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## How Does Dielectric Solvation Affect the Size of an Ion?

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The effect of solvation by a continuum dielectric on the size of an ion is examined using electronic structure calculations. Various measures correlated with size are considered, including the root-mean-square radius of the electronic charge density, the amount of solute charge penetrating outside the cavity, the electronic radial distribution function, the nucleus–electron potential energy, and the electron–electron potential energy. Calculations are made on several representative ionic solutes, and it is found that every measure indicates that the application of a dielectric makes the cations larger and the anions smaller. These counterintuitive trends are examined, and a plausible explanation is offered for the observed behavior.

### I. Introduction

Ionic solutes typically have large interaction energies with dipolar solvents. This is mainly due to the solute charge inducing a large number of solvent dipoles to partially reorient themselves for favorable electrostatic interactions with the ion. A cationic solute will produce a field to which a dipolar solvent will respond by partially reorienting the solvent dipoles to preferentially have their negative ends pointing toward the solute, while an anionic solute will cause solvent dipoles to preferentially reorient to have their positive ends pointing toward the solute. The main aspects of such solvent polarization can be effectively described with simple dielectric continuum models of the electrostatic interactions.<sup>1–5</sup> For example, the well-known Born model of a spherical ion gives the free energy of solute–solvent interaction as

$$\Delta G_{\text{Born}} = -\left(\frac{\epsilon - 1}{\epsilon}\right)\frac{Q^2}{2R_{\text{Born}}}$$

where  $\epsilon$  is the bulk dielectric constant of the solvent,  $Q$  is the net charge of the solute, and  $R_{\text{Born}}$  is the radius of an appropriate cavity that encloses the charge density  $\rho(\mathbf{r})$  of the solute.

It has long been appreciated<sup>6</sup> that the size of the cavity should not be taken simply as the size of the solute itself, but rather as a measure of how closely solvent molecules approach the solute. While solute size is undoubtedly the major factor in how closely solvent molecules approach, the cavity size will also depend to some extent on other influences as well. For example, it can be expected to also depend on the strength of the solute–solvent interaction, which for a given cavity radius is governed in the Born model by the factor  $(\epsilon - 1)/\epsilon$  that ranges from zero in the gas phase to nearly unity in a high dielectric solvent. An increase in dielectric constant will increase the solute–solvent attractive interaction for both cations and anions and so can be expected to pull solvent molecules in closer and thereby decrease the cavity size in both cases.

The solute can also change in response to its interaction with solvent. In comparison to the gas phase, intuition suggests that the electron charge density in a cation will be polarized by being pushed somewhat inward away from the nearby negative ends of the solvent dipoles. The cation will thereby become a little smaller, reinforcing to some extent the expected concomitant

decrease in solute cavity size discussed above. Conversely, the electron charge density in an anion will be polarized by being pulled somewhat outward toward the nearby positive ends of the solvent dipoles. The anion will thereby become a little larger, counterbalancing to some extent the expected concomitant decrease in cavity size discussed above. The essential point is that even while cavity size depends mainly on solute size they should not be equated to one another, and in fact they may change in either the same or opposite directions with change in dielectric constant.

In general, the dielectric continuum result can be obtained by solving the Poisson equation that governs the electrostatic response of a classical polarizable dielectric. The solution is often represented in terms of certain apparent charge distributions that reproduce the same electric field acting on the solute as does the actual polarized dielectric. If all the solute charge density is contained inside the cavity, then the solution can be represented by an apparent charge density lying on the cavity surface, which ultimately leads to the Born result quoted above. Thus, a spherically symmetric cation will produce a distribution of constant negative apparent surface charge, and a spherically symmetric anion will produce a distribution of constant positive apparent surface charge, each thereby mimicking the influence of the polarized dielectric that was described qualitatively above.

The situation is modified if some solute charge density penetrates outside the cavity, as it necessarily does in any unconstrained quantum mechanical calculation of the electronic structure. In that event, in addition to an apparent surface polarization charge density there also exists an apparent volume polarization charge density which influences both the surface polarization charge density and the free energy of solvation.<sup>7</sup> The volume polarization charge density resides only outside the cavity and is essentially a damped mirror image of the actual solute charge density there. It therefore serves to screen and diminish the influence of the outlying solute charge density. The qualitative arguments made above on how the solute sizes are expected to respond to a change in dielectric constant therefore still hold essentially unchanged when the effect of outlying charge is taken into account.

