Connecting Cluster Anion Properties to Bulk: Ion Solvation Free Energy Trends with Cluster Size and the Surface vs Internal Nature of Iodide in Water Clusters

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There is disagreement in the literature on whether small water clusters (up to ∼60 waters) accommodate an excess iodide anion at the surface, in the interior, or in states intermediate between the two extremes. Small cluster solvation data, the results of ion simulations in model polar solvent clusters of intermediate size, and limiting continuum dielectric trends at large cluster size have been combined to illustrate the progression of the free energy of ion solvation from the smallest cluster size to bulk, establishing a set of general expectations for cluster ion solvation properties vs cluster size. The surface vs internal state issue for iodide in water clusters is examined in the context of the cluster ion properties of solvation thermochemistry, electron vertical detachment thresholds, and vertical detachment energies with specific regard to variation with cluster size and extrapolation to bulk. In aqueous systems, the anionic cluster property of vertical detachment threshold is shown to bear a better correspondence than the cluster vertical detachment energy (peak center) to the bulk property of the anionic defect photoemission threshold. It is concluded that in aqueous iodide clusters there is a gradual progression from surface states at small cluster size to internal states at large cluster size with the intervening region exhibiting an intermediate degree of surface character. Small $I^-(H_2O)_n$ clusters are unlike bulk $I^-(aq)$ in this regard, yet meaningful extrapolations of the photodetachment data to the bulk behavior can be made.

Introduction

Clusters undoubtedly play a fundamental role in the activity of connecting molecular properties to bulk; however, the advent of both large cluster range experiments[1−10] and of nanoparticle synthetic methods[11−16] reminds us that the activity is also a timely and practical one. It is currently scientifically[17] and technologically[18] important to examine how physical and chemical properties evolve from gas phase monomers to bulk and to characterize how cluster properties are both distinct and related to their bulk counterparts. In solution many important properties of chemical species at bulk are often different or even reversed from the properties of the gas phase monomer species.[19,20] Such bulk properties result from the collective interactions of solvation and cannot be inferred from the properties of the monomer species alone. Are small hydrated clusters of solutes representative of the bulk entities? At what cluster size do such systems become representative? The issue of surface vs internal states of charged species in small aqueous clusters is currently a topic of interest and controversy.[21,22] At bulk, iodide is considered a defect state[23] that is internal by definition. Are small hydrated clusters of these species internally solvated as at bulk, do they exist as surface states, or should a range of intermediate states be considered which gradually change with cluster size?

Photoelectron experiments on $I^-(H_2O)_{n=0-15}$ involving fixed frequency lasers and kinetic energy analysis of photoelectrons performed by Cheshnovsky and co-workers[24] determined vertical detachment energies (VDEs, from peak centers) as a function of cluster size. The apparent change in the trend of VDEs vs n was initially interpreted as solvent shell closure at $n = 6$. Since the VDEs for $n = 0-15$ extrapolate on an $n^{-1/3}$ plot to 7.28 eV, a value close to the bulk photoemission threshold for $I^-(aq)$ of 7.2 eV,[25−27] the data were interpreted (by analogy with experimental hydrated electron cluster work[28,29]) as evidence for internal solvation of I^- in the larger clusters. The trends in VDE (but not total energy) calculated with ab initio methods[30] supported this interpretation; however, molecular dynamics simulations using a polarizable model for water by Perera and Berkowitz,[22,31,32] Caldwell and Kollman,[33] and Dang and Garrett[34] conclude that the larger halides exist on the surface of small water clusters for $n < 15$. Recent work[35,36] on the solvation enthalpy and free energy of I^- in $(H_2O)_{n=1-5}$ does not extrapolate on an $n^{-1/3}$ plot to the bulk values, suggesting that these clusters are not internal states. New work by Cheshnovsky and co-workers[37] impressively extends to $n = 60$ and considers surface, internal, and intermediate possibilities.[38] Fitting of the experimental binding energies to a simple electrostatic model was found[37] to be "consistent with surface solvation". They state,[37] "In spite of considerable calculational effort on the energetics of the solvation of halides in water, final conclusions about their structure are still lacking."

In this paper, some fundamental relationships are established between anionic cluster properties extrapolated to bulk and observables of inherently neutral bulk systems. Large cluster properties can often be predicted using continuum theories and bulk properties, but there may be little guidance regarding how cluster properties will deviate from continuum expectations. For several typical ions, small cluster solvation data, the results of ion solvation simulations in model polar solvent clusters of intermediate size, and limiting continuum dielectric trends at large cluster size have been combined to illustrate the progression of the free energy of ion solvation from the smallest cluster size to bulk, thereby characterizing the deviations from continuum expectations and connecting small cluster trends to those of large clusters. When aqueous iodide cluster trends of solvation thermochemistry (ΔE_{sol}, ΔH_{sol}, and ΔG_{sol}), photoelectron vertical detachment thresholds (VDTs), and photoelectron vertical detachment energies (VDEs, from peak centers) are evaluated in terms of this framework, a consistent picture emerges about the surface/internal issue.

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The Bulk Picture

The I^-(aq) defect state can be referenced to the top of the valence band of pure water and KI(g) by virtue of the enthalpy of solvation of KI(g), ΔH_{sol}[KI(g)], which is estimated[39] as 1.80 eV from a thermochemical cycle. This defect state lies beneath the vacuum level of the solution by about 5.6 eV by virtue of the adiabatic electron affinity of gaseous iodine (AEA[I(g)] = 3.059 eV[40]), minus the solvation enthalpy of iodide ($\Delta H_{sol}[I^-] = -2.55$ eV[35,36,41]), plus the unknown but small solvation enthalpy of neutral iodine atom ($\Delta H_{sol}[I] \approx 0.0$ eV[42]). The process of bulk photoemission from iodide is a vertical process that cannot access the conduction band edge (bottom of the conduction band) due to the large difference in optimal arrangement of solvent molecules about iodide vs iodine. The bulk photoemission threshold of iodide[25-27] (7.2 eV) accesses the solution's conduction band about 1.6 eV above the vacuum level, so there is more than 1.6 eV (in fact, ~2.5 eV) of reorganization energy associated with the arrangement of solvating water molecules about an iodide at bulk.

Large Cluster Ions: Dielectric Sphere Trends for Limiting Behavior near Bulk

As cluster ions get very large, the stabilization gained by adding another solvent molecule depends very little on the molecular details governing the accommodation of the charge. In the very large size regime solvent molecules far from the ion can be expected to interact very weakly with the ion in a manner that is accurately described by a linear response theory (continuum dielectric theory[43]) using the dielectric properties of the bulk material. In the dielectric sphere approach (DS), cluster ions are modeled as a central charge within a uniform dielectric sphere with dielectric constants of the bulk solvent. The number of cluster components is related to cluster size by adding up the bulk volume associated with each component and calculating the effective spherical radius associated with that volume. A number of properties are expected to progress toward bulk with a linear reciprocal relation to cluster radius and, consequently, $(n + \xi)^{-1/3}$, where ξ represents the ion's contribution to cluster volume in units of the solvent's volume. If, for instance, the ion had the same volume as the solvent molecule, then $\xi = 1$. Note that at large cluster size where continuum expressions are expected to be valid $(n + \xi)^{-1/3} \approx n^{-1/3}$.

