and ion pairing, are critically examined. A short assay on the ion size concept, in general and as related to the

present study, is provided in the Discussion section. An illustration of the complexity of this concept in reality even for the relatively simple case of NaCl in water is given in Appendix A. Appendix B further elaborates on the essence of the ISP and how it affects the range (as m , M , or I) of effective fit of DH–SiS with experiment.

2. COMPUTATION

A Methods section is limited here to a note on the computation in regard to the choice of ISPs; the rest of the Methods section is as in Part 1¹ and should not be repeated.

The computation–experiment fits were done using the conventional literature experimental values of γ_{\pm} vs m .^{7,8,18} The same ISP notation, b_+ , b_- , and a , is used for both models for the closest approach distances of positive co-ions, negative co-ions, and counterions, respectively. These ISPs are compared with the crystallographic or thermochemical diameters (hereinafter, the “calculated diameters”) of the cation, d_+ , and the anion, d_- . The model–experiment fits were performed with essentially only one adjustable ISP: In MC–UPM, b_+ and in DH–SiS, a . The MC–UPM fit in this comparison is based on the assumption that the size of the anion is its calculated diameter, and on obeying the ISP additivity requirement $a = 1/2(b_+ + b_-)$. The anions compared here are only the univalent anions Cl^- , Br^- , I^- , ClO_4^- , and NO_3^- . In the DH–SiS computation, I have assumed that, as much as possible, both b_+ and b_- are equal to the corresponding calculated diameters, and they are ideally nonadjustable. Divalent and trivalent cations may be somewhat larger than their crystallographic size,³ perhaps due to strong partial hydration, in which case the fit is subject to a secondary, usually limited, ISP adjustment. In sharp contrast with MC–UPM, DH–SiS assumes *a priori* that any ion retains a constant size in the presence of different counterions, and the only adjustable parameter is the counterion's distance of closest approach, a ; this is so since the DH–SiS fit is based on the premise that ISP additivity is not a rule. As before, all computations and experimental data^{2,3,7,8,18} are for aqueous solutions at 25 °C. Calculated ionic dimensions are from the standard literature.^{19,20}

3. RESULTS

Let us first check the ISP differences between the Lewis–Randall (LR) and McMillan–Mayer (MM) scales. Table 1 presents these differences for the six representative electrolytes of the comparison of Part 1,¹ as analyzed by DH–SiS. For the 3–1 electrolyte LaCl_3 , all three ISPs are identical in both scales. For the 1–1 electrolytes, a is somewhat larger in the MM scale than in the LR scale, but the difference (~ 10 pm) is miniscule compared with that between ISPs of parallel cases in DH–SiS and MC–UPM. The two calcium electrolytes representing the 2–1 family (Table 1) give ~ 20 -pm smaller a and ~ 30 -pm smaller b_+ values in the MM scale than in the LR scale; b_+ is

Table 1. Difference between Ion-Size Parameters (ISPs)^a of the DH–SiS Best Fit in the LR and MM Scales

family	electrolyte	d_+	$b_+(\text{LR})$	$b_+(\text{MM})$	$a(\text{LR})$	$a(\text{MM})$	Δa^b	Δb_+^b	$\Delta d/2^c$
1–1	NaCl	194	194	194	344.0	352.5	8.5	0	8.0
1–1	KCl	266	266	266	343.0	355.5	12.5	0	12.5
1–1	NaClO_4	194	194	194	337.0	353.5	16.5	0	16.5
2–1	CaCl_2	198	226	198	361.0	339.0	–22.0	–28.0	–8.0
2–1	$\text{Ca}(\text{ClO}_4)_2$	198	226	198	406.0	388.0	–18.0	–26.0	–5.0
3–1	LaCl_3	212	212	212	325.0	325.0	0	0	0

^aIn pm. ^b $[a, b_+; \text{in MM}] - [a, b_+; \text{in LR}]$. ^c $d \equiv 2a - b_+ - b_-$. Δd , difference between d in MM and d in LR.

Table 2. Comparison of the Monte Carlo Simulation of the UPM (MC–UPM) with the Smaller-Ion Shell Model Computation (DH–SiS): Best-Fit ISPs^a and Fit Range (M/m) of Model–Experiment Fit of γ_{\pm} (MC–UPM) and γ_{\pm} (DH–SiS) against Concentration for Various 1–1, 2–1, and 3–1 Electrolytes in Water at 25 °C

electrolyte	d_+	$d_- (= b_-)$	MC–UPM, MM scale				DH–SiS, LR scale			
			b_+	$b_+ - d_+$	a	fit limit, M[m] ^b	b_+	$b_+ - d_+$	a	fit limit, m[M] ^b
HCl		362	440		401	1.92	116		361	3.0
HBr		392	450		421	2.50	116		390	5.0
HI		440	464		452	1.80	116		438	0.8
HClO ₄		480	370		425	1.40	116		375	>2.0
LiCl	136	362	420	284	391	1.92	136	0	364	1.4
LiBr	136	392	410	274	401	3.00	136	0	378	1.0
LiI	136	440	450	314	445	1.20	136	0	435	1.2 ^c
LiClO ₄	136	480	400	264	440	2.50	136	0	425	1.4
LiNO ₃	136	358	420	284	389	1.20	136	0	345	3.5
NaCl	194	362	336	142	349	0.96[0.98]	194	0	344	1.8[1.7]
NaBr	194	392	336	142	364	0.98	194	0	364	1.1
NaI	194	440	336	142	388	0.98	194	0	387	0.5
NaClO ₄	194	480	204	10	342	0.49[0.50]	194	0	337	>2.5[>2.2]
KCl	266	362	270	4	316	0.78[0.80]	266	0	343	1.8[1.7]
KBr	266	392	268	2	330	0.70	266	0	356	>1.4
KI	266	440	268	2	354	0.40	266	0	386	1.4
RbCl	294	362					294	0	333	1.6
RbBr	294	392					294	0	330	1.8
RbI	294	440					294	0	331	1.4
MgCl ₂	132	362	590	458	476	0.98	212	80	361	0.8
MgBr ₂	132	392	620	488	506	1.00	212	80	384	0.7
MgI ₂	132	440	618	486	529	1.00	212	80	404	0.7
Mg(ClO ₄) ₂	132	480	600	468	540	0.93	212	80	414	0.9
Mg(NO ₃) ₂	132	358	590	458	474	0.95	212	80	357	0.9
CaCl ₂	198	362	548	350	455	0.80[0.82]	226	28	361	0.9[0.88]
CaBr ₂	198	392	580	382	486	0.80	226	28	378	0.6
CaI ₂	198	440	594	396	517	0.60	226	28	403	0.7
Ca(ClO ₄) ₂	198	480	530	332	505	1.10[1.2]	226	28	406	0.8[0.75]
AlCl ₃	102	362	720	618	541	1.00	220	118	347	0.2–0.7
LaCl ₃	212	362	640	428	501	0.97[1.0]	212	0	325	1.0[0.97] ^d

^aISPs and ionic diameters are given in pm; for both models $b_- = d_-$. ^bMolar for MC–UPM, molal for DH–SiS; for the meaning of “fit limit”, see text and Part 1.¹ ^cFair fit, $\pm 1.3\%$. ^dFit within $\pm 2\%$.

identical (as desired!) with d_+ of Ca²⁺.¹⁹ Still the ISP differences for the 2–1 electrolytes, due to the concentration scale, are very small *vis-à-vis* those between the two models compared in the present study. The conclusion from Table 1 is that the model comparison of ISPs is insensitive to the type of concentration scale, whether LR or MM, and converting from one scale to the other is not essential in regard to the ISPs of best fit. In other words, one can effectively compare MC–UPM in the MM scale with DH–SiS in the LR scale, and it is legitimate to compare ISPs of the LR scale with those of the MM scale.

Table 2 lists “best-fit” ISPs and concentration fit range of selected common electrolytes, for MC–UPM in the MM scale² and for DH–SiS in the LR scale.^{3,21} The main observations in Table 2 are summarized in the following subsections.