In this work we computationally test these simple intuitive hypotheses on how solute size is expected to change with dielectric solvation and *find them to be incorrect*. Instead, the quantum mechanical calculations indicate that cations typically

become a little larger and anions a little smaller when allowed to relax in the presence of a polarizable dielectric. A plausible explanation for this initially surprising behavior is also suggested.

To avoid nonessential complications involving solute geometry and shape, we treat here only spherically symmetric atomic ions, although the qualitative conclusions are expected to be quite general and to hold for nonspherical polyatomic molecules as well. Our computational methods are described in the next section. This is followed by a section presenting results and then by a section discussing the significance of the results. The paper ends with a brief conclusion section.

## II. Computational Methods

With unconstrained quantum mechanical calculation, there is no unique way to define the size of the solute charge density, because in principle it tails off to infinity. To allow for concrete discussion, we select two reasonable measures related to solute size. A direct measure is the root-mean-square radial distance  $R_{\text{rms}} = \langle r^2 \rangle^{1/2}$  of the solute electronic charge density from the nucleus. We also consider in this context the amount of solute charge  $Q_{\text{out}}$  penetrating outside the cavity. While  $Q_{\text{out}}$  does not directly measure solute size, its change upon applying a dielectric should indicate the direction of the change in solute size.

We also report the radius  $R_{\text{Born}}$  that would make the simple Born expression for the solvation energy reproduce either the experimental or the quantum mechanically calculated solvation energy. This is included strictly for reference purposes, since as noted in the Introduction the Born radius should not be taken as a physical measure of solute size. The value of  $R_{\text{Born}}$  would be infinite in the gas phase, corresponding to zero solvation energy, so this measure is not useful to correlate changes in solute size upon solvation either.

A more detailed picture of the solute size is provided by plotting the spherically symmetric radial distribution function  $D(r) = 4\pi r^2 \rho(r)$ . The usual normalization convention is adopted that  $D(r)$  integrates to the number of solute electrons.

The cavity surface is taken to be a sphere whose radius  $R_{\text{cav}}$  is the distance from the nucleus to the widely used  $0.001 \text{ e}/a_0^3$  isodensity contour of the gas phase solute charge density. While it is common practice to instead allow the cavity to relax by defining it to be at the specified isodensity contour of the solute charge density that is actually determined in the presence of dielectric, doing so might tend to complicate the interpretations sought in this work. In the event, calculations not reported here show that allowing the cavity to relax in that way ultimately leads to the same trends, with only small quantitative differences, as the results that are determined with a fixed cavity. Additional calculations not reported here with smaller cavities based on the  $0.002 \text{ e}/a_0^3$  contour and with larger cavities based on the  $0.0005 \text{ e}/a_0^3$  contour also give similar results and identical trends.

The SVPE (surface and volume polarization for electrostatics) method<sup>7–9</sup> is used to account for dielectric solvation effects. It includes a surface polarization contribution arising from the abrupt change in dielectric constant from unity inside the cavity to  $\epsilon$  outside the cavity and also includes a volume polarization contribution arising from solute charge density that penetrates outside the cavity. Although not reported here in detail, we remark that results very similar to those obtained with SVPE are also obtained from the SS(V)PE (surface and simulation of volume polarization for electrostatics) method,<sup>10</sup> which is equivalent in principle<sup>11,12</sup> to a modification<sup>13,14</sup> of the original IEF-PCM (integral equation formalism—polarized continuum model), and which invokes just a surface polarization contribu-

**TABLE 1: Calculated and Experimental Properties Related to Ion Cavities<sup>a</sup>**

ion	$\Delta G_{\text{solv}}$		$R_{\text{Born}}$		$R_{\text{cav}}$
	calc	expt	calc	expt	calc
Be <sup>+</sup>	−92.7	—	1.768	—	1.834
Mg <sup>+</sup>	−85.3	—	1.921	—	2.041
Ca <sup>+</sup>	−80.6	—	2.034	—	2.309
F <sup>−</sup>	−85.1	−104.4	1.926	1.570	1.864
Cl <sup>−</sup>	−68.3	−74.6	2.400	2.197	2.285
Br <sup>−</sup>	−64.1	−68.2	2.557	2.404	2.412