The original formulations[43] were in terms of free energy and adapted[44] to dielectric spheres as a simple electrostatic model of the solvation free energy of a cluster of size n

$$\Delta G_{sol,n} = \Delta G_{sol,\infty} + \frac{e^2}{2r_s}\left(1 - \frac{1}{D_s}\right)(n + \xi)^{-1/3} \tag{1}$$

where $\Delta G_{sol,\infty}$ is the bulk solvation enthalpy, r_s is the effective bulk radius of a solvent molecule, D_s is the bulk static dielectric constant of the solvent, ξ is the ratio of the ion's effective volume to that of the solvent, and e is the electron charge. When converted to solvation enthalpy,[45] a similar expression results:

$$\Delta H_{sol,n} = \Delta H_{sol,\infty} + \frac{e^2}{2r_s}\left[\left(1 - \frac{1}{D_s}\right)\left(1 + \frac{\partial \ln r_s}{\partial \ln T}\right) - \frac{1}{D_s}\frac{\partial \ln D_s}{\partial \ln T}\right](n + \xi)^{-1/3} \tag{2}$$

where $\Delta H_{sol,\infty}$ is the bulk solvation enthalpy and T is the temperature. Corresponding equations can be given for the cluster anion vertical detachment energy (VDE) involving the conversion of a free energy to internal energy and Marcus' separation of the electronic component of the polarizability:[43]

$$\mathrm{VDE}_n = \mathrm{VDE}_\infty - \frac{e^2}{2r_s}\left[\left(1 + \frac{1}{D_{op}} - \frac{2}{D_s}\right)\left(1 + \frac{\partial \ln r_s}{\partial \ln T}\right) + \frac{1}{D_{op}}\frac{\partial \ln D_{op}}{\partial \ln T} - \frac{2}{D_s}\frac{\partial \ln D_s}{\partial \ln T}\right](n + \xi)^{-1/3} \tag{3}$$

$$\mathrm{VDE}_n \approx \mathrm{VDE}_\infty - \frac{e^2}{2r_s}\left(1 + \frac{1}{D_{op}} - \frac{2}{D_s}\right)(n + \xi)^{-1/3} \tag{4}$$

where VDE_∞ is the bulk VDE and D_{op} is the bulk optical dielectric constant of the solvent.

At room temperature, the limiting DS slopes of $\Delta G_{sol,n}$, $\Delta H_{sol,n}$, and VDE_n with respect to $(n + \xi)^{-1/3}$ as $n \rightarrow \infty$ of ions in water are 3.68, 3.83, and 5.89 eV, respectively. The parametrized temperature dependence for these quantities is given in the Appendix. When substituted into eqs 1−3, these relations determine that the temperature dependence of the limiting $(n + \xi)^{-1/3}$ slope of $\Delta G_{sol,n}$, $\Delta H_{sol,n}$, and VDE_n varies by less than 7% over the temperature range from 125 to 375 K. Therefore, when dealing with differences from limiting trends to bulk greater than 7%, the issue of ice-like vs water-like clusters is not critical. Also note that the ratio of the limiting DS $(n + \xi)^{-1/3}$ slope of solvation enthalpy to that of the VDE is

$$\frac{\text{slope } \Delta H_{sol,n}}{\text{slope } \mathrm{VDE}_n} \approx \frac{1 - D_s^{-1}}{1 + D_{op}^{-1} - 2D_s^{-1}} \tag{5}$$

which is 0.643 for the case of water at 298 K using $D_s = 78.5$ and $D_{op} = 1.78$. If, for instance, the solvation enthalpy data were at 298 K, but the VDEs were of unknown temperature, then this ratio would still vary by less than ~7%.

Small Cluster Size Regime

The small cluster size regime is readily approachable with both theoretical and experimental methods. The following cluster reaction describes solvation of species X,

$$X + (H_2O)_n \rightarrow X(H_2O)_n \tag{6}$$

The free energy of this reaction is the solvation free energy of X which is analogous to bulk solvation when $n = \infty$ and can be written as the difference between summations of stepwise solvent additions to build up the clusters on each side eq 6:

$$\Delta G_{sol,n} = \sum_{i=1}^{n} \Delta G_{i-1,i}[X] - \sum_{i=1}^{n} \Delta G_{i-1,i}[H_2O] \tag{7}$$

Small cluster $(n + \xi)^{-1/3}$ trends can be different than the limiting trends of the DS model, and the manner in which the small cluster trend evolves into the limiting DS trend can be characteristic of the basic solvation physics exhibited with increased clustering. Thermochemical data available from high-pressure, cluster ion mass spectrometry experiments[46-48] have been combined with neutral water cluster data using Coe's method,[35] as detailed in Cowen's Ph.D thesis,[36] to provide the small cluster solvation free energies and bulk single ion solvation free energies[36,49,50] plotted in Figure 1 and presented in Table 1 for iodide, hydroxide, and lithium ion.

As cluster ions get smaller, the DS model breaks down because the cluster is dominated by strong ion−solvent interactions with a structure very different from bulk water, and therefore, the energetics are not well described by the dielectric

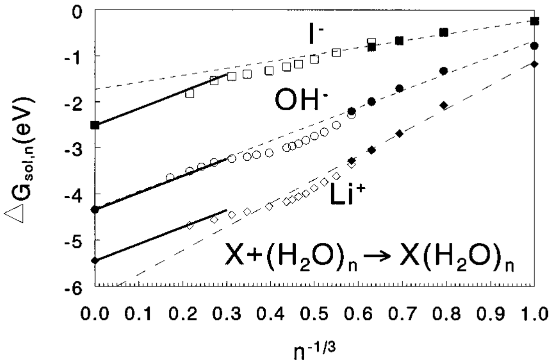

Figure 1. Single ion solvation free energies vs $n^{-1/3}$ where n is the number of solvating water molecules. At large cluster size (small values of $n^{-1/3}$) the DS trend is drawn from the bulk value with a solid line. At small cluster size experimental measurements are used (filled symbols) from refs 35 and 36. These data have been linearly fit (dotted lines) to show how the small cluster trends deviate from the continuum DS expectations. The intermediate size region (open symbols) is bridged with the Stockmayer, polar solvent simulations of Lu and Singer (ref 52 and data in Table 1). For this plot, offsets of 0.466, −0.363, and 0.155 eV were added to the Lu and Singer data sets in the intermediate cluster size range for the small ion (Li$^+$), the medium ion (OH$^-$), and the large ion (I$^-$), respectively, because the ion sizes investigated by Lu and Singer were not chosen to model Li$^+$, OH$^-$, and I$^-$, specifically. With nothing but the offsets, the polar solvent simulations of Lu and Singer connect the varying small cluster trends to the DS large cluster trends.