3.1. Correlation between Ion Size and Fit Range in Halides with Large Cations. For potassium halides, the MC–UPM fit is very range-limited (<0.8 M); this appears without reason except that the experiment shows almost no increase in γ_{\pm} (γ_{\pm}) beyond its minimum. Therefore, there has to be a very small repulsion effect even though the sum of the cation and anion radii (i.e., $d_+/2 + d_-/2$) is at least 314 pm (for KCl). Unless using unphysically small ionic sizes, MC–UPM exaggerates the γ_{\pm} value at increasing ionic concentration, compared with the experiment. Thus, the concentration range

of good fit is limited, implying no core repulsion since the number density of the ions is small. The lack of fit at higher concentration (e.g., >0.78 M for KCl, Table 2) has been attributed by Abbas et al. to ion association² but without proof or evidence; the result of such an effect is reduction in ion number density. In contrast, the DH–SiS fit for potassium halides extends to ~ 1.4 m or higher (Table 2) if a is allowed to somewhat exceed the sum of ionic radii, e.g., by $\sim 9\%$ for KCl. This reflects a weak polarization of the X^- (halide) ion by the K^+ ion.

With the large, singly charged K^+ ion, b_+ of best fit in MC–UPM is close to the crystallographic value, so K^+ is not hydrated; this is also expected of the larger alkali metal ions (Rb^+ , Cs^+), but, as mentioned by Abbas et al.² (albeit not shown), a best fit for RbX and CsX requires unphysically small cationic sizes (smaller than Pauling’s). This is an inherent problem in fits of the PM and theories based on it (e.g., MSA; see the Introduction of ref 3 and Discussion in Part 1¹) when the γ_{\pm} -vs- m (or γ_{\pm} -vs- M) curve declines monotonically up to high electrolyte concentration and does not pass a minimum, or when it exhibits a very shallow minimum. In contrast, DH–SiS can deal effectively with both RbX and CsX : The results for the RbX series are presented in Table 2, and they show the expected general trend as found with the smaller alkali metal halides. The

CsX series belongs to the group of “Type II” electrolytes (see footnote 12 in ref 5) and will be dealt with, presented, and discussed in a forthcoming paper.

3.2. Size of Small Cations (MC–UPM). For the smaller ions H^+ , Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , and La^{3+} , MC–UPM gives *very large* cationic diameters (Table 2). According to Abbas et al.,² such excessive sizes reflect high-coordination states of hydrated ions and, in some cases, more than one “shell” (or sheath) of coordinating water molecules. For example, a good fit for AlCl_3 is obtained with $b_+ = 720$ pm (Table 2). Abbas et al. have interpreted² this ISP as the diameter of *hydrated* Al^{3+} with two sheaths of water molecules around the bare ion.²² But to what extent can water molecules of the second sheath be distinguished from the water molecules of the bulk water solvent? A few related questions readily arise:

(1). What physical hardness does a “hard sphere” have when it comprises an Al^{3+} cation of negligible volume surrounded by water molecules that contribute 99.7% to the volume of the hydrated-ion sphere?

(2). How rigid can this arrangement of water molecules around Al^{3+} be?

(3). Furthermore, how can two colliding ionic hard spheres of mostly water sustain themselves as such at a distance of closest approach of over 700 pm?

Let us try to rationalize (a) ion sizes that are larger than expected based on crystallographic data and (b) the correlation between ion–ion contact distances, as reflected by ISPs, and hard-core effects. Figure 1 provides schematic sketches of different ions of different size, both nonhydrated (bare) and hydrated, with respect to their contact (or “collision”) distance. Upon interionic collision, a small cation strongly polarizes a large anion thereby deforming its shape, and, as a result, the core repulsion effect becomes smaller (Figure 1, case d) than if the anion were not deformed (Figure 1, case c). Due to the strong polarization, the portion of the anion in *direct contact* with the cation reflects much smaller sphere (depicted by the dashed circle in d). Dispersive forces are weak because most of

the anionic electrons are diffused away from the cation; this is due to the involvement, at short ion–ion distance, of covalent bonding effects.²³ Thus, the larger counterion contact distance (center-to-center) is *diminishing* the hard sphere repulsion effect, which becomes more similar to that of case a.

Hydrated ions are represented in Figure 1 by sketches e and f (see similar illustrations in ref 10). Here there is a weak core effect when two such ionic bodies approach each other since what in fact approach are two water molecules of the hydrated shell. (The shell’s effective size is represented by the large circles.) A larger body of a hydrated ion is assumed² to have a second water sheath. This sheath contains loose water molecules in contact with the coordinating water molecules of the first sheath. An interionic collision here is not very different from a collision of two free water molecules of “bulk water”. Therefore, the core effect created by the mutual approach of such “hydrated ions” loses its physicochemical meaning along with the concept of “hard sphere”.

Clearly, as deduced from the sketches of hydrated ions in Figure 1, core effects are small for a “multi-water sphere” in contact with another such sphere since the *actual* collision is between water *molecules* and not between the entire spherical arrangements of the many “hydrating” water molecules grouped together around the M^{n+} (say, Al^{3+}) ion. Phrased differently, it is hardly believable, considering the physical principles of chemical bonding, that a tiny M^{n+} (e.g., Al^{3+}) ion would tie up water molecules together very strongly through “fixing” them behind its first coordination shell, where they are placed ~ 3 Å away from that ion.

Yet, another complication with the assumption of highly hydrated ions is that it is not consistent with a concentration-independent ion size, as offered in ref 2. The effect of increasing electrolyte concentration on diminishing the size of hydrated ions has been discussed in the literature.^{13,14,24} Over a large concentration range, as covered by the MC–UPM study,² the extent of hydration varies, and this should cause the effective size of the hydrated ion to change: There are less hydration water

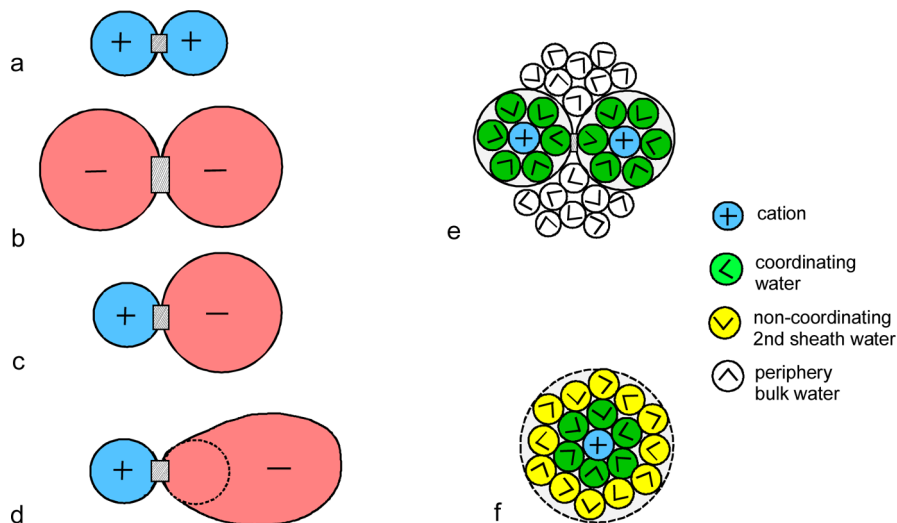


Figure 1. Two-dimensional schematic presentation of the limitation of the core potential concept as related to the size of two charged spherical bodies in solution, at a distance of closest approach; “boxes” at contact points represent schematically the extent of “core effect”. a – Two small positive (e.g., Na^+) ions (blue spheres); even though such ions are truly “hard spheres”, when they approach each other, the core effect produced is very small. b – Two large monatomic negative ions (red spheres), e.g., Br^- ions; a large anionic sphere, when approaching another such sphere, creates a quite strong core repulsion effect. c and d – A small cation (say Na^+) and a large anion (say Br^-) collide (blue sphere with red sphere; see text). e – Hydrated ion spherical bodies. I. f – Hydrated ion spherical bodies. II. See text for explanation.

molecules around an ion at higher ionic concentration than at lower concentration, and, as a result, hydrated ions should be smaller at high concentration than at low concentration; but more extensive “hydration” is a needed fitting tool in MC–UPM especially at higher ionic concentration.