<sup>a</sup>  $\Delta G_{\text{solv}}$  is the free energy of solvation in kcal/mol,  $R_{\text{Born}}$  is the corresponding effective Born radius in Å, and  $R_{\text{cav}}$  is the cavity radius in Å determined from the gas phase  $0.001 \text{ e}/a_0^3$  isodensity contour of the solute.

tion that is designed in a way to exactly simulate everywhere inside the cavity the influence of the actual volume polarization.

The solvent dielectric constant  $\epsilon$  was set to 78.34 to be representative of bulk water or to 1.0 to represent the gas phase.

Free energies of solvation are calculated under the convention of Ben-Naim,<sup>15</sup> wherein a solute is transferred from a fixed position in gas to a fixed position in solvent. Thus, the gas and solvent standard states are taken to have the same solute concentration. The reported experimental free energies of solvation are based on the cluster-pair approximation using experimental cluster-ion solvation data<sup>16</sup> and have been converted here to the Ben-Naim convention.

All calculations were carried out with the GAMESS program,<sup>19</sup> as locally modified to report some of the information needed for this study.

Solute charge densities are determined from Hartree–Fock (HF) calculations. It is to be remarked that, although not presented here, we have found very similar results and identical trends upon including electron correlation effects by using various common density functional theory methods. For cations, we used the cc-pVTZ basis set<sup>17</sup> that is of triple- $\zeta$  quality in the sp valence space and also includes polarization functions. For anions, we used the aug-cc-pVTZ basis set<sup>18</sup> that further includes diffuse functions.

Solute internal energies  $E_{\text{int}}$  are separated into individual contributions from kinetic energy  $T_{\text{kin}}$ , nucleus–electron potential energy  $V_{\text{ne}}$ , and electron–electron potential energy  $V_{\text{ee}}$ . We note that the value for  $V_{\text{ee}}$  that is printed in the GAMESS output file is not correct when dielectric is present, although sufficient information is given to construct it properly.

## III. Results

For cations, we study the singly charged alkaline earths Be<sup>+</sup>, Mg<sup>+</sup>, and Ca<sup>+</sup>. Although these are generally believed to form dications in water, we choose to examine instead the singly charged ions because the latter retain an electron in the same outer shell as is occupied in the corresponding neutral atoms and should therefore be more representative of the behavior of typical polyatomic cations. Calculations not presented here on the alkali metal cations Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> as well as on the spherical cations O<sup>+</sup>, S<sup>+</sup>, and Se<sup>+</sup> having half-filled p-shells show the same trends, although with smaller magnitude changes, as those presented for the singly charged alkaline earths. For anions, we study the halogens F<sup>−</sup>, Cl<sup>−</sup>, and Br<sup>−</sup>. Calculations not presented here on the spherical anions C<sup>−</sup>, Si<sup>−</sup>, and Ge<sup>−</sup> having half-filled p-shells show the same trends, although with larger magnitude changes, as those presented for the halogens.

Table 1 presents the calculated free energies of solvation, the corresponding effective Born radii  $R_{\text{Born}}$ , and the cavity radii

**TABLE 2: Calculated Properties Related to Ion Sizes in Gas and in Dielectric Model of Solvent and Their Difference<sup>a</sup>**

ion	$R_{\text{rms}}$			$Q_{\text{out}}$		
	gas	solv	diff	gas	solv	diff
Be <sup>+</sup>	1.355	1.405	0.049	-0.109	-0.132	-0.022
Mg <sup>+</sup>	1.981	2.064	0.083	-0.164	-0.208	-0.044
Ca <sup>+</sup>	2.961	3.164	0.203	-0.284	-0.393	-0.108
F <sup>-</sup>	2.116	2.093	-0.023	-0.113	-0.098	0.015
Cl <sup>-</sup>	3.281	3.243	-0.038	-0.197	-0.169	0.028
Br <sup>-</sup>	3.868	3.826	-0.042	-0.235	-0.202	0.033

<sup>a</sup>  $R_{\text{rms}}$  is the root-mean-square distance in Å of the solute electronic charge density from the nucleus, and  $Q_{\text{out}}$  is the amount of solute charge in units of  $|e|$  lying outside the cavity.