TABLE 1: Single Ion Solvation Free Energies (eV) vs $n^{-1/3}$

	experimental values			Lu and Singer polar solvent simulations^{d,e}			
n	OH$^{-\,a}$	I$^{-\,a}$	Li$^{+\,a}$	n	small ($\sigma = 0.5^c$)	medium^b ($\sigma = 1.0^c$)	large ($\sigma = 1.5^c$)
1	−0.776	−0.234	−1.179	4	−3.507	−1.640	−0.863
2	−1.332	−0.482	−2.069	5	−3.825	−1.926	
3	−1.713	−0.669	−2.693	6	−4.084	−2.142	−1.084
4	−1.991	−0.807	−3.058	7	−4.210	−2.295	
5	−2.203		−3.282	8	−4.342	−2.380	−1.237
				9	−4.461	−2.474	
∞	−4.342	−2.507	−5.450	10	−4.527	−2.549	−1.340
				11	−4.593	−2.600	
				12	−4.637	−2.636	−1.405
				16	−4.740	−2.751	−1.486
				20		−2.789	
				24	−4.852	−2.831	−1.559
				33	−4.921	−2.873	−1.612
				50	−5.028	−2.958	−1.703
				70		−3.053	
				100	−5.153	−3.146	−1.977
				200		−3.283	

[a] Reference 35 (details method with enthalpies data), ref 36 (method using free energy data). [b] Reference 52 shows plot of results for medium case. [c] σ is the ratio of the ion diameter to the solvent diameter in the Stockmayer particle model. [d] The reduced energy of ref 52 is multiplied by 0.018 97 to get eV. [e] Offsets of 0.466, −0.363, and 0.155 eV were added to the small (Li$^+$), medium (OH$^-$), and large (I$^-$) data sets, respectively, when plotted in Figure 1.

properties of neutral bulk water. At bulk, an ion may have a well-defined volume (and ξ value) due to its roughly equivalent confinement in all directions; however, an ion's volume may change in small clusters. Cluster ξ values are not known exactly, may change with cluster size, are different for different isomers, and can be very different from bulk by virtue of structure (imagine elongated cluster structures without waters enclosing large ions), and different investigators will likely favor different values. The difference between $n^{-1/3}$ and $(n + \xi)^{-1/3}$ is not important for large clusters (since $n \gg \xi$) in the region where DS models can be expected to be good, but the value of ξ is both problematic and most important at small cluster sizes where the DS model (which gave rise to it) is no longer valid. Reasonable values of ξ fall within a range determined from self-volumes based on Pauling crystal radii[49] (1.406, 0.814, and 0.030 for I$^-$, OH$^-$, and Li$^+$, respectively) and partial molar volumes[49] (3.302, 1.077, and 0.651, respectively). The range of reasonable ξ values for iodide is large enough to obtain a small cluster $(n + \xi)^{-1/3}$ slope which varies widely (in ref 37 a value of $\xi = 2$ was used for iodide assuming a volume fraction of 0.7 for iodide in its first solvation layer—a good assumption that may have little to do with the actual structure of the small clusters), so the comparison of small cluster trends requires a consistent treatment of ξ values for different ions. For all of the above reasons, it has been found more useful to make the cluster plots vs $n^{-1/3}$ (which can be done by anyone and without knowledge of ξ) instead of $(n + \xi)^{-1/3}$ and to consider the ion's self-volume as just one reason for deviation from the $n^{-1/3}$ trend—particularly when comparing the trends of different ions (with different ξ values). The data in Figure 1 have been examined using ξ values[51] of 2.31, 1.37, and 0.61, without affecting the presently drawn conclusions. Bear in mind that any small cluster $n^{-1/3}$ slope can be converted to an $(n + \xi)^{-1/3}$ slope, given a cluster size range and an agreed upon value of ξ. The difficulty associated with picking a best value of ξ limits the usefulness of a simple comparison of the small cluster trend to the continuum DS trend for a single ion such as iodide; and so the data for a representative set of ions are examined.

The cluster data must eventually come into the bulk values with the same limiting DS slope (solid lines in Figure 1). The dotted lines represent linear fits to the small cluster data which have been extended in order to illustrate how the small cluster trends differ from the limiting, continuum, DS trend. The small cluster $n^{-1/3}$ slopes are 1.52, 3.64, and 5.13 eV for I$^-$, OH$^-$, and Li$^+$, respectively. The $(n + \xi)^{-1/3}$ slopes are 4.42, 6.79, and 7.36 eV, respectively, using ξ values of 2.31, 1.37, and 0.61, respectively. Note also that the iodide $(n + \xi)^{-1/3}$ slope with $\xi = 2$ is 4.01 eV. In general, the small cluster trends increase in magnitude on going from I$^-$ to OH$^-$ to Li$^+$, reflecting the expected increase in ion−solvent interaction strength as the ion gets smaller. The small cluster trends can be bigger or smaller than the continuum DS trend depending on the chosen value(s) of ξ. These small cluster trends, which are dominated by ion−solvent interactions, must grow into similar-sloped continuum trends, which are dominated by solvent−solvent interactions. The intermediate region is particularly interesting as it reveals how the transition from ion−solvent structure to solvent−solvent dominated structure proceeds.

Intermediate Size Cluster Regime

The intermediate size regime is in many ways the most difficult to approach. There is currently no predictive theory that can characterize the deviations of the cluster trends from continuum expectations. How does the small cluster trend evolve into the DS trend? At what size can cluster trends be rigorously extrapolated to bulk? Rips and Jortner have attempted to introduce molecular structure into the electrostatic model using the bulk radial distribution function of a charged hard sphere within a dipolar hard sphere solvent in the mean spherical approximation,[52] but this theory is not predictive as tested against the appropriate model simulations.[53] In the absence of a predictive theory, the simulations by Lu and Singer on solvated ions (Lennard-Jones plus monopole interactions) in model polar clusters of Stockmayer particles (Lennard-Jones plus point dipole interactions) have been very instructive.[53−55] This work bridges the gap between what is known at small cluster size and what must be so at very large cluster size.

Clearly, the energetic distinction between surface and internal states is subtle. Any of the following properties could be critical in deciding the surface/internal nature of a cluster ion system: solvent polarity and dielectric strength, relative size of solute vs solvent, cluster size, and temperature.

