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Cluster Ion Thermodynamic Properties: The Liquid Drop Model Revisited

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The liquid drop (LD) model is revisited to assess the reliability of its predictions for thermodynamic properties of cluster ions and to examine the rate of convergence of such properties to their bulk counterparts. The model predictions are in very good agreement with both available experimental data and simulation results for $Na^+(H_2O)_n$ clusters, surprisingly for all cluster sizes, and the stepwise cluster thermodynamic properties are found to converge only slowly to their bulk counterparts. The LD model allows a natural partitioning of the cluster ion thermodynamic properties into various components, one of which (the solvation part) is of prime importance in connecting cluster solvation properties to the bulk limit. The latter LD model component is found to be entirely analogous to the so-called dielectric sphere theory, and as implied in earlier work, the results of dielectric models suggest that ion solvation is also a very slow process to converge to the bulk limit. In addition, a form alternative to the customary interior ion LD model is proposed, where the ion resides at the surface of a solvent droplet, and the resulting model successfully predicts that surface ion $I^-(H_2O)_n$ clusters are thermodynamically very likely and that large halide ions tend to be located, if not at the surface, very close to it in large clusters of polar solvent molecules. Conversely, small ions such as Na^+ are predicted to be interior in water clusters. Further, large ions such as I^- are predicted to have interior but near-surface locations in acetonitrile clusters. Even though it seems to work better for smaller ions and solvents such as water, the LD model, despite its simplicity, generally appears to properly describe cluster ion thermodynamic properties over a wide range of cluster sizes and even for relatively small cluster sizes.

I. Introduction

There has been a long-standing interest in determining how physical and chemical properties of clusters evolve with cluster size, since one often thinks of clusters as bridging the gap between the gas and condensed phases.[1,2] The properties of chemical species in solution often differ drastically from those of the gas-phase monomer species, and thus, important issues include the identification of possible transitions between the gas-phase and condensed-phase behavior of clusters or the determination of how large a cluster needs to be for its properties to even approach the bulk limit. In this article, we will focus on a rather fundamental issue: the solvation of simple ions in clusters, with particular emphasis on the rate of convergence of the cluster ion thermodynamic properties, such as cluster enthalpies and free energies, to their bulk counterparts. The latter bulk properties are experimentally known,[3−5] but the cluster thermodynamic properties are known from gas-phase thermochemistry experiments only for small clusters.[6,7] Computer simulations can be and have been used to predict cluster ion thermodynamic properties,[8−10] but it would be computationally unrealistic to calculate cluster properties over a very wide range of cluster sizes. An alternative approach advocated in early work by Castleman and co-workers[1,11,12] uses the liquid drop (LD) model,[11−14] based on macroscopic properties, to estimate reliable cluster thermodynamic properties over a wide range of cluster sizes. A major goal of the present work is to assess the general applicability and reliability of the LD model to estimate cluster ion thermodynamic properties. A second goal is introduced and described in the next few paragraphs.

Early studies[1,11] seemed to indicate that experimental enthalpies of cluster ions[6] converge quite rapidly as a function of cluster size and approach the bulk ion solvation enthalpy for clusters containing only five solvent molecules. Stepwise cluster ion enthalpies, calculated with the LD model, were also shown[12] to reach a plateau fairly rapidly with increasing cluster size. These early observations seem to suggest that cluster thermodynamic properties such as total cluster enthalpies converge quite rapidly to their bulk counterparts for cluster sizes as small as, say, $n \approx 5$ (n being the number of solvent molecules in the cluster). For most of the simple ions investigated, such as monovalent cations, the number roughly corresponds to the number of solvent molecules in the ion first solvation shell.

A different picture of convergence emerges in connection with the relationship of cluster solvation properties to their bulk counterparts,[15,16] a topic of much interest in studies of chemical reactions in clusters[17] to understand microsolvation effects on chemical systems. In a study of aqueous solvation dynamics via molecular dynamics (MD) simulations of ion−water clusters,[18] clusters containing 256−512 water molecules were found to be adequate for describing the bulk solvation dynamics. Yet, simple continuum dielectric arguments indicate that, for these cluster sizes, the cluster solvent molecules only account for 70−80% of the bulk solvation free energy of small charged solutes,[18] suggesting that ion solvation is quite slow to converge to the bulk limit. Thus, in simulations of ionic solvation, finite-size corrections for, for example, solvation free energies of ions in bulk solution are quite important and cannot be neglected.[19]

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Indeed, continuum dielectric arguments confirm that the deviation from the bulk limit of the solvation free energy of large cluster ions is inversely proportional to the cluster radius.[20,21] Along similar lines, a mean spherical approximation treatment of halide ion−water cluster thermodynamics indicated that two complete solvation shells account for only 55−70% of the bulk ion solvation.[20] Even though not clearly stated or emphasized in earlier work, it is obvious from the above that the solvation thermodynamic properties of cluster ions are very slow to approach the bulk limit.