$R_{\text{cav}}$  used in the solvation calculations. The  $R_{\text{Born}}$  and  $R_{\text{cav}}$  results for the cations are seen to be comparable to one another, with  $R_{\text{cav}}$  systematically being a little larger. Experimental solvation free energies are known for the anions, and these are also included in Table 1 along with their corresponding effective Born radii. The calculated free energies are about 19, 6, and 4 kcal/mol less than experiment for F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> respectively. Thus, as should be expected, the very compact charge of F<sup>-</sup> produces larger specific effects with first shell solvent molecules that are not properly described by a dielectric continuum model than are found in the larger Cl<sup>-</sup> and Br<sup>-</sup> ions. Since the present dielectric model recovers 82–94% of the experimental solvation energies, it can be taken as a useful model for all the anions. The experimental and calculated  $R_{\text{Born}}$  radii for the anions are close to one another, except for a discrepancy as large as 0.34 Å for the case of F<sup>-</sup>, with the experimentally derived values being consistently smaller. The  $R_{\text{cav}}$  radii lie between the calculated and experimental  $R_{\text{Born}}$  radii in all cases.

Table 2 reports the values of  $R_{\text{rms}}$  and  $Q_{\text{out}}$  calculated for each ion, giving for each the gas phase value, the value found in dielectric, and the gas to dielectric difference. With cations, the  $R_{\text{rms}}$  radii become larger by 0.04–0.17 Å upon applying the dielectric. Consistent with this, the amount of solute charge penetrating outside the cavity is seen to increase by 13–33%, again indicating that the cations become larger. For anions, the  $R_{\text{rms}}$  radii all become smaller by about 0.02–0.04 Å upon applying the dielectric. Consistent with this, the amount of solute charge penetrating outside the cavity is seen to decrease by 10–12%, again indicating that the anions become smaller.

Detailed pictures of the changes in cation charge densities are shown by the radial distribution functions  $D(r)$  in the left panel of Figure 1. The inner region clearly shows the shell structures of the ions, but the differences between gas and solvent are too small to be resolved on the main plots. These differences are most significant in the region around the cavity surface, which is blown up for the plots shown in the inset. The latter plots show that in each cation applying the dielectric causes some depletion of charge density from a region inside the cavity, and a concomitant accumulation in a region that is mostly outside the cavity, with the crossover point lying slightly inside the cavity for Be<sup>+</sup> and Mg<sup>+</sup> and essentially at the cavity surface for Ca<sup>+</sup>. The net amount of charge depleted inside the crossover point by the dielectric influence is 0.027, 0.048, and 0.108  $|e|$  for Be<sup>+</sup>, Mg<sup>+</sup>, and Ca<sup>+</sup>, respectively. These redistributions of charge density are similar to the changes in  $Q_{\text{out}}$  and give clear visual demonstrations confirming yet again that the cations become larger in the presence of dielectric.

The anion radial distribution functions  $D(r)$  are shown in the right panel of Figure 1. Again the main plots show the shell

structures of the ions but are unable to resolve the differences between gas and solvent. And again these differences are most significant in the region around the cavity surface, which is blown up for the plots shown in the inset. In the latter plots the accumulations of charge density inside the cavity are still spread out so much that they cannot be readily seen on the scale of the figure, but the concomitant depletion of charge density outside the cavity can be clearly discerned. The crossover point lies slightly inside the cavity in each case. The net amount of charge gained inside the crossover point by the dielectric influence is 0.022, 0.033, and 0.037  $|e|$  for F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup>, respectively. These redistributions of charge density are similar to the changes in  $Q_{\text{out}}$  and confirm yet again that the anions become smaller in the presence of dielectric.