Lu and Singer[53] used parameters for Stockmayer solvent particles which bracket the properties of water as best as possible. ($\epsilon = 250$ K and $\sigma = 2.9$ Å for the Lennard-Jones potential and a reduced solvent dipole moment of $\mu^* = 2$ which corresponds to a bulk static dielectric constant of ∼80 as in eqs 3 and 4 of ref 53.) They write, "while the directional hydrogen bonds of water are not described by the Stockmayer fluid, the simple model does provide a scenario for the response of a strongly ordered solvent cluster to an ionic solute". The ion solvation free energies calculated by Lu and Singer with the reduced parameter for charge of $Z^* = 16$ is most pertinent because this value corresponds approximately to a unit electron charge. They plot the results for the case of an ion with the same volume as the solvent in ref 52 (Figure 10), while the numerical results for the cases of an ion 1.5, 1.0, and 0.5 times the solvent diameter are reported here in Table 1. These data are used in Figure 1 to connect the small cluster data to the limiting DS trend for iodide (ion larger than solvent), hydroxide (same size as solvent), and lithium ion (smaller than solvent). The calculations were performed with reduced units, so the reduced energies were scaled by a factor of 0.018 97 such that the limiting DS slope was the same as that for the experimental small cluster data in electronvolts. Since the ion/solvent size ratios studied in the simulations were not chosen as models of the ions presently studied and since ion radius in known to be the primary factor[56] in determining the bulk intercept of these trends, small offsets (+0.155, −0.363, and +0.466 eV for I^-, OH^-, and Li^+, respectively) were added to these data in the Figure 1 plots in order to best connect the small cluster data to the limiting DS trend (solid line). In all three cases the simulation results connect the small cluster data to the limiting DS trend, effectively mapping out the free energy of solvation over the complete cluster size regime, from the smallest cluster to bulk.

The model polar solvent simulations of Lu and Singer also provide a framework for understanding the size evolution of the small cluster trends into bulk. Polar solvent molecules will align their dipoles about an ionic charge producing a different structure than that of pure solvent which is dominated by solvent−solvent interactions. As a cluster ion grows, the ion and its solvation shell(s) become increasingly dilute; i.e., solvent arranged around the ion represents a diminishingly small fraction of the water. The process of bringing additional solvent to an ionic cluster involves a transition from structure dominated by ion−solvent interactions to a structure dominated by solvent−solvent interactions. It is the solvent−solvent dominated structure that exhibits properties which are well modeled by dielectric continuum properties. The nature of the trend toward bulk depends on the strength of the ion−solvent interactions which are treated here in three cases:

(1) Small ions relative to the solvent molecule, such as lithium ion, can get closer to the solvent molecules and experience stronger ion−solvent interactions. Such interactions can be strong enough to maximally align all of the solvent molecules in a small cluster—effectively saturating the solvent response producing the dip or high slope in the $\Delta G_{\mathrm{sol},n}$ vs $n^{-1/3}$ curves. As polar solvent molecules are added, the ion−solvent structure may persist to larger distances from the ion (i.e., larger cluster size), requiring more solvent molecules before sufficient dilution of the ion−solvent structure is obtained to produce the DS slope characteristic of solvent−solvent structure.

(2) Solvent size ions, such as hydroxide, tend to exhibit ion−solvent interactions which are intermediate between the small and large ion extremes. Such ions may not be able to completely saturate the solvent response at as large a cluster size as a small ion, so the "dips" in the $\Delta G_{\mathrm{sol},n}$ vs $n^{-1/3}$ curves are less pronounced, and it takes less solvent to dilute the ion−solvent structure to a level sufficient to produce the DS slope. The facts—that strong ion−solvent interactions produce small cluster $n^{-1/3}$ trends greater than the DS value and that weak ion−solvent interactions produce small cluster $n^{-1/3}$ trends less than the DS value—conspire to produce an intermediate case with a small cluster $n^{-1/3}$ trend close to the DS value. The observation of similar small and large cluster $n^{-1/3}$ behavior for OH^- is a useful characterization, but it is not an application of DS theory to small clusters. Notice that the intermediate cluster size region displays deviations (as a "dip") from the similar small and large cluster trends. To further emphasize this point, consider that a plot made vs $(n + \xi)^{-1/3}$ will not show a small cluster $(n + \xi)^{-1/3}$ trend (6.79 eV for OH^- with $\xi = 1.37$) that is the same as the DS trend (3.68 eV).

(3) Larger ions relative to the solvent molecule, such as iodide, tend to have smaller ion solvent interactions, perhaps even smaller than solvent−solvent interactions mediated by a surface ion. There is a competition between surface ion structures which do not have to sacrifice solvent−solvent hydrogen bonds and structures dominated by ion−solvent interactions (more internalized ion structures) which do sacrifice solvent−solvent hydrogen bonds. Certainly, any cluster ions with ion−solvent pairwise interactions that are weaker than the solvent−solvent pairwise interactions will favor surface ion structures; however, the additional stability gained by the surface ion-cluster interaction produces a situation where ions with ion−solvent interactions somewhat stronger than solvent−solvent interactions will still favor the surface ion states. The ΔH for adding an iodide to a water molecule (−0.46 eV) is considerably smaller in magnitude than the same quantities for OH^- and Li^+ (−1.14 and −1.47 eV, respectively)[35] and comparable in magnitude to the bulk heat of vaporization of water (0.456 eV/molecule).[39] Ions with small cluster $n^{-1/3}$ trends less than the bulk DS value or small cluster $(n + \xi)^{-1/3}$ trends about the same size as the DS value fall into this category where surface state structures may be most stable at small cluster size. Unlike experiments, one nice feature of calculations is that one knows the position of the ion. The simulations of Lu and Singer for the large ion show the ion on the surface of the cluster at small cluster size as do other models[22,31−34] and in agreement with the total energies calculated by ab initio methods.[30] With increased clustering, the Lu and Singer calculations show a gradual change to more internalized states (i.e., internal surface states[38]), eventually reaching fully internal states analogous to bulk. If one expects small iodide clusters to be surface states and large clusters to be internal states as at bulk, then it is particularly important to discern a transition in the data. This issue can be subtle. For example, a plot of the small cluster, iodide solvation enthalpy data in Table 2 against $(n + \xi)^{-1/3}$ with $\xi \approx 2$, exhibits the DS limiting slope (approximately), but the small cluster data do not extrapolate (nor should they) to the known bulk value. There must be a "kink" in the progression to bulk in order to eventually go into to bulk with the proper DS continuum slope. The calculations of Lu and Singer characterize this "kink" for a simple polar solvent model. This "kink" can be sought in the photodetachment data, although it may not be as evident as with an adiabatic property.

TABLE 2: Solvation Enthalpy (eV), Photoelectron Threshold (VDT, eV) and Vertical Detachment Energy (VDE, eV) vs Cluster Size for $I^-(H_2O)_n$

n	$\Delta H_{\mathrm{sol},n}$[a]	VDT[b,c]	VDE[c]	n	$\Delta H_{\mathrm{sol},n}$[a]	VDT[b,c]	VDE[c]
1	0.455	3.37	3.51	15		5.21	5.69
2	0.681	3.67	3.92	16			5.74
3	0.846	3.83	4.29	20		5.38	5.87
4	0.984	4.19	4.59	24			6.06
5	1.097	4.42	4.77	25		5.48	6.10
6		4.46	5.11	30		5.61	6.18
7		4.63	5.20	33			6.22
8		4.78	5.28	35		5.71	6.25
9		4.80	5.40	37			6.28
10		4.93	5.46	40		5.73	6.40
11		4.95	5.49	44		5.72	6.45
12		5.09	5.55	49		5.73	6.47
13		5.15	5.63	53		5.81	6.44
14		5.21	5.64	60		5.87	6.58

[a] References 35 and 36. [b] Determined by graphically extrapolating to the base line a line tangent to the main photoelectron peak's low-binding-energy-side inflection point. [c] References 24 and 37.