3.3. Counterion Distance of Closest Approach. The a in MC–UPM (as $b_+/2 + b_-/2$) and a in DH–SiS are similar for 1–1 electrolytes (Table 2). For 2–1 electrolytes, a of DH–SiS is about 100 pm smaller, and for 3–1 electrolytes, it is ~ 200 pm smaller. MC–UPM has average a that is far larger than the sum of the calculated radii ($d_+/2 + d_-/2$); it is also larger than the average of counterion sizes in the DH–SiS case [as $(b_+ + b_-)/2$, usually equal to $(d_+ + d_-)/2$]. For example, for NaCl, the MC–UPM optimized a value is 349 pm, as $(b_+ + b_-)/2$; in DH–SiS, $(b_+ + b_-)/2 = 278$ pm. In MC–UPM, a is necessarily larger than the sum of the calculated radii of counterions (since $b_+ > d_+$); this is because of the need to account for a considerable core repulsion potential. Differences between best-fit b_+ and b_- are small in MC–UPM since ion size differences do not serve any purpose in the PM. In other words, the PM is “blind” to a possible effect of the size difference between the positive and negative ions. In contrast, in DH–SiS the $b_- - b_+$ difference (usually equal to $d_- - d_+$) is a major drive for the electrostatic repulsion (in addition to larger a), and core repulsion effects are ignored.

3.4. Essence of Nonadditivity in DH–SiS. A positive ISP nonadditivity ($d > 0$) in halide electrolytes is attributable to polarization effects^{3,21,25} exerted by a small cation on a larger halide ion upon mutual approach and collision. It is well-known²³ that such polarization elongates the contact distance between the positive and negative centers of the counterions; this is attributed to an increased covalency of the ion–ion bonding interaction. To some extent, oxo ions may also be polarized (e.g., NO_3^- , Table 2), but the elongation of a may then be somewhat mitigated by the closer ion–ion contact distance when the cation approaches the anion between adjacent oxygens instead of “head-to-head”. Since a smaller cation is more strongly polarizing and a larger anion is more polarizable, the elongation of a – the factor $a - (b_+ + b_-)/2$ ($\equiv d/2$) – changes along the order of increasing cationic size, $\text{H}^+ < \text{Li}^+ < \text{Na}^+ < \text{K}^+$, as follows (Table 2).

Cl^- : 122, 68, 66, 29 pm

Br^- : 136, 107, 71, 27 pm

I^- : 160, 149, 70, 33 pm

A parallel elongation of a is observed with alkaline earth halides. For very large cations, for example, Rb^+ , $d/2$ may become negative (e.g., in RbBr , RbI ; Table 2); this may be due to ion-shape deformation arising from formation of quasi-covalent transient bonding that involves overlap of larger-shell atomic orbitals (e.g., p - d hybrids).

An alternative explanation for the elongation of a (in DH–SiS), according to a referee, is that upon mutual approach, two counterions may “capture” a solvent molecule between them; for example, a $\text{Na}^+ - \text{H}_2\text{O} - \text{Cl}^-$ collision structure can be formed instead of $\text{Na}^+ - \text{Cl}^-$ in which the shape of the chloride ion is deformed by polarization. Such an explanation, although qualitatively plausible, is difficult to reconcile with the varying extent to which a elongates in series of related electrolytes, as shown above. There is not sufficient “free” space for a water molecule between the positive and negative ions, when the ions

are “at contact distance”; also, the excess a length ($d/2$) is not constant, as would be expected if water molecules occupied the free space between counterions.

3.5. Ion-Size Consistency. MC–UPM cannot keep b_+ of a given small cation constant; b_+ varies with the change in counterion. For example, for H^+ , the b_+ value, for various counteranions, changes between 370 and 464 pm (Table 2), a 25% variation; in contrast, the H^+ diameter in DH–SiS (Table 2) is constant regardless of the type of anion and is very small –116 pm – as may be expected from a hydronium ion (H_3O^+).^{21,26,27} As another example, b_+ of Ca^{2+} varies in MC–UPM (Table 2) between 530 and 594 pm, depending on the counteranion; that is, the b_+ variability is 12%. Sodium electrolytes in the MC–UPM fit² give best-fit b_+ of 336 pm for all halides, and this value is assumed² to represent a hydrated sodium cation; but b_+ is only 204 pm (i.e., that of unhydrated Na^+) for the perchlorate, for which the fit limit is ~ 0.5 M (Table 2), and for the nitrate.² If Na^+ is hydrated in the presence of halide counteranions, why would it not in the presence of other univalent anions? The DH–SiS fit is, in contrast, achievable for many sodium electrolytes, with a constant b_+ value of 194 pm (Table 2), equal to the crystallographic diameter (d_+) of Na^+ .

3.6. Comparison Summary of Table 2. MC–UPM and DH–SiS give the same fit with experiment when the core potential and the net electrostatic repulsion potential are both small. This happens (1) at low concentration and (2) when ions are small (less hard-sphere effect) and/or counterions are of similar size (smaller SiS). An example of a relatively good agreement between the two models is the potassium halides, but fit quality and fit range are better in the DH–SiS case (see Part 1;¹ also, Table 2).

The cation size order (as b_+) as found by MC–UPM is $\text{Al}^{3+} > \text{La}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{H}_3\text{O}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+$; for DH–SiS, this order is $\text{K}^+ > \text{Ca}^{2+} \approx \text{Mg}^{2+} \approx \text{La}^{3+} \approx \text{Al}^{3+} > \text{Na}^+ > \text{Li}^+ > \text{H}_3\text{O}^+$ (Table 2). The DH–SiS analysis thus provides an ion-size order that is (1) very different from that of the “recommended ionic radii” of Abbas et al.² and (2) in better agreement with literature values (e.g., Pauling’s). In the case of small, highly charged cations, ionic sizes of DH–SiS (b_+ ’s) exceed the crystallographic values (d_+ ’s), perhaps due to partial – but strong – hydration (Table 2). In both models – MC–UPM and DH–SiS – the anion sizes (as b_- ’s) are the calculated diameters (d_- ’s),^{19,20} so all anions of the current comparison are assumed to be entirely unhydrated.

4. DISCUSSION

In the context of the present analysis, the ISP is ideally considered as the closest dynamic contact distance between ions, that is, the collision distance. The dynamic process of ionic collisions in the DH theory, due to formation and dissipation of the ion atmosphere, occurs at a time domain of picoseconds.¹⁰ Therefore, the collision should usually be between bare – not hydrated – ions unless ions are very strongly bonded chemically to water molecules; for example, this is the case for H^+ that is essentially H_3O^+ in solution at any time domain.^{4,5,21,26,27} Ion sizes derived from physical measurements (such as some spectroscopic techniques) may have different values if measured at a different time scale compared with that of the ionic model, say microseconds. Such measured sizes, especially when reflecting hydrated ions, are outside the realm of both the PM and the DH model.

The goodness of the fit with experiment, e.g., γ_{\pm} (γ_{\pm}) vs I ,¹ is only one criterion for the effectiveness of electrolyte models and theories; another is achieving best fit with ISPs that genuinely represent ionic size and structure. Traditionally, electrolyte theories such as the DH theory, HNC, and MSA (see Introduction) have been tested for their fit with experiment using ISPs as the crystallographic diameters of ions, and when the fit required larger ISPs, ions were claimed to be hydrated. It is *a priori* very appealing to assume that ions are hard spheres, and their contact distances are sums of their known radii, preferably the crystallographic radii. This is apparent in the literature (e.g., ref 20 and references therein). Moreover, even though crystallographic radii are derived from solid-state measurements and calculations, they are believed to also represent ions in liquid solution.²⁸

When comparing MC-UPM with DH-SiS, it is in order to ask what the ion-size term really means in each case. For MC-UPM, Abbas et al. stated² that “mapping of the MC simulation results... will serve... to obtain reliable effective ionic radii” [that] “in the present context” [are meant to be] “the sizes of ions by which the activity and osmotic coefficients of a specific salt solution can reliably be predicted within a specific concentration range”. Obviously, such a statement concedes that ISPs, as fitting parameters, may not represent genuine ionic dimensions; instead, they are given enough flexibility to be of *any value*, even outside the acceptable range of ionic dimensions, just in order to fit a model/theory to experiment. The optimized “sizes” may then be claimed to include electrostriction, hydration shell overlapping, and exclusion volumes;² but this only relates to *cation sizes* since in the MC-UPM fit, anionic ISPs (b_- 's) are chosen as the respective calculated ion diameters (d_- 's).