Internal energies of the various solutes are given in Table 3, along with a breakdown into individual contributions. Results are given separately for the ions in gas and in dielectric solvent and the gas to solvent difference. In all cases, the changes from gas to solvent are much smaller in magnitude than the values in gas or solvent separately. Nevertheless, these changes show some interesting and consistent trends. For cations, solvation makes the magnitudes of all the components smaller,  $T_{\text{kin}}$  becoming less positive,  $V_{\text{ne}}$  less negative,  $V_{\text{ee}}$  less positive, and  $E_{\text{int}}$  less negative. For anions, trends opposite to those of the cations are seen for  $T_{\text{kin}}$ ,  $V_{\text{ne}}$ , and  $V_{\text{ee}}$ , but the same trends as cations for  $E_{\text{int}}$ . In any event, the changes to  $E_{\text{int}}$  upon solvation are very small for both cations and anions, despite large changes in their individual components. This is related to the fact that the changes in  $E_{\text{int}}$  upon solvation would be exactly zero if the virial theorem were satisfied throughout. The virial theorem is indeed satisfied in the gas phase calculations but is not perfectly satisfied in the presence of dielectric due to the nonlinear nature of the effective Schrödinger equation that includes dielectric effects and the resulting manner in which the solvation free energy is determined.

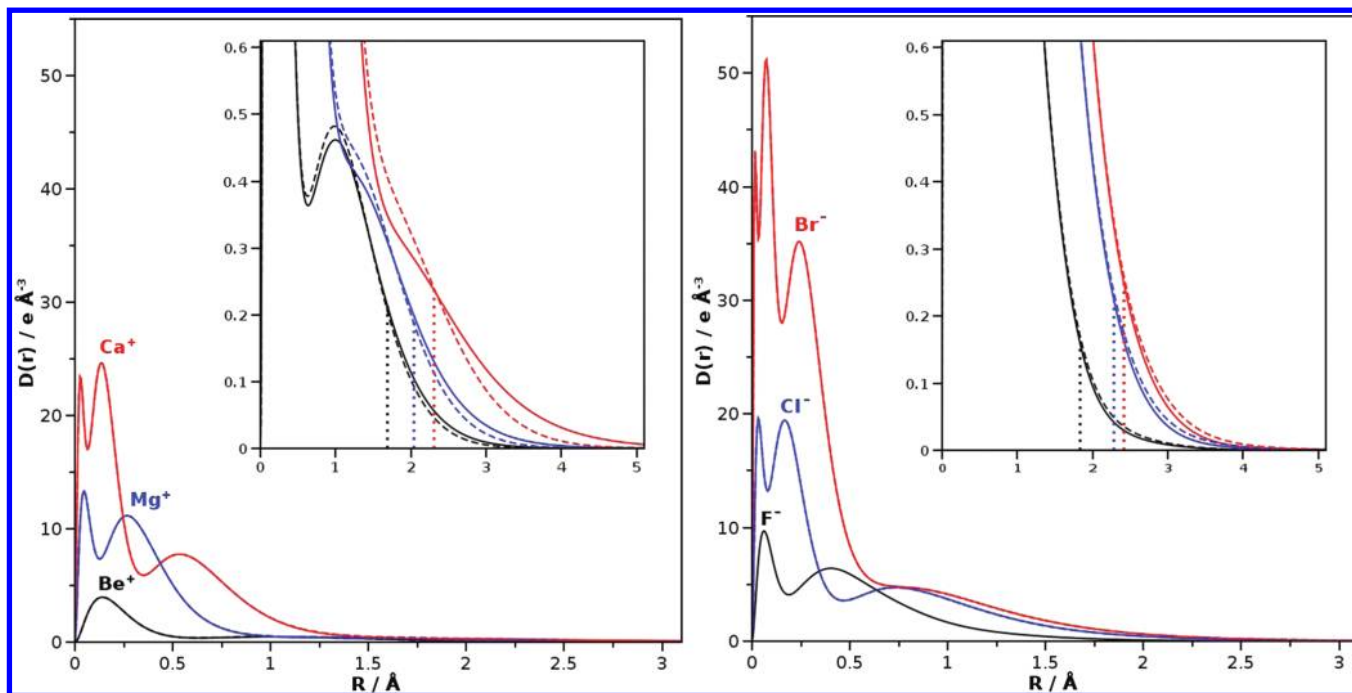
The changes upon solvation calculated for the potential energy components of  $E_{\text{int}}$  are consistent with the cations becoming larger and the anions becoming smaller. Thus, if the electronic charge distribution expands, the electrons will, on average, be a little further from the nucleus and also further from one another, leading to reductions in the magnitudes of both  $V_{\text{ne}}$  and  $V_{\text{ee}}$ , just as seen in Table 3 for the solvation effects on cations. Conversely, if the electronic charge distribution contracts, the electrons will, on average, be a little closer to the nucleus and also closer to one another, leading to increases in the magnitudes of both  $V_{\text{ne}}$  and  $V_{\text{ee}}$ , just as seen in Table 3 for the solvation effects on anions.