Corresponding Bulk Observables and Cluster Properties

The extrapolation of cluster data to appropriate bulk values with the appropriate continuum slopes indicates that the clusters are chemically similar to their bulk counterparts, which are by definition internal in nature. Conversely, the properties of surface state clusters (or completely saturated ions with respect to solvent orientation of hydrated clusters) should not extrapolate to bulk values even though they may display, for instance, $n^{-1/3}$ linearity over a limited size regime. The previous two sections have now provided a framework for the following observations concerning the connection of anionic cluster and bulk properties:

An adiabatic property (such as solvation enthalpy, free energy, or internal energy) of internal cluster states should extrapolate to the bulk value at large cluster size with the DS model trend. The cluster adiabatic electron affinity (AEA_n) can also be linked to the cluster solvation internal energy ($\Delta E_{\mathrm{sol},n}[\mathrm{X}^-]$, which is a negative quantity), the monomer gas phase adiabatic electron affinity (AEA_0), and the solvation internal energy of the anionic defect's corresponding neutral ($\Delta E_{\mathrm{sol},n}[\mathrm{X}]$) as

$$\mathrm{AEA}_n = \mathrm{AEA}_0 - \Delta E_{\mathrm{sol},n}[\mathrm{X}^-] + \Delta E_{\mathrm{sol},n}[\mathrm{X}] \qquad (8)$$

where the bulk relation is obtained when $n = \infty$. Note that, for the case of the excess electron, AEA_0 and $\Delta E_{\mathrm{sol},n}[\mathrm{X}]$ are by definition zero, and the cluster AEA_n and $-\Delta E_{\mathrm{sol},n}$ are equivalent. It is important to recognize that AEA_∞ (the bulk extrapolation of the molecular adiabatic electron affinity which corresponds to the energy difference between the anionic defect state and the vacuum level) is not the quantity called the liquid electron affinity or $-V_0$ in the condensed phase literature. This quantity, unfortunately (for those relating to cluster anion detachment) called the liquid electron affinity ($-V_0$), is the energy of promoting a conducting electron, e^-(cond), of minimal energy to the gas phase or vacuum level with zero kinetic energy. V_0 has a value[57,58] often estimated from +1.0 to about −1.3 eV in water. The value of $\mathrm{AEA}_\infty[\mathrm{I}^-(\mathrm{aq})]$ is about 5.6 eV (uncertain by the small solvation energy of iodine atom) and quite different than $-V_0$.

Regarding vertical properties, water will always have a large reorganization energy in response to charge; i.e., solvating water molecules will compromise their hydrogen-bonded structure to better align their dipoles to the charge. If the reorganization energies of ions in water could be ignored, then AEA_∞ and VDE_∞ would be the same. But reorganization energies are typically in the range of 1.6 to more than 5 eV and cannot be ignored, so photoemission thresholds from anionic defects in water will correspond to neither AEA_∞ nor VDE_∞, but rather something in between. This type of effect is well-known in the photodetachment of small gas phase anions[59] such as NO^- whose equilibrium bond length is very different than its corresponding neutral, photodetachment product (NO). In the case of NO^-, photoelectron peak intensities are governed by vibrational Franck−Condon factors primarily between the ground vibrational level of NO^- and the various vibrational levels accessed in the NO product, but in the present case photoemission intensity is governed by the wave function overlap (or lack thereof) of the ion−solvent structure of the anionic defect and the very different equilibrium solvation structure of the corresponding neutral product. In water, there will be no vertical access to the lowest energy configurations of the corresponding neutral product of a photoemission process. These same considerations, i.e., difference in equilibrium solvent organization between aqueous anionic clusters and their uncharged photodetachment products, are of course at work in the cluster anion detachment data. Therefore, in the case of *aqueous* cluster anions, the extrapolation of cluster vertical detachment thresholds (VDT_∞) should be expected to have a better correspondence to the bulk photoemission threshold of the corresponding anionic defect than the extrapolated value of the vertical detachment energies (VDE_∞).

Much attention has been focused on comparing the extrapolated value of cluster vertical detachment energies[24,37] from peak centers (VDE_∞) to bulk photoemission thresholds (PET). While this is a good start, i.e., the VDE_∞ should be in the vicinity of the corresponding PET, this approach has three problems: (1) the effect of the large solvent reorganization energy about charge is ignored; (2) if the extrapolated photoelectron peak center corresponds to a bulk photoemission threshold, then roughly half of the peak width or band width corresponds to photon frequencies which will detach electrons even though they are supposedly below the threshold; and (3) experimental observables are not presently available for this property from aqueous solutions. Any feature in bulk photoemission spectra that might be correlated to the VDE_∞ is marred by dispersion effects of radiation in water; i.e., all of the features above threshold observed in bulk photoemission spectra of solutions are due to water itself and not to any solutes placed in the water.[60] Since there are no solute-dependent features above threshold in solution photoemission spectra, the important observation to make concerning VDEs is the $n^{-1/3}$ slope they exhibit upon going to bulk. Internal bulklike states should progress to bulk with the DS model trend. The cluster VDE_∞ of internal states represents a unique measurement that ultimately will reveal the bulk solvent reorganization energy about the subject ion. Without an available bulk observable for VDE_∞, more attention should be paid to the threshold behavior in the extrapolated cluster data, even though photoelectron thresholds are in some ways less satisfactory to work with compared to peak centers since empirical definitions are required.

A recent reexamination[61] of the V_0 value of water in view of hydrated electron cluster work[28,29] shows that $V_0 \geq -0.12$ eV, which is considerably smaller in magnitude than the value of −1.3 eV obtained from photoionization of aqueous indole[58] and other similar experiments. However, this smaller value of V_0 is in good agreement with the theoretically determined values of Henglein[62] (−0.2 eV) and Jortner[63] ($-0.5 \text{ eV} \leq V_0 \leq 1.0$ eV). Since the reorganization energies about charge in water are so large, the vacuum level is not vertically accessible. Therefore, the thresholds for photoemission are also governed by the availability of sufficient overlap of solvent configurations

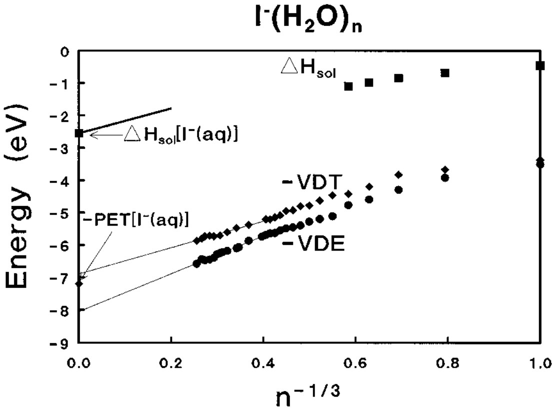

Figure 2. Plot of cluster solvation enthalpy (ΔH_{sol}), electron detachment thresholds (VDT, derived graphically from data in refs 24 and 37), and vertical detachment energies (VDE, from refs 24 and 37) vs $n^{-1/3}$ where n is the number of solvating water molecules. The bulk solvation enthalpy (−2.55 eV) and photoelectron emission threshold (~7.2 eV) are also shown. The VDT and VDE data of the Cheshnovsky group for $n > 15$ (ref 37) have been fit to an $n^{-1/3}$ line to see how it extrapolates to bulk. VDE(eV) = $8.06-5.84n^{-1/3}$ and VDT(eV) = $6.90-4.09n^{-1/3}$. It is the detachment thresholds (VDTs) that should and do extrapolate to the bulk photoemission threshold as the iodide internalizes, not the VDEs.