In DH-SiS, the ISPs are ideally chosen as the calculated diameters for *both* the cations and anions. Optimization of the fit with experiment sometimes requires adjustment of the cationic diameter, especially for small and highly charged cations (see Table 2). Also, the counterion's distance of closest approach (a) may not be the sum of the respective radii, thus reflecting specific effects, e.g., a deformation of the spherical shape of a large anion due to its polarization by a small cation.^{23,25}

An inherent difficulty in using the concept of “ion size”,^{20,29,30} even if not merely to “assign” a physical role to an adjustable parameter in theoretical derivation of excess functions, is that the concept is vague, inconsistent, and often quite confusing. It is based on how we *visualize* an ion instead of what the ion *really is*. Therefore, any attempt to find a constant, “universal” value for the “size” of an ion is doomed to fail, as has been extensively argued and discussed in the literature.^{29,30} Specifically, determining where an ion “ends” in a given space, such as in solution or in a solid lattice, as we move from the center of this ion toward the center of an adjacent ion, is arbitrary. This is especially so for distances of closest approach between counterions because for co-ions we can simply *define* the ionic diameter as the center-to-center contact distance. In polyatomic ions, the interionic distance of co-ions is an effective average ionic diameter of somewhat compromised physicochemical meaning; this is due to the different possible orientations of ion-ion approach. For counterions, we intuitively assume that as we go along the straight line connecting the positive and negative ionic centers, one ion “ends” just where the other “begins” but this is not so, at least as a general rule.

The SiS treatment is unique in providing co-ion ISPs – the b 's – as (by definition) “true” ionic diameters, while clearly

distinguishing them from counterion ISPs – the a 's that, as mentioned above, are usually *not* sums of ionic radii. In MC-UPM, b_+ is adjustable and a always equals $1/2(b_+ + b_-)$. Whether adjustable a 's (in DH-SiS) and b_+ 's (in MC-UPM and sometimes in DH-SiS) reflect a physical reality can be inferred from their constancy when relating to the same ion (say, in different electrolytes) and consistency when exhibiting trends in ionic series (e.g., alkali metal cations). As shown in Table 2, in MC-UPM there is a lack of consistency in b_+ , hence the additive a , in series of electrolytes with the same cation. If b_+ represents hydrated cations, as suggested by Abbas et al.,² why is it not constant at the same cationic concentration for different counteranions? Also, why does the assumed hydrated ion not vary in shape and size with electrolyte concentration over many orders of magnitude of molarity/molality?

The ISPs of DH-SiS, especially the b 's, whenever reflecting naked ions and even when somewhat adjusted for best fit, are not necessarily less “correct” than other ionic “sizes”, such as calculated diameters, bearing in mind that the former distances are dynamic whereas the latter are usually lowest-energy *equilibrium* distances between ions, (as, for example, between an ion of interest and O^{2-} anion²⁰). The fact that the ISPs in DH-SiS are constant over electrolyte concentration ranges of many orders of magnitude (e.g., 10^{-4} – 1 M) is further support for my argument that these ISPs do bear physicochemical meaning.

5. CONCLUSION

In this Part 2 of the comparison between MC-UPM and DH-SiS, the emphasis has been on the ISPs that provide model-experiment best fit for activity coefficients as functions of concentration (or ion strength) and on the meaning of those ISPs in both models. For small cations ($d_+ < \sim 200$ pm), the fit optimization of MC-UPM always results in sizes that are much larger than the crystallographic diameters. Due to the inherent ISP additivity in MC-UPM, the corresponding ISPs of counterions (a 's) are far larger than the sums of the respective crystallographic radii. In fitting the PM with experiment, large ISPs are needed to enable strong repulsion-type core potential. As “hard spheres”, ions in the PM are only defined by their *size*; the type, number, and geometric arrangement of atomic constituents in the ions, and atom-atom bonding characters, are all ignored. Cation sizes larger than the corresponding crystallographic values are attributed to ion hydration, and the limitation of the fit to low concentration is explained as resulting from ion pairing occurring at higher concentration.² Also, in most cases compared in the present study, MC-UPM fits have given, as optimized parameters, varying cation “diameters”.² Such ISPs are inconsistent with model assumptions and with reality in (1) being too large to be considered as those of “hard spheres”, (2) changing with the counteranion without apparent reason, and (3) being constant at varying ionic concentration albeit assumed to represent hydrated ions.

According to the present analysis, hydration and ion-association arguments are overused in MC-UPM in explaining what appears to be modeling deficiencies; as such, these arguments are unjustified and misleading, compromising our ability to unravel the real physicochemical nature of electrolyte systems. Spectroscopic measurements of ionic solutions, e.g., neutron diffraction or scattering,^{10,31,32} should be carefully assessed for their ability to explain the deviation of electrolyte solutions from thermodynamic ideality. Even if ion hydration and ion pairing are indicated by some spectroscopic technique,

their very existence does not necessarily imply that they play role in dynamic ion–ion interactions in solution. In solution, ions can hop from one hydration state to another as naked ions, so ion–ion collisions occur between naked ions even if hydration and ion pairing do exist. Obviously, hydration reactions with ions depend on the *time domain* at which ionic solution phenomena are observed or modeled.^{10,31}

Unlike MC–UPM, DH–SiS is very effective in representing real electrolyte solutions (see also Part 1¹); co-ion ISPs are usually in full accord with crystallographic data (i.e., $b_+ = d_+$ and $b_- = d_-$), and they do not change for different counterions. Since the ISPs of DH–SiS do not agree with the “recommended ionic radii”² of MC–UPM (unless identical with calculated radii), due diligence is required when evaluating those radii as quantities of physicochemical essence. In particular, the current study emphasizes the risk of forcing a fit between an electrolyte model (or theory) and experiment; not only may this lead to a false conviction that the model (or theory) is “correct”, but it may also result in optimized ISPs of no actual meaning. Very large ISP values obtained by fitting the PM with experiment (e.g., 720 pm in the Al^{3+} case²) should be considered with great caution before interpreted as those of hydrated ions.²²

■ APPENDIX A

Ion Sizes in NaCl Solutions – A Test Case

The complexity of the ion size concept, as discussed above, and its relevance to ionic models and theories can be illustrated for the classical case of aqueous NaCl. Ion sizes of Na^+ and Cl^- in NaCl solutions are subject to the states of these ions, whether naked or solvated (e.g., hydrated). Sizes in theoretical computations are ISPs that vary with the type and method of computation. At least three “kinds” of size have to be considered for *naked* ions:

- (1). The size related to the electrostatic minimum ion–ion distance that may be best represented by the crystallographic size.
- (2). The covalent–ionic size that arises from overlapping of atomic orbitals of the approaching ions, which partially creates quasi molecular orbitals. (This is especially important in the case of ionic polarization.)
- (3). The equilibrium diameter or kinetic diameter (“sigma”) due to electron dispersion, as reflected, e.g., by the Lennard–Jones (L–J) potential.

The present test case analyzes the work of Lyubartsev and Laaksonen (L&L)³³ and its comparison with MC–RPM/MC–UPM and with DH–SiS. The above authors derived effective

interaction potentials between Na^+ and Cl^- from radial distribution functions (RDFs) in MD simulations of NaCl solutions. They then applied MC simulations to calculate activity and osmotic coefficients for the ions. They employed the simple point charge (SPC) water model of Toukan and Rahman³⁴ and used – as L–J constants [the distance parameter (“sigma” in literature notation) and the energy constant (“epsilon”)] – the values given by Smith and Dang for ion–water and ion–ion interaction.³⁵ They next derived the RDFs for two rather concentrated solutions, 0.9 and 4 M, and found effective potentials that have 1–2 oscillations, which they have associated with the molecular nature of the solvent (water). Lyubartsev and Laaksonen provided six different MC computation “runs” of excess functions, each with a different combination of system parameters. Summarizing their findings, they stated that the “important outcome from this study is that the osmotic and activity coefficients can be obtained without adjustable parameters such as hydration radii, and are in good agreement with experiment”. This statement leaves an impression that ion radii are available “somewhere out there” and therefore should not be adjusted for a successful treatment that includes both the electrostatic (coulomb) and dispersion (L–J) contributions to the excess functions in the UPM; this is so when the latter model is modified for a more realistic dispersion contribution. If Lyubartsev and Laaksonen are correct, then the entire comparison of the present article (main text) is meaningless since the two theoretical methods compared here, MC–UPM and DH–SiS, optimize the computed activity coefficients by *adjusting* ISPs.