#### IV. Discussion

As indicated in the Introduction, the intuitive expectation is that applying a dielectric will make cations smaller and anions larger. However, all the evidence collected in this work by actual calculation on gas to solvent changes in  $R_{\text{rms}}$ ,  $Q_{\text{out}}$ ,  $D(r)$ ,  $V_{\text{ne}}$ , and  $V_{\text{ee}}$  indicate the opposite behavior, namely, that cations become larger and anions smaller. These counterintuitive findings therefore point to the existence of some other effect that more than balances the intuitive expectation.

We hypothesize that this other effect is descreening or screening by the dielectric of the inherent electron–electron repulsions in the vicinity of the cavity surface. For example, with a cation the repulsion between electrons that lie near the cavity surface will be somewhat reinforced by the negative apparent surface charge, leading to an expansion of the electronic charge density in the outer regions and thereby making





**Figure 1.** Radial distribution functions calculated for cations (left panel) and anions (right panel). Insets blow up the regions near the cavity surfaces. Dashed lines show gas phase results, and solid lines show results in dielectric. Vertical dotted lines show the cavity boundaries.

**TABLE 3: Calculated Components of Ion Internal Energies in Gas and in Dielectric Model of Solvent and Their Difference<sup>a</sup>**

ion	component	gas	solv	diff
Be <sup>+</sup>	$T_{\text{kin}}$	8958.4	8937.9	-20.5
	$V_{\text{ne}}$	-20009.3	-19973.5	35.8
	$V_{\text{ee}}$	2091.7	2077.0	-14.7
	$E_{\text{int}}$	-8959.1	-8958.5	0.6
Mg <sup>+</sup>	$T_{\text{kin}}$	125097.9	125064.4	-33.5
	$V_{\text{ne}}$	-298093.4	-297965.5	127.9
	$V_{\text{ee}}$	47888.6	47795.4	-93.1
	$E_{\text{int}}$	-125106.9	-125105.7	1.2
Ca <sup>+</sup>	$T_{\text{kin}}$	424559.2	424503.1	-56.1
	$V_{\text{ne}}$	-1002910.5	-1002580.8	329.7
	$V_{\text{ee}}$	153797.4	153527.6	-269.7
	$E_{\text{int}}$	-424553.9	-424550.1	3.8
F <sup>-</sup>	$T_{\text{kin}}$	62390.3	62406.8	16.5
	$V_{\text{ne}}$	-152749.5	-152818.9	-69.4
	$V_{\text{ee}}$	27952.9	28006.0	53.2
	$E_{\text{int}}$	-62406.3	-62406.1	0.2
Cl <sup>-</sup>	$T_{\text{kin}}$	288386.1	288409.7	23.5
	$V_{\text{ne}}$	-690702.5	-690830.0	-127.6
	$V_{\text{ee}}$	113929.6	114034.1	104.4
	$E_{\text{int}}$	-288386.7	-288386.3	0.4
Br <sup>-</sup>	$T_{\text{kin}}$	1614302.7	1614331.3	28.7
	$V_{\text{ne}}$	-3869373.1	-3869626.9	-253.8
	$V_{\text{ee}}$	640781.3	641006.9	225.6
	$E_{\text{int}}$	-1614289.2	-1614288.8	0.4

<sup>a</sup>  $T_{\text{kin}}$  is the electron kinetic energy,  $V_{\text{ne}}$  the nucleus–electron potential energy,  $V_{\text{ee}}$  the electron–electron potential energy, and  $E_{\text{int}}$  the total internal energy of the solute, all given in kcal/mol.

the cation larger. By analogous reasoning, with an anion the repulsion between electrons that lie near the cavity surface will be somewhat counteracted by the positive apparent surface charge, leading to a contraction of the electronic charge density in the outer regions and thereby making the anion smaller.