and not by the vacuum level. Furthermore, considering that V_0 is small in water, both photoconductivity thresholds and photoemission thresholds of similar defects can be expected to access similar regions [energetically within ~0.1 eV (the small V_0 value) plus surface potential effects] of the conduction band well above the vacuum level. In view of these considerations, it is presently proposed that the value of *aqueous* cluster anion vertical detachment thresholds extrapolated to bulk (VDT_∞) corresponds to both the bulk photoemission threshold (PET) of the anionic defect and, in a more approximate way, due to the small V_0 value of water, to the bulk photoconductive threshold (PCT),

$$\mathrm{VDT}_\infty = \mathrm{PET} \approx \mathrm{PCT} \qquad (9)$$

These relations are approximate, perhaps good to ~0.1 eV. This assertion is interesting for two reasons: (1) the cluster property of VDT_∞ is connected to the intrinsic bulk property of PCT without requiring a surface, and (2) if the VDTs connect to the PCT and PET, then the vertical detachment energies (VDEs) cannot. The above relation broadens the scope of important bulk observables. For example, there exists for iodide an experimental PET[I^-(aq)][25−27] = 7.2 eV, but not a PCT[I^-(aq)] value, while for hydrated electron, there exists an experimental PCT[e^-(ice)][64] = 2.3 eV, but not a PET[e^-(aq)].

Detachment and Solvation Data on $I^-(H_2O)_n$

Experimental values of three hydrated iodide cluster properties, including −VDTs and −VDEs from the data of Cheshnovsky and co-workers[24,37] (n = 1−60) and solvation enthalpies[35,36] (n = 1−5), are plotted vs $n^{-1/3}$ in Figure 2 and listed in Table 2. The set of VDTs are not given in ref 37; they have been obtained from the spectra in Figs. 3 and 10 of ref 37 and Fig. 2 of ref 24 by graphically extrapolating to the base line a line tangent to the main peak (low-binding-energy side) at the inflection point. No claim is made that the set of thresholds obtained in this manner is the "best" or even a "good" set of data; such a set can only be expected to come from the original investigators should they be compelled by the arguments presented herein. The "rough" set of VDTs offered in this work are good enough, however, to demonstrate the usefulness of considering this property in these deliberations. In the following, the trends of each data set are examined within the framework established in the earlier sections of this paper.

Bulk values for the solvation enthalpy ($\Delta H_{\mathrm{sol},\infty}$) of many ions including I^- are known. The most recent determination[35] is $\Delta H_{\mathrm{sol},\infty}(I^-) = -2.55 \pm 0.08$ eV. Other reported values include −2.8 ± 0.4 eV from Friedman and Krishnan,[49] −2.78 ± 0.17 eV from Randles,[65] and −2.71 ± 0.11 eV from Klots.[50] A dark line is drawn from the bulk $\Delta H_{\mathrm{sol},\infty}(I^-)$ in Figure 2 with the DS slope, showing that it cannot go into the small cluster data. The small cluster $\Delta H_{\mathrm{sol},n}$ data extrapolate to −1.93 eV (0.62 eV shy of the bulk solvation enthalpy) with a slope of 1.51 eV (only 39% of the 3.83 eV DS slope). If examined in terms of an $(n + \xi)^{-1/3}$ slope, the small cluster data reveal a value of 4.11 eV with $\xi = 2.31$ or 3.75 eV with $\xi = 2.00$, which is about the same as the DS value (3.86 eV). The data most importantly reveal the necessity of a "kink" or transition region in connecting the small cluster and large cluster trend, even if the small and large cluster $(n + \xi)^{-1/3}$ slopes are similar. The small cluster trend is characteristic of surface states as modeled by the Stockmayer particle simulations of Lu and Singer[53] for ion diameters 1.5 times that of the solvent, as found in the polarizable water simulations of Perera and Berkowitz[22] and in agreement with the energetic results of ab initio calculations[30] which find the surface states to be more stable.

Threshold photoelectron emission spectra from the work of Delahay and co-workers are also available for bulk aqueous halide solutions including I^-. Thresholds of 7.2 ± 0.1,[26] 7.19 ± 0.03,[25] and later 7.4 eV[24,25,27] have been reported for I^-(aq). The VDT data in the small cluster range for n = 1−15 (data from the Cheshnovsky group's first paper)[24] extrapolate to 6.49 eV, which is ~0.7 eV shy of the bulk PET[I^-(aq)] value. The VDT data in the intermediate range for n = 16−60 (new values from the Cheshnovsky group's second paper)[37] extrapolate to 6.90 eV, which is only 0.3 eV shy of the bulk PET value for iodide. The VDT data vs $n^{-1/3}$ gradually increase in magnitude as the clusters get larger and eventually (at the largest cluster sizes available) almost point to the expected bulk property, PET[I^-(aq)]. Similar observations can be made from the $(n + \xi)^{-1/3}$ perspective, however with opposite deviations. The VDT data for $n < 15$ extrapolate to 7.71 eV with $\xi = 2.00$ or 7.87 eV with $\xi = 2.31$ overshooting PET[I^-(aq)], while the data for $n > 15$ extrapolate to 6.98 eV with $\xi = 2.00$ or 6.99 eV with $\xi = 2.31$, which is much closer to the bulk PET[I^-(aq)] value. In general, there is a gradual change in which the largest cluster sizes head increasingly toward the corresponding bulk property, PET[I^-(aq)]. The value of VDT_∞ is between 6.9 and 7.0 eV.