Note, however, that even though Lyubartsev and Laaksonen indeed did not adjust their ISPs, these ISPs *were* adjusted by Smith and Dang through optimization of the SPC model.³⁵ Therefore, the L&L ISPs for Na^+ and Cl^- were not derived by independent measurements. Also, the “good agreement with experiment”³³ was obtained without checking the sensitivity of the computation to variations in ionic sizes. It is, thus, unknown what results would have been obtained had the *crystallographic* sizes of Na^+ and Cl^- been employed. There is also no information from Smith and Dang on the sensitivity of the RDFs to different choices of the L–J parameters.

Table A1 compares the L&L data³³ with the “unoptimized” ISPs, on the one hand, and, on the other hand, data derived from the PM:² MC–RPM and MC–UPM, and from DH–SiS:³ DH–SiS(1) with the respective optimized ISPs (as above), DH–SiS(2) with the crystallographic ionic sizes and ISP additivity, and DH–SiS(3) with the L&L ISPs. (Note that γ_{\pm} has been converted here to γ_{\pm}^{\pm} ; this was not done by Lyubartsev

Table A1. γ_{\pm} of Aqueous NaCl Solution at 25 °C As a Function of Molarity: Computed vs Experimental Values^a

M	exp ^b	MC–RPM	MC–UPM	DH–SiS(1)	DH–SiS(2)	DH–SiS(3)	L&L range
0.001	0.965	0.9641	0.9641	0.9651	0.9647	0.9650	0.963–0.965
0.01	0.903			0.9027	0.8994	0.9013	0.890–0.905
0.1	0.779	0.7704	0.7703	0.7791	0.7580	0.7691	0.76–0.78
0.3	0.714	0.7039	0.7041	0.7130	0.6683	0.6891	0.68–0.72
0.6	0.680			0.6810	0.6121	0.6407	0.64–0.67
1	0.669	0.6864	0.6865	0.6680	0.5738	0.6087	0.62–0.67
1.5	0.677			0.6685			0.61–0.70
2	0.694	0.7772	0.7780	0.6740			0.61–0.73

^aISPs are 349 pm for MC–RPM (ref 2), the respective parameters in Table 2 for MC–UPM, the respective parameters in Table 1 for DH–SiS(1), the crystallographic diameters for DH–SiS(2), and 235, 337.5, and 440 pm for the $\text{Na}^+–\text{Na}^+$, $\text{Na}^+–\text{Cl}^-$, and $\text{Cl}^-–\text{Cl}^-$ closest distances, respectively, in the case of DH–SiS(3) and L&L (ref 33). ^bExperimental values, converted from the LR to the MM scale (see text).

and Laaksonen who compared their computed γ_{\pm} with literature's γ_{\pm} .) In comparing the various computations, Table A1 can be split into three concentration regions. In the first, up to ~ 0.1 M, the L&L results are very good, but there is almost no effect of ISPs (in this case, the respective L-J distance parameters), and the γ_{\pm} range mostly reflects differences between computation runs. DH-SiS(3), with the same sigma values for Na^+ and Cl^- , gives the same fit! DH-SiS(1) provides, of course, a better fit, but even DH-SiS(2), with full additivity of the crystallographic ("electrostatic") ISPs, gives a fairly decent fit.²⁵ MC-RPM and MC-UPM both exhibit the same result with the fit being at least as good as the L&L fit, and this further proves that the computation is almost insensitive to the ISP choice and to whether ions are size-similar or size-dissimilar. In the second, middle concentration region, 0.1–0.6 M, the L&L fit is still quite good, but it is again as good as the DH-SiS(3) fit and so has no advantage due to considering a combination of the electrostatic, dispersion, and solvent effects. DH-SiS(1) is once again much better, but DH-SiS(2) now loses its ability to fit with experiment. In the third concentration region, 1–2 M, the L&L fit seems to gain considerable advantage over DH-SiS(3) and DH-SiS(2), as expected, but DH-SiS(1) is still quite good up to ~ 1.5 M. In this M range, both MC-RPM and MC-UPM clearly exaggerate γ_{\pm} as has been discussed earlier.¹ However, at ≥ 1 M, the L&L data of different runs fluctuate too much (bottom of last column in Table A1) to be considered as providing a "fit".

It is thus demonstrated here that the L&L modeling work is not really contributing to the understanding of how the NaCl solution behaves thermodynamically since this modeling cannot distinguish between different ISP choices and it does not have an advantage over the simpler MC simulations of the PM² and the very simple computation of DH-SiS that ignores the nonelectrostatic effects.³ The L&L study only indicates that one can use the L-J parameters of Smith and Dang to calculate excess functions but without proving that those parameters are correct or that others are incorrect. The idea that there is advantage in the use of unadjusted parameters for calculating excess functions³³ is also unconvincing (see ref 25); this is in addition to the fact that the unadjusted parameters used by Lyubartsev and Laaksonen are, in fact, optimized parameters, albeit those of other researchers who did the optimization previously and on whose work the L&L analysis is based.

Other modeling efforts of aqueous NaCl include the MD simulation studies of Degreève and da Silva,³⁶ of Aziz et al.,³⁷ and of Bouazizi et al.²⁴ In the first study, the stability of ion pairs in 1.0 M NaCl solution was examined and, in terms of "maximum lifetimes", found to be 0.13, 0.14, and 0.27 ps for the $-$ $-$, $+$ $-$, and $+$ $+$ pairs, respectively; non-neutral ion pairs were found to be stabilized by the counterions and water molecules. Considering that the formation and dissipation of the ionic atmosphere in the DH model is apparently in the range of hundreds of picoseconds, ion pairs according to Degreève and da Silva may not be "seen" in such a formation–dissipation cycle because within this cycle, they are at full dynamic equilibrium with the free ions. In the study of Aziz et al.,³⁷ Na^+ – H_2O and Na^+ – Cl^- distances in aqueous NaCl were calculated through modeling near-edge X-ray (NEXAFS) spectra at the Na *K* edge. Using different models applying to different hydration clusters, the values they obtained for Na^+ – Cl^- distances were 3.9 Å (390 pm) or higher. An *a* value of 3.9 Å is considerably larger than the crystallographic value (2.8 Å) but only 0.4 Å larger than the optimized *a* in the DH–

SiS fit of γ_{\pm} , as shown in Table A1 for DH–SiS(1). Bouazizi et al.²⁴ compared their MD simulations with X-ray scattering results over a wide range of NaCl concentration in water (0–4 m). Their study suggests that the cationic (Na^+) hydration number decreases with increase in salt concentration, in agreement with previous literature claims.^{13,14}

APPENDIX B

Influence of ISPS on the DH–SiS Fit Limit

The underlying assumption in the SiS treatment in regard to the core and other nonelectrostatic potentials is that, to a first approximation, the contribution of those potentials to the thermodynamic nonideality of electrolyte solutions can be ignored at sufficiently small concentration at which ions, on average, are separated from one another by a free distance of the order of magnitude of their average diameter. This is illustrated in Figures B1 and B2, representing two somewhat different analyses of the relative effect of the coulomb and dispersion potentials at very small *r* (*r*, radial distance from the origin). Table B1 compares various analyses (see details below)

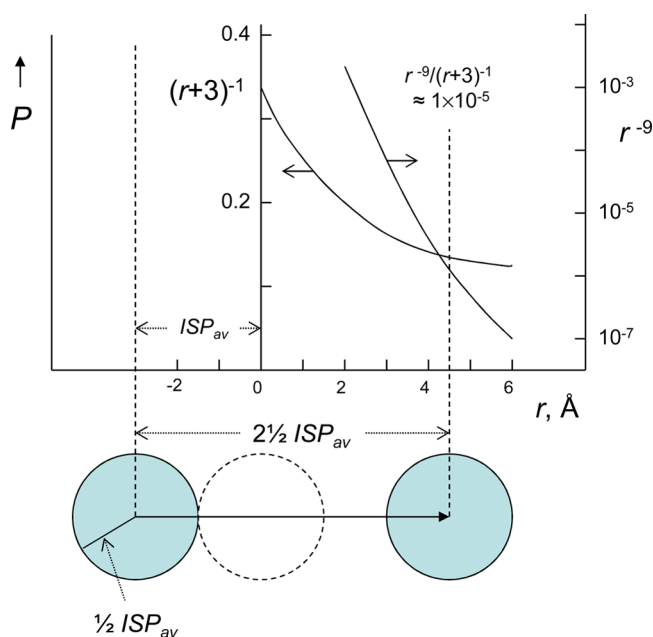


Figure B1. A qualitative schematic illustration of the relationship between the attractive coulomb potential ($-r^{-1}$) and the London repulsive dispersion potential (here as $+r^{-9}$) between two counterions. This relationship is for moderate ionic concentration (~ 0.1 M).

on the extent of contribution of the nonelectrostatic potential to the total ion–ion interaction potential, as a function of the "free distance" between neighboring ions.