Finally we should ask: Are these changes in size physical? Do ions really change their size in different solvents? The dielectric continuum model considered here accounts for the important long-range electrostatic influence of bulk polar solvent

on an ion, but in nature there are many other effects as well. These questions are therefore difficult to answer. Some hints might be obtained from considering other approaches made in the literature.

There is no direct experimental measure of how solvent affects the size of a solute. The closest relevant experimental information comes from measurements of partial molar volumes, which determine how the total volume of a solution changes when a small amount of solute is added. A comprehensive review<sup>20</sup> has been made of the many analyses of the huge amount of data available for partial molar volumes of electrolytes dissolved in polar solvents. The consensus interpretation that has emerged<sup>20</sup> is that the data can be satisfactorily modeled by postulating two factors. One factor is the intrinsic volumes of the electrolyte ions themselves, which are considered to have the same size in any and all solution environments and which are usually taken as the effective sizes of the ions in crystals. The other factor is a change in the density of those solvent molecules in the near vicinity of the ions due to electrostriction caused by the strong electric fields produced by the ions. With simple models of the latter, satisfactory descriptions have been obtained with this picture for partial molar volumes of ions in several nonaqueous polar (both aprotic and hydrogen bonding) solvents<sup>21</sup> and in water over the full liquid temperature range.<sup>22</sup>

For present purposes, the important point to be taken from the literature on modeling of experimental partial molar volume data is that there is no compelling evidence for solvent-induced changes in the sizes of ionic solutes. However, that does not necessarily preclude the possibility of small changes in ionic size such as are found in this work. The changes in  $R_{\text{rms}}$  obtained here in passing from gas phase to high dielectric solvent amount to 3–6% for the cations and 1% for the anions. But the experiments do not include information about changes from the gas phase, rather only information from different polar solvents. Increasing the solvent dielectric constant in the computations will evidently produce changes in the same direction as changing from gas to strong dielectric, but with smaller magnitude. For rough estimation purposes we note that in passing from one

polar solvent to another, say from extremes in  $\epsilon$  of 10 to 100, the factor of  $(\epsilon - 1)/\epsilon$  that characterizes the solvent dependence in the Born model changes from 0.90 to 0.99, i.e., only a 10% variation. Thus, over a wide range of polar solvents with different dielectric constants,  $R_{\text{rms}}$  would change by only 0.3–0.6% for the cations and by only 0.1% for the anions examined. One then needs to inquire whether the experimental analyses would be able to notice changes of less than 1% in ionic radii.

Experimental values for partial molar volumes range from about  $-20$  to  $+50 \text{ cm}^3 \text{ mol}^{-1}$  for univalent ions<sup>21</sup> and are subject to errors from several sources. One source is the extra-thermodynamic assumption required to separate electrolyte data into separate contributions from cations and anions, which by itself contributes about  $\pm 2 \text{ cm}^3 \text{ mol}^{-1}$  to the uncertainty,<sup>21</sup> and of course additional errors arise from the laboratory measurements. We may therefore conservatively estimate the typical errors in experimental partial molar volumes of individual ions to be at least 10%. Taking the cube root, we would then estimate that changes in ionic radii on the order of 3% would have a barely noticeable effect on the experimental results. We conclude that analyses of experimental partial molar volumes are not sensitive to such small changes in radii as are determined in this work.