Since there is currently no experimental bulk observable for comparison to the extrapolation to bulk of cluster vertical detachment energies (VDE_∞), these data must be evaluated in terms of their $n^{-1/3}$ trend toward bulk. The VDE data in the small cluster range for n = 1−15 (data from the Cheshnovsky group's first paper)[24] proceed to bulk with an $n^{-1/3}$ slope of 4.03 eV, which is only 69% of the DS value. Also, the ratio of the slope of ΔH_{sol} data to that of the small cluster VDEs (n = 1−15), which should be less sensitive to temperature effects, is 0.44, which is only 69% of the DS ratio (eq 5). The data in the intermediate range from n = 16−60 (new data from the Cheshnovsky group's second paper)[37] proceed to bulk with an average $n^{-1/3}$ slope of 5.84 eV, which is essentially the DS value (5.89 eV). Since there can apparently (see the next paragraph) be an overshoot in the progress of the $n^{-1/3}$ slope toward bulk, the agreement of the slope with the DS value does not necessarily mean that the internalization process is entirely complete. From the $(n + \xi)^{-1/3}$ perspective, the slope of the

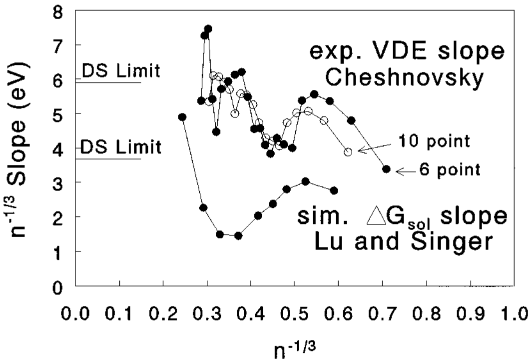

Figure 3. Characterizing the deviations from continuum expectations. There should be a "kink" in the progression of the cluster ion properties considered herein as the small cluster data gives way to the larger cluster trends, even if the small cluster $(n + \xi)^{-1/3}$ trend is similar to the bulk trend as is the case with iodide. Smoothed derivatives of the vertical detachment energy (VDE) vs $n^{-1/3}$ of experimental photodetachment data on $I^-(H_2O)_n$ of the Cheshnovsky group (refs 24 and 37) are presented with the derivative of solvation free energy vs $n^{-1/3}$ for simulations on water-like Stockmayer particles by Lu and Singer (ref 52). There is at least one set of local maxima and minima, i.e., the "kink", imposed upon the overall $n^{-1/3}$ trend of a gradual increase with increasing cluster size to the DS value as predicted by the free energy simulations of Lu and Singer and exhibited by the photodetachment data of the Cheshnovsky group.

small cluster data starts out greater than the DS value and gets closer as the clusters get larger. The $(n + \xi)^{-1/3}$ slope for $n < 15$ is 7.41 eV with $\xi = 2.00$ or 7.88 eV with $\xi = 2.31$, which is much greater than the slope of the $n > 15$ data, 6.39 eV with $\xi = 2.00$ or 6.47 eV with $\xi = 2.31$, which is still a bit more than the DS value (5.89 eV). When the $n^{-1/3}$ and $(n + \xi)^{-1/3}$ trends are considered together, they reveal gradual progress toward DS behavior at larger cluster size. This trend is consistent with a gradual transition from surface character at small cluster size to internal character at larger cluster size. Extrapolation of the $n > 15$ data set with both $n^{-1/3}$ and $(n + \xi)^{-1/3}$ methods produces a VDE_∞ value of 8.06−8.21 eV, which is about 0.9 eV greater in magnitude than $PET[I^-(aq)]$.

Considering that different small cluster trends are obtained with different ξ values, it becomes important to look for transitions or "kinks" in the trends as opposed to absolute comparisons of small cluster trends to DS values. A more careful inspection of the trends can be made by calculating the $n^{-1/3}$ local slope of the data vs $n^{-1/3}$. If only adjacent cluster sizes are used, the noise in the experimental VDEs produces an unacceptable amount of noise in the local slopes, so both 6 and 10 adjacent points were used to define a linear slope for cluster size ranges about the experimental data as plotted in Figure 3. Also included are the local slopes from adjacent points in the solvation free energies of the simulations of Lu and Singer. Inspection of Figure 3 supports the observation that there is an overall gradual increase in the $n^{-1/3}$ slope of the data toward the DS value. The experimental data in Figure 3 also begin to reveal deviations from this general trend which are modeled to some extent in the simulations of Lu and Singer. The simulations with Stockmayer particles cannot be expected to capture the directionality of hydrogen bonding, so exact agreement is not expected. However, both the simulated and experimental data sets of slopes exhibit a "kink" with increasing cluster size. There is initially an increase in the $n^{-1/3}$ slopes with increasing cluster size, a local maximum which gives way to a local minimum, and finally an increasing trend possibly overshooting the DS limiting value. If one chooses a ξ value that produces a small cluster average slope that is the same as the DS value, then the "kink" is the only indication that a transition occurs. The observation of this "kink" in both the experimental data and the simulations suggests that some (perhaps much) of the solvation physics important for capturing the deviations from continuum expectations is embodied in the Stockmayer particle simulations.

Discussion

There now exists a compelling set of reasons favoring surface structures for small aqueous iodide clusters: (1) the small magnitude of $n^{-1/3}$ or $(n + \xi)^{-1/3}$ slopes in the small cluster size regime relative to other ions corroborates weak ion−solvent interactions, (2) a "kink" is evident in the derivative of the VDEs vs $n^{-1/3}$ in Figure 3 indicating a transition, even though such a transition is not obvious upon casual inspection of the VDE data in Figure 2, and (3) all of the recent theoretical approaches find surface ion structures to be adiabatically most stable for the small clusters. The only recent/serious calculation which has claimed (in words) otherwise[30] actually found that the surface states were more stable in terms of total energy! It was only the vertical properties of the internal states which seemed to bear better correspondence to the contemporaneous interpretation of the original experimental data set[24] as internal states, and this interpretation was essentially abandoned in the next paper.[37] And so at some cluster size, there must be a transition from surface iodide character at small cluster size to the internal character of $I^-(aq)$ at bulk.

It has been shown in this work that there is overall, gradual progress of the cluster properties that have been examined toward continuum expectations. The first confusing issue in this matter was that the VDEs (not VDTs) of the original photodetachment data set[24] ($n = 1-15$) extrapolated to a value (7.28 eV) very close to the bulk $PET[I^-(aq)]$. This was interpreted as evidence for internal states in the initial work by analogy to the experimental hydrated electron photodetachment data. However, the arguments made in the hydrated electron cluster work were devised to contrast the VDE_∞ of theoretical calculations,[66] which were more than 2 eV higher than experiment, not to distinguish VDT_∞ and VDE_∞. More recently,[37] it has been shown that the VDE data can also be fit by an electrostatic model of the anion at the surface of the cluster, i.e., on the boundary of a spherical solvent cluster. This model predicts that an ion positioned on the boundary of a spherical solvent cluster can have an $(n + \xi)^{-1/3}$ slope for VDEs, which is the same as the limiting DS value of an internalized ion. This would be inconsistent with the present interpretation if observed vs $n^{-1/3}$; however, the $(n + \xi)^{-1/3}$ parameter shifts the scale compared to $n^{-1/3}$. Such an $(n + \xi)^{-1/3}$ slope still indicates the low end of the range of ion−solvent interaction strengths, as can be seen by the small cluster $(n + \xi)^{-1/3}$ slopes of the solvation free energy data on the left side of Table 1 (4.42, 6.79, and 7.36 eV for I^-, OH^-, and Li^+, respectively, using ξ values of 2.31, 1.37, and 0.61, respectively). The boundary ion model is very interesting and provides justification that surface states can produce the observed small cluster slopes, but the model is unsatisfactory as an explanation over the whole cluster range because it necessarily predicts a bulk state at the bulk−vacuum interface which cannot be the familiar electrochemical species $I^-(aq)$. Taken over the whole cluster range, the surface (boundary ion) interpretation requires that $I^-(H_2O)_n$ clusters have little to do with their bulk counterpart, $I^-(aq)$. Taken at the worst, this interpretation suggests that $I^-(aq)$ is unstable; i.e., I^- should work its way to the surface of bulk water. There must be a transition from surface character to internal character. The "kink" in the VDE data, as demonstrated in Figure 3, reveals that a transition is underway [even if the $(n + \xi)^{-1/3}$ trend is the same before and after the "kink"]. Clearly, the "kink" is an essential and subtle feature indicating the gradual transition from surface to internal behavior in a manner captured in the simulations of Lu and Singer. Such a "kink" might be more evident in the adiabatic properties like $\Delta G_{\mathrm{sol},n}$ or $\Delta H_{\mathrm{sol},n}$, if such data could be extended into the intermediate cluster size region.