The average ion–ion separation distance can be estimated by the $(V/N)^{1/3}$ criterion,⁹ V/N being the average volume of the electrolyte solution per single ion (see below). A term ISP_{av} can be defined as $ISP_{av} \equiv (\nu_+ISP_+ + \nu_-ISP_-)/\nu$, with $ISP_+ \equiv (\nu_+b_+ + \nu_-a)/\nu$ and $ISP_- \equiv (\nu_+a + \nu_-b_-)/\nu$, ISP_+ and ISP_- being the average ISPs of the positive and negative ions, respectively. Following is a step-by-step description, in section B1, of the derivation of the ISP_{av} value below which dispersive hard-core effects cannot be ignored. In section B2, I show how this ISP_{av} limit is related through $(V/N)^{1/3}$ to the concentration (or ionic strength) limit of the effectiveness of the SiS treatment (DH–SiS).

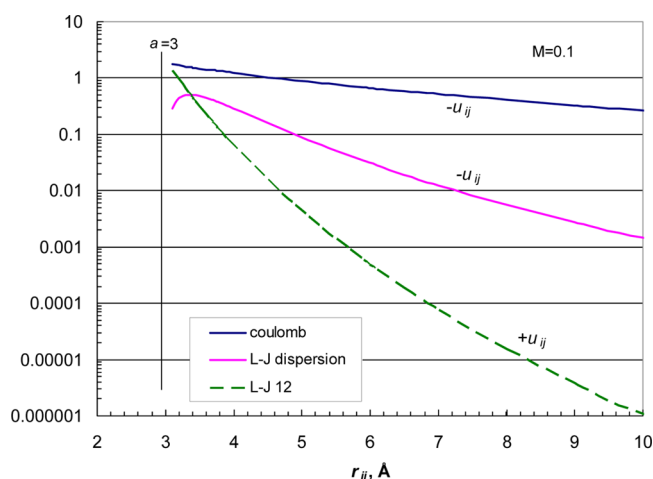


Figure B2. Comparison of the electrostatic DH potential with $a = 3 \text{ \AA}$ (blue upper line), with the L-J 12–6 potential with a distance parameter of 3 \AA and an energy constant of 0.5 kJ/mol (magenta lower line); the green broken line is the 12-portion of the L-J potential. Concentration: 0.1 M .

Table B1. Estimated Percent Contribution of the Dispersive Potential to the Total Interionic Interaction Potential As a Function of Ion–Ion Average Distance

method	$1.25 \text{ ISP}_{\text{av}}$	$1.5 \text{ ISP}_{\text{av}}$	$1.75 \text{ ISP}_{\text{av}}$	$2.0 \text{ ISP}_{\text{av}}$	$2.5 \text{ ISP}_{\text{av}}$
Figure B1		10	0.5	0.06	0.0008
ref 38	69	~8		~0	
Figure B2 ^a		13	8	4	1.8
Figure B2 ^b		2	0.38	0.086	0.008

^aEntire L-J potential, see text. ^bOnly repulsion portion of the L-J potential.

B.1. Estimation of the Core Potential Contribution to the Total (Electrostatic + Core) Potential as a Function of the Average Ion–Ion Distance

In Figure B1, the dispersive attraction potential (r^{-6}) is ignored because it adds to the coulomb attraction potential; a simplified picture can thus be derived without the additional uncertainty of the r^{-6} potential due to its unknown coefficient. On the specific diagram of Figure B1, the ion–ion electrostatic (coulomb) potential is chosen as $(r+3)^{-1}$, with $3 -$ in \AA – being the distance of closest approach, or ISP_{av} between two colliding equal-size (size-averaged) ions approximated as hard spheres. The repulsion core potential due to electron dispersion forces is assumed to be r^{-9} , without a weighting factor combining the coefficient of the coulomb potential with that of the r^{-9} dispersion potential (i.e., approximating this factor as 1). The two potentials are placed on their respective (different) scales. The negative ninth power of r is so chosen to increase the core contribution at a given r , as compared with higher negative powers. The two potentials are presented here as functions of ISP_{av} as P -vs- r curves in which P is $-u_{ij}$ for the attraction coulomb potential and $+u_{ij}$ for the dispersion (repulsion) 9-potential. At an internuclear distance of $(r+3) \approx 2.5 \text{ ISP}_{\text{av}}$ or at $r \approx 4.5 \text{ \AA}$ (7.5 \AA away from the center of the reference ion), the contribution of the dispersion potential is thus estimated to be only about 0.0008% of the entire ion–ion interaction potential (electrostatic plus nonelectrostatic). At $(r+3) = 2.0 \text{ ISP}_{\text{av}}$ the core potential contributes 0.06% , and at $(r+3) = 1.75 \text{ ISP}_{\text{av}}$ 0.5% ; at $(r+3) = 1.5 \text{ ISP}_{\text{av}}$ the core contribution is 10% (Table B1).

Friedman³⁸ did similar calculations; he also used a core repulsion function with r^{-9} and ignored the r^{-6} attraction component, but he added Gurney's cosphere overlap potential. Without the latter potential, the core potential contribution to the entire potential (core plus electrostatic) in Friedman's analysis (Table B1) is $\sim 0\%$ at $2.0 \text{ ISP}_{\text{av}}$, $\sim 8\%$ at $1.5 \text{ ISP}_{\text{av}}$ and 69% at $1.25 \text{ ISP}_{\text{av}}$. Due to differences in the details of the computations, there are understandably some numerical differences between the current analysis and Friedman's on the extent of contribution of the core effect; but the two analyses nonetheless provide similar results, and they both agree that above $\sim 2.0 \text{ ISP}_{\text{av}}$ the core contribution is practically negligible, whereas below $\sim 1.75 \text{ ISP}_{\text{av}}$ the core contribution cannot be ignored.

In another analysis, with the full 12–6 L-J potential, the picture is somewhat different, but it gives essentially the same outcome; this is presented in Figure B2. Here, I assume that the coulomb potential can be chosen as that of the DH theory. This is based on the analysis of Card and Valteau,³⁹ who compared radial distribution functions (RDFs) derived from the DH electrostatic potential with those computed from potentials obtained by MC simulations of the PM; the agreement between such sets of RDFs at different concentrations was fair even at very small r . If one assumes that the L-J distance parameter is 3 \AA and the energy constant is 0.5 kJ/mol (see ref 33 and Appendix A), then the contribution of the L-J potential (sum of dispersive repulsion and dispersive attraction terms) can be compared with the coulomb contribution (Table B1). At ionic concentration of 0.1 M (Figure B2), at $r = 7.5 \text{ \AA}$, i.e., $2.5 \text{ ISP}_{\text{av}}$ of Figure B1, the L-J potential is 1.8% of the entire potential; at $r = 6.0 \text{ \AA}$ ($2.0 \text{ ISP}_{\text{av}}$) it is 4% ; at $r = 5.25 \text{ \AA}$ ($1.75 \text{ ISP}_{\text{av}}$), 8% ; and at $r = 4.5 \text{ \AA}$ ($1.5 \text{ ISP}_{\text{av}}$), 13% ; see Table B1. Somewhat higher values (not shown) are obtained at 1 M . The results based on Figure B2 suggest more dispersion potential contribution than in the case of Figure B1, and, obviously, when including the attraction portion of the dispersion potential in the computation, the overall dispersion contribution is smaller. Nevertheless, the above conclusion that the core effect cannot be ignored below about $1.75 \text{ ISP}_{\text{av}}$ appears correct, and the choice of $2.5 \text{ ISP}_{\text{av}}$ as the limit of the effective fit range of DH–SiS is supported also by this second analysis (Figure B2).