As an aside, we note that hydration energies of singly charged ions are typically in the range of about  $-50$  to  $-100 \text{ kcal/mol}$ , with estimated uncertainties of about  $2\text{--}3 \text{ kcal/mol}$ .<sup>23,24</sup> Thus, if one were to use the simple Born formula to estimate the ionic radius from the experimental solvation energy, there would be an uncertainty in the radius of about  $2\text{--}6\%$ , which is just about the same as the actual changes in  $R_{\text{rms}}$  radii we calculate on passing from gas to high dielectric solvent. Thus, the small changes calculated here are comparable to the uncertainties in radii that would naively be determined from the effective experimental Born radii.

Considerable success in reproducing experimental solvation energies has been obtained using a generalized Born model to treat bulk electrostatic effects, along with inclusion of nonelectrostatic and nonbulk electrostatic effects via surface tension terms<sup>25</sup> and other models.<sup>26</sup> These efforts are able to closely reproduce solvation energies of both neutrals and ions in various solvents having quite different dielectric constant by using fixed atomic radii that are independent of solute charge and of solvent. At first glance this might seem to argue against ionic size changing with solvent. However, the extensive empirical parametrization of surface tension terms may largely correct for any shortcomings in other parts of the description. Furthermore, the so-called atomic radii in such models actually play a role that is analogous to defining a cavity, and as argued in the Introduction the solute size and cavity size are distinct things that may not correlate perfectly with one another. In fact, it seems quite possible that within these approaches a more direct measure of solute size, such as  $R_{\text{rms}}$ , might well show similar trends as are found here.

Some other solvation models adjust the cavity size parameters directly to empirically fit experimentally observed solvation energies. Works of this kind have consistently found<sup>27–30</sup> that the cavity size must be made smaller for ions than for the corresponding neutrals. Such changes in empirical cavity size are to be expected because of stronger solute–solvent interactions with ions than with neutrals, and the cavity radii so obtained should not be regarded as the ionic solute radii.

## V. Conclusion

In this work we have considered several measures of how dielectric solvation influences ion size, including the root-mean-square radius of the electronic charge density  $R_{\text{rms}}$ , the amount of solute charge penetrating outside the cavity  $Q_{\text{out}}$ , the electronic radial distribution function  $D(r)$ , the nucleus–electron potential energy  $V_{\text{ne}}$ , and the electron–electron potential energy  $V_{\text{ee}}$ . All these measures indicate that dielectric solvation causes cations to become larger and anions smaller. Furthermore, additional calculations not presented here in detail indicate that these trends are robust with respect to including electron correlation effects by using common density functional methods instead of Hartree–Fock, to considering ions from other regions of the periodic table, to using a different dielectric continuum model, and to allowing the cavity size to relax in the presence of dielectric instead of holding it fixed.

These size changes found upon dielectric solvation are contrary to intuitive expectations based on the direct attractive or repulsive interactions of solute charge density with polarized dielectric. A plausible hypothesis to explain the trends is offered in terms of an opposite and apparently stronger indirect influence of the apparent surface charge either descreening or screening the inherent repulsive interactions between electrons that lie near the cavity surface.

Experimental evidence from partial molar volumes shows no compelling evidence for an effect of solvent on ionic size, but it is argued that the magnitude of the size changes found here would probably be too small to be noticed in the analysis of such experiments. In the case of solvation models that utilize some form of dielectric continuum theory either with or without additional terms, there are models in the literature that postulate cavities being dependent on solute charge and on solvent, as well as models that do not. However, that point is not directly relevant to the present work, because cavity size should not be equated with solute size, and any connection between the two is further weakened if the cavity size is treated by empirical parametrization.

The long-range influence of dielectric polarization is generally the largest effect of solvation on a charged solute in a polar solvent. However, there are also various short-range effects of solvation which are not properly described by dielectric continuum models. Whether such short-range effects may also have a significant influence on ionic size in solution is an interesting and open question for further investigation.

In summary, it has been found that applying a dielectric continuum to solvate quantum mechanically described spherical monatomic ions leads cations to become larger and anions to become smaller. While the changes are fairly small, corresponding to no more than a few percent in the effective ionic radii upon passing from the gas phase to high dielectric solvent, they are consistent and significant. These qualitative trends are expected to be quite general and to hold for nonspherical polyatomic ions as well. This interesting and counterintuitive behavior deserves further attention.

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