The availability of the experimental data set extended to $n = 60$ of Cheshnovsky and co-workers[37] is certainly key to untangling this problem. The experimental VDTs are increasingly pointed toward the bulk PET[I^-(aq)] with increasing cluster size, although they have not quite gotten there by $n = 60$. In this data set, the VDEs are no longer headed toward the bulk value of PET[I^-(aq)], but rather to a higher value, perhaps ~8.1 eV. It has been proposed, argued, and demonstrated as reasonable by the iodide cluster trends that the vertical detachment thresholds (VDTs) are better related to the bulk photoemission threshold (PET) than the vertical detachment energies (VDEs from peak centers). The value of anionic cluster vertical detachment energies extrapolated to bulk, VDE_∞, represents a unique measurement of a bulk property which would be otherwise very difficult to obtain. The reorganization energy of solvent about a charged defect is obtained when the AEA_∞ (which can be obtained using eq 8) is subtracted from VDE_∞. The assumption that $\Delta E_{\mathrm{sol},n}$[I] is ~0.0 eV produces a value of 2.5 eV for the reorganization energy of solvating molecules about iodide in water. This value is about 0.9 eV larger than the minimum value implied by PET[I^-(aq)]. The fact that for iodide the $\mathrm{VDE}_\infty = 8.1$ eV $>$ PET[I^-(aq)] $= 7.2$ eV $\gg$ $\mathrm{AEA}_\infty = 5.6$ eV emphasizes both the importance of considering reorganization energy about charge in water and the fact that a vertical photoemission (or photoionization) process in water is unlikely to access the lowest energy levels of the corresponding product. The difference of 0.9 eV between VDE_∞ and PET[I^-(aq)] serves as a useful estimate of how big this difference can be expected to be in similar systems, perhaps allowing more accurate estimates of the reorganization energies of other halides.

Currently in water, the connection of small cluster data to limiting continuum trends is an area largely devoid of predictive theory. The incorporation of the work of Lu and Singer on model polar solvent systems in the intermediate size regime with the experimental data of solvation free energies provides a valuable framework for interpreting cluster trends from the very smallest clusters to bulk. Both the Cheshnovsky experimental data and the simulations of Lu and Singer begin to show how the cluster data deviates from continuum expectations. The competition between solvent–solvent structure and ion–solvent structure as a cluster grows in size can be understood in terms of the strength of ion–solvent interactions vs solvent–solvent interactions, of which it is well-known[56] that a primary factor is ion size relative to the solvent. Iodide–water interactions are about the same magnitude as water–water interactions, so small water clusters gain the most stability by engaging a large iodide ion without breaking the solvent–solvent hydrogen bonds. In general, over extended cluster size ranges, the DS model represents an upper $n^{-1/3}$ limit for the trend toward bulk [the distinction between $n^{-1/3}$ and $(n + \xi)^{-1/3}$ being important in this argument considering that the $(n + \xi)^{-1/3}$ average trends can be much larger than the DS values]. Ions will only exceed the $n^{-1/3}$ slope in limited and predictable cluster size regimes. Any calculations which predict $n^{-1/3}$ slopes greater than the DS value over an extended size range should be quantitatively suspect, such as QUPID calculations[66] on the VDEs of $(H_2O)_n^-$ showing an $n^{-1/3}$ slope of 9.8 eV that is ~170% of the DS value. These considerations, garnered from the solvation free energy trends in Figure 1 and evident in the detachment data of Figures 2 and 3, have been used to distinguish whether or not iodide clusters are behaving like their bulk counter parts. By the largest experimentally available cluster size ($n = 60$), it appears that the transition to continuum behavior is nearly, but not quite complete. The aqueous iodide cluster data reveal a gradual change from surface character at small cluster size to internal character over the size regime that has been experimentally investigated ($n = 1-60$) with decreasing surface character exhibited with increasing cluster size.

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Appendix

The temperature dependence[67] of the density and dielectric constants can be fit to obtain the following relations in atomic units for liquid water:

$$r_s\ (\mathrm{bohr}) = 3.9452 - 2.327 \times 10^{-3}T + 4.420 \times 10^{-6}T^2 \tag{10}$$

$$D_s = 248.95 - 7.8950 \times 10^{-1}T + 7.2809 \times 10^{-4}T^2 \tag{11}$$

$$D_{\mathrm{op}} = 1.9236 - 4.962 \times 10^{-4}T \tag{12}$$

$$\frac{\partial \ln r_s}{\partial \ln T} = -2.5548 \times 10^{-1} + 9.385 \times 10^{-4}T \tag{13}$$

$$\frac{\partial \ln D_s}{\partial \ln T} = 4.806 \times 10^{-2} - 4.6848 \times 10^{-3}T \tag{14}$$

$$\frac{\partial \ln D_{\mathrm{op}}}{\partial \ln T} = 3.4261 \times 10^{-1} - 1.3169 \times 10^{-3}T \tag{15}$$

where T is the temperature (K) using data over the range from 273 to 373 K. The effective radius of the solvent molecule, r_s, is determined by assuming a spherical form for the volume per water molecule at bulk. This value has not been modified to fit any particular model of water. A similar procedure for ice using data from 123 to 273 K gives

$$r_s\ (\mathrm{bohr}) = 3.7190 - 1.8 \times 10^{-6}T + 3.72 \times 10^{-7}T^2 \tag{16}$$

$$D_s = 851.80 - 5.7535T + 1.0906 \times 10^{-2}T^2 \tag{17}$$

$$D_{\mathrm{op}} = 1.7405 - 1.00 \times 10^{-4}T \tag{18}$$

$$\frac{\partial \ln r_s}{\partial \ln T} = -7.1493 \times 10^{-3} + 7.6930 \times 10^{-5}T \tag{19}$$

$$\frac{\partial \ln D_s}{\partial \ln T} = -10.204 - 3.7102 \times 10^{-2}T \tag{20}$$

$$\frac{\partial \ln D_{\mathrm{op}}}{\partial \ln T} = 2.962 \times 10^{-4} - 5.9429 \times 10^{-5}T \tag{21}$$

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