In Figure B2, there is also a plot of the positive (repulsion) portion of the 12–6 potential. An analysis as above (Figure B1) on the relative contribution of the nonelectrostatic repulsion potential gives 0.008% , 0.086% , 0.38% , and 2.0% for $2.5 \text{ ISP}_{\text{av}}$, $2.0 \text{ ISP}_{\text{av}}$, $1.75 \text{ ISP}_{\text{av}}$, and $1.5 \text{ ISP}_{\text{av}}$, respectively (Table B1). These percentages are similar to those of Figure B1 with the small differences (within the same order of magnitude in each case) arising from the differences between the potentials chosen in the two sets of potentials. Note also that for the L-J potential, the coordinate origin is the center of the reference ion (or atom) in the collision with an approaching ion, whereas a London dispersion potential is computed from the outer surface of that ion (Figure B1).

B.2. Electrolyte Concentration Limits for Effective Use of DH–SiS

Table B2 presents fit limit estimates for various common representatives of different electrolyte valence families; the estimates have been obtained by employing the average ion–ion distance limit of $2.5 \text{ ISP}_{\text{av}}$ (section B.1). In relating ISP_{av} to ion size, I use the relation $(V/N)^{1/3} = 2.5 \text{ ISP}_{\text{av}}$. For example, the limiting average interionic distance for NaCl (LR-scale fit) is 777.5 pm (i.e., $2.5 \times 311 \text{ pm}$). It can be assumed that at this

Table B2. High Concentration Limit Conditions for Electrostatic Model (DH–SiS)^a

family	example	system	ISP_{av}	N/V	M_i^b	M^b	$m_{obs}(M_{obs})$	I^c	I_{obs}
1–1	HCl	LR	300.0	2.4	3.94	1.97	~3	1.98	~3
1–1	NaCl	LR	311.0	2.1	3.53	1.77	1.8	1.77	1.8
		MM	315.2	2.0	3.39	1.70	1.5	1.70	1.5
1–1	NaClO ₄	LR	337.0	1.7	2.78	1.39	>2.5	1.39	>2.5
		MM	345.2	1.5	2.58	1.29	1.5	1.29	1.5
2–1	CaCl ₂	LR	346.4	1.5	2.56	0.85	0.9	2.56	2.7
		MM	333.5	1.7	2.86	0.95	~1.0	2.86	~3
1–2	Na ₂ SO ₄	LR	270.7	3.2	5.36	1.78	1.2	5.36	3.6
3–1	LaCl ₃	LR/MM	338.7	1.6	2.73	0.68	~1.0	4.10	~6
1–3	K ₃ Fe(CN) ₆	LR	329.5	1.8	2.97	0.74	0.6	4.46	3.6
2–2	MgSO ₄	LR	311.5	2.1	3.52	1.76	~1.6	7.03	~6.4
1–4	K ₄ Fe(CN) ₆	LR	325.0	1.9	3.10	0.62	~0.5	6.19	~5.0
3–2	In ₂ (SO ₄) ₃	LR	342.1	1.6	2.65	0.53	0.4	7.96	6.0

^a ISP values are in pm, V in nm³. m_{obs} (or M_{obs}) and I_{obs} (on m or M scale) are the corresponding high limits, as observed by fitting theory with experiment. The HCl fit is from ref 21; all others fits on the LR scale are from ref 3; MM fits are of the present work. ^b M_i – ionic molar (molarity, $M \times$ total number of ions in an electrolyte “molecule”). ^c I calculated from either molality (LR) or molarity (MM), depending on the case.

distance, the contribution of London-type dispersion forces is negligible when compared with the contribution of coulomb forces. According to Table B2, the calculated “high concentration limit” for the all-electrostatic SiS model is overall in good agreement with the observed limit for selected electrolytes of different families (m_{obs} on LR scale, M_{obs} on MM scale). Thus, the SiS model should be valid especially when ions, on average, are separated from one another by an internuclear distance equal at least to about $2.5 ISP_{av}$.

Table B2 thus indicates that the nonelectrostatic potentials (ignored in DH–SiS) contribute very little up to I value of at least about 2, the actual value being dependent on the particular electrolyte. Within the crude nature of the calculation of the fit limit, the agreement with the actual limit in both LR and MM scales is reasonable. In some cases, the fit exceeds the expected “limit”, e.g., in HCl, NaClO₄, and LaCl₃; in others, it is below the expected value, e.g., in Na₂SO₄, K₃Fe(CN)₆. The trend, however, is clear: For 1–1 electrolytes, DH–SiS should generally fit with experiment up to about 1.5 M, and for higher valence electrolytes, the fit limit should usually be smaller, ~0.5–1 M. This is confirmed in Table 2 of the main text. Thus, up to ~1.5 M in 1–1 electrolytes and ~0.5–1 M in the other electrolyte families, nonelectrostatic (core) effects are small and, to a first approximation, negligible.

Table B2 also shows that for many electrolytes the model–experiment fit is effective up to a concentration $N/V \approx (2.5 ISP_{av})^{-3}$, corresponding to ~1.5–3 ions in 1 nm³ volume. Obviously, more ions can reside in this unit volume at the fit limit when they are, on average, smaller. [Compare, e.g., HCl (ISP_{av} = 300 pm) with NaClO₄ (ISP_{av} = 345 pm); the two counterions of HCl are considerably smaller than those of NaClO₄.] Therefore, when the criterion for the fit limit is similar average ion–ion distance, for a given valence family, electrolytes with smaller ions (e.g., HCl) should exhibit a higher concentration fit limit than electrolytes with larger ions (e.g., NaClO₄), as confirmed in Table B2 (and Table 2). Past the N/V limit of $(2.5 ISP_{av})^{-3}$, calculated and measured activity coefficients lose their agreement rapidly, and the computed values gradually diverge from the experimental values (see Figure 7 in Part 1¹).

There is thus a simple explanation, based on the conversion of m (or M) to I , for the fact that in the case of DH–SiS, the fit between computed and experimental activity coefficients extends to $I \approx 6$ for higher-valence electrolytes ($|z_+z_-| \geq 3$),

whereas lower-valence electrolytes (1–1, 1–2, 2–1; $|z_+z_-| \leq 2$) usually lose that fit at a lower I (~1.5–2.5). The loss of fit at a I_{obs} value substantially smaller than the anticipated one (Table B2) indicates ion association (e.g., in Na₂SO₄) that increases the value of γ_{\pm} (or γ_{\pm}) due to the overall decrease in the ionic content in the solution. In general, however, the gradual loss of agreement between theory (DH–SiS) and experiment above $N/V \approx (2.5 ISP_{av})^{-3}$ is mostly due to the increasing role of nonelectrostatic repulsion potentials; therefore, this expected deviation of theory from experiment at higher concentration supports the validity of DH–SiS, that is, its being effective but only up to electrolyte concentration beyond which core effects cannot be neglected.

The above analysis of the ionic concentration range at which the core contribution is small is not applicable to MC–UPM in which a departure from a good computation–experiment fit is solely blamed on ion association.² Since ion association is assumed to vary from one electrolyte system to another, MC–UPM has ample flexibility in explaining the fit limit of any particular electrolyte. Also, the analysis in this Appendix does not apply for a case in which the cation size is allowed to be an adjustable parameter, as in MC–UPM.²

Nomenclature of This Article and of Part 1,¹ Combined

Abbreviations/Acronyms

DH	Debye–Hückel
DHEE	DH extended equation
HNC	hypernetted chain (equation)
ISP	ion-size parameter
L-J	Lennard-Jones (potential)
L&L	Lyubartsev & Laaksonen
LR	Lewis–Randall
MC	Monte Carlo
MD	molecular dynamics
MM	McMillan–Mayer
MPB	Modified Poisson–Boltzmann (theory)
MSA	mean spherical approximation (theory)
PB	Poisson–Boltzmann (equation)
PM	primitive model
RDF	radial distribution function
RPM	restricted PM
SiS	Smaller-ion Shell
SPC	simple point charge (water model)
UPM	Unrestricted PM

Mathematical and other notations

A	empirical factor in Appendix A of Part 1 ¹
a	an ISP; distance of closest approach between any two ions in RPM or DH model; of counterions in DH–SiS model
\mathcal{A}, \mathcal{B}	DH theory constants
b	an ISP; distance of closest approach between co-ions
C	concentration in molar scale (M)
d	ionic diameter, when with subscript + or –; or, a size-difference parameter, $2a - b_+ - b_-$ (a elongation)
g	correlation function
I	ionic strength
k	Boltzmann's factor
M	molar
m	molal
N/V	number of ions per unit volume of nm ³
P	potential (general notation)
q	ionic charge (fundamental charge times ion valence)
R	ion–ion contact distance
r	distance from coordinate origin
T	absolute temperature, in K
U	potential energy, eq 1 of Part 1 ¹
u	interaction potential between ions
W	molecular weight
w	effective ionic interaction potential
y	molar activity coefficient
z	ion charge number, or valence

Greek notations

α	ion of the 1 st atmosphere, or as defined specifically in the text (Part 1 ¹)
β	central, singled-out ion at the coordinate origin
γ	molal activity coefficient
ϵ	permittivity
ϕ	osmotic coefficient; or, ionic interaction potential
κ	reciprocal screening length
μ	chemical potential
ν	number of ions in the molecular formula of an electrolyte
σ	density; or, kinetic diameter

Superscripts

o	reference (“zero”) state
clc	calculated
exp	experimental

Subscripts

\pm	mean ionic
$+, -$	of positive (+), negative (–) ion
0	of solvent
av	average
α	of α ion; or, per definition in text for eq 1 in Part 1 ¹
β	of β ion
el	of electrostatic
i, j	of ion i, j
obs	observed
s, l	of smaller (s), larger (l) ion
sol	of solution
ν	of “volume-molar”
w	of “weight-molar”

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Fraenkel, D. *J. Chem. Theory. Comput.* **2014**, DOI: 10.1021/ct5006938.
- (2) Abbas, Z.; Ahlberg, E.; Nordholm, S. *J. Phys. Chem. B* **2009**, *113*, 5905.
- (3) Fraenkel, D. *Mol. Phys.* **2010**, *108*, 1435.
- (4) Fraenkel, D. *J. Chem. Thermodyn.* **2014**, *78*, 215.
- (5) Fraenkel, D. *J. Chem. Phys.* **2014**, *140*, 054513.
- (6) Debye, P.; Hückel, E. *Phys. Z.* **1923**, *24*, 185.
- (7) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959.
- (8) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold Publishing Corp.: New York, 1958.
- (9) Davidson, N. *Statistical Mechanics*; McGraw-Hill: New York, 1962; Chapter 21.
- (10) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*, Vol. 1, 2nd ed.; Plenum Press: New York, 1998; Chapter 3; also 1st ed., 1970; Chapter 3.
- (11) Rasaiah, J. C.; Friedman, H. L. *J. Chem. Phys.* **1968**, *48*, 2742.
- (12) Triolo, R.; Grigera, J. R.; Blum, L. *J. Phys. Chem.* **1976**, *80*, 1858.
- (13) Lu, J.-F.; Yu, Y.-X.; Li, Y.-G. *Fluid Phase Equilib.* **1993**, *85*, 81 and references therein.
- (14) Tikanen, A. C.; Fawcett, W. R. *J. Electroanal. Chem.* **1997**, *439*, 107.
- (15) Outhwaite, C. W. *J. Chem. Phys.* **1969**, *50*, 2277.
- (16) Outhwaite, C. W.; Molero, M.; Bhuiyan, L. B. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1315 and references therein.
- (17) Rasaiah, J. C. *J. Chem. Phys.* **1970**, *52*, 704.
- (18) *CRC Handbook of Chemistry and Physics*, 85th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2004–2005; 5-99–5-103.
- (19) *CRC Handbook of Chemistry and Physics*, 58th ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1977–1978; F-213.
- (20) Marcus, Y. *Chem. Rev.* **1988**, *88*, 1475.
- (21) Fraenkel, D. *J. Phys. Chem. B* **2011**, *115*, 557.
- (22) In analyzing hydrated Al^{3+} , Abbas et al.² concluded that there are two water layers around the ion. A referee has commented that a 720-pm diameter of hydrated Al^{3+} “does not seem to be exaggerated”, and it fits well with one water layer. This is since the (formal) diameter of a free water molecule in liquid water is ~ 300 pm. However, the analysis of Abbas still has merit since it goes beyond the specific case of the current discussion (ISPs as ion diameters), and therefore this analysis deserves close attention. From the free molar volume of water, 30 \AA^3 , one infers a molecular diameter of 310 pm, but in electrolyte solution, just the effect of electrostriction reduces this diameter to 271 pm (based on ref 10, p 185). Other effects, such as overlapping of hydration layers, ion–dipole interactions (causing charge separation hence shape deformation in the water molecule) and dipole–dipole interactions, further shrink the effective diameter of water *directly coordinating with an ion*. It is not unimaginable that in aqueous ionic solution, the diameter of a hydration water molecule is close to the self-diffusion value of 230 pm (ref 7, p 13). Considering the deformation (elongation) of the water molecule due to the above factors, and to its alignment with the ion to which it coordinates, say in an octahedral arrangement, deep interstices between the coordinating water molecules are created, and, as a result, the effective average diameter of say $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ is ~ 500 pm [as $\sim (2 \times 200 + 1 \times 100)$ pm]. The water molecules of the second sheath are contributing apparently much less to the overall size of hydrated Al^{3+} , ~ 200 pm, because they fit deep in the interstices of the first sheath. This rationalizes two water layers around Al^{3+} (vs one layer around Li^+ , Ca^{2+} , etc.; see Table 2), as suggested by Abbas et al.² However, it does not reflect my own view that the 720-pm ISP is not the diameter of hydrated Al^{3+} but an artifact due to imperfections of MC–UPM. Note also that modeling of the essence and structure of hydrated ions (and solvated ions, in general) is highly speculative and quite naïve, especially when relying on an electrolyte model that is based on an implicit solvent.
- (23) Silberberg, M. A. *Chemistry*, 3rd ed.; McGraw-Hill: Boston, 2003; p 549.

- (24) Bouazizi, S.; Nasr, S.; Jaidane, N.; Bellissent-Funel, M.-C. *J. Phys. Chem. B* **2006**, *110*, 23515.
- (25) Fraenkel, D. *J. Chem. Phys.* **2011**, *134*, 157101.
- (26) Fraenkel, D. *J. Phys. Chem. B* **2012**, *116*, 11662.
- (27) Fraenkel, D. *J. Phys. Chem. B* **2012**, *116*, 11678.
- (28) Masterton, W. L.; Bolocofsky, D.; Lee, T. P. *J. Phys. Chem.* **1971**, *75*, 2809.
- (29) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; Appendix 4, p 1301.
- (30) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; p 71.
- (31) Barthel, J. M. G.; Krienke, H.; Kunz, W. *Physical Chemistry of Electrolyte Solutions, Topics in Physical Chemistry 5*; Steinkopff: Darmstadt, 1998.
- (32) Enderby, J. E. *The Physics and Chemistry of Aqueous Ionic Solutions*; Bellissent-Funel, M.-C., Neilson, G. W., Eds.; Reidel Publishing Company: Dordrecht, 1987; p 129.
- (33) Lyubartsev, A. P.; Laaksonen, A. *Phys. Rev. E* **1997**, *55*, 5689.
- (34) Toukan, K.; Rahman, A. *Phys. Rev. B* **1985**, *31*, 2643.
- (35) Smith, D. E.; Dang, L. X. *J. Chem. Phys.* **1994**, *100*, 3757.
- (36) Degreè, L.; da Silva, F. L. B. *J. Chem. Phys.* **1999**, *111*, 5150.
- (37) Aziz, E. F.; Zimina, A.; Freiwald, M.; Eizebitt, S.; Eberhardt, W. *J. Chem. Phys.* **2006**, *124*, 114502.
- (38) Friedman, H. L. *Modern Aspects of Electrochemistry*, No. 6; Bockris, J. O'M., Conway, B. E., Eds.; Plenum Press: New York, 1971; p 1.
- (39) Card, D. N.; Valleau, J. P. *J. Chem. Phys.* **1970**, *52*, 6232.