At this stage, one may be puzzled by the apparent paradox, or at least discrepancy, arising from the fact that total cluster enthalpies seem to converge quite rapidly to their bulk counterparts, while the solvation free energies of cluster ions are very slow to approach the bulk limit. Part of this article aims to resolve this discrepancy or ambiguity. In the earlier analyses of total cluster enthalpies,[12] an approximate ion-independent form of the LD model was used to compare the model predictions to experimental measurements for a collection of cluster ions. A more quantitative approach will be used here. The attractive feature of the LD model is that it allows a natural partitioning of the cluster properties into various components, only one of which is associated with ion solvation. As will become clear presently, fast convergence of the total cluster thermodynamic property to the bulk limit would by no means imply that the ion solvation component would itself be fast to approach its bulk limit. To resolve these convergence issues, we shall examine the rate of convergence of the total cluster ion thermodynamic properties to the bulk limit, as well as that of the ion solvation component of the thermodynamic properties.

The ion solvation component of the LD model employs a continuum dielectric description of the solvent, and most attention has been paid to its applicability for larger clusters. For example, a recent analysis by Coe[16] of small iodide−water cluster solvation data, results of ion simulations in model polar solvent clusters of intermediate size and continuum dielectric asymptotic trends, suggests that the transition to continuum behavior is nearly but not quite complete for cluster sizes of $n \approx 60$ and that this transition might be associated with a change from the peculiar surface character of small iodide−water clusters to the bulklike interior character of larger clusters.[16] Similarly, the continuum dielectric (CD) model was found to properly describe the solvation free energy of halide ion−water clusters only for large cluster sizes ($n \geq 125$) when compared to a more refined mean spherical approximation treatment.[20] Since the LD model is based on macroscopic rather than microscopic properties and since the continuum dielectric model seems questionable for small clusters, we will investigate the reliability of the LD model predictions over a wide range of cluster sizes from small clusters to the bulk and for cluster ions other than halide−water clusters. We pause to stress our perspective here. There is no doubt that, even if one rules out the very smallest clusters, the LD model assumptions are easy to criticize for small clusters: the neglect of molecular aspects; the neglect of nonlinear effects of the ionic field; the neglect of various polarizabilities; etc. Ideally, one would like to have a more molecular-based theory,[22] which currently does not exist. Our approach here is simply to use the simple LD model to investigate if, despite its obvious underlying shortcomings, it can nonetheless provide a useful framework for characterizing ionic cluster systems.

Finally, we will introduce and test a slightly modified LD model that takes into account the peculiar structural aspects, mentioned above, of surface ion clusters such as clusters of water and the larger halide ions.[9,10,16,23] The conventional LD model assumes that the ion is located at the center of a spherical solvent droplet, which is questionable for this class of clusters. As we shall see, this surface ion LD model successfully predicts that surface ion $I^-(H_2O)_n$ clusters are thermodynamically very likely and that large halide ions tend to be located, if not at the surface, then very close to the surface in large clusters of polar solvent molecules while smaller, less spatially disruptive ions such as sodium tend to exhibit interior cluster structures.

The outline of the present article is as follows: we first briefly present in section II the various ingredients of the LD model[11−14] that we use to describe cluster thermodynamic properties and we reexamine the rate of convergence of the latter properties to their bulk counterparts. We then turn to the general applicability of the LD model in section III, where, in turn, the model predictions are compared to both experimental and computer simulation data, connection is made between the LD model and a recently proposed cluster solvation model known as dielectric sphere (DS) theory,[15,16] and a surface ion LD model is introduced to take into account the peculiar structural properties of a certain class of cluster ions such as the larger halide ion−water clusters. Other solvents such as acetonitrile are discussed here, as are the possible limitations of the LD model in general. Concluding remarks follow in section IV.

II. Cluster Thermodynamic Properties and Convergence to the Bulk Limit

A. Liquid Drop Model. The classical LD formulation of Thomson[11−14] that we will use to examine cluster thermodynamic properties expresses the free energy of formation of ionic clusters in terms of the solvent macroscopic properties. The Thomson equation has been used earlier in the context of cloud physics[14] to predict energy barriers of ion-induced nucleation processes[24] or to investigate cluster ion thermodynamic properties,[12] but we feel it has been perhaps inappropriately neglected ever since, especially given the recent activity in the field of cluster science. A number of refinements and corrections for the Thomson equation have been proposed, and a more precise treatment of the microscopic droplet surface tension[25,26] or the inclusion of polarization effects[27,28] has been considered for the smallest clusters for which the macroscopic parameters of the Thomson equation are expected to fail.[29] These various corrections have been found to be most significant for clusters containing a single solvent molecule and, in general, only substantial for clusters containing less than a few solvent molecules.[12] Thus, for simplicity, we retain the original “primitive” form of the LD model and investigate over what range of cluster sizes the LD model predictions may be reliable, keeping in mind that the model very likely cannot perform well for the very smallest clusters.

In the LD model, the free energy of forming an ion−solvent cluster of size n from its monomer constituents can be written as a sum of solvent *condensation*, droplet *formation* and ion *solvation* terms:

$$\Delta G_n = \Delta G_{\mathrm{cond}} + \Delta G_{\mathrm{form}} + \Delta G_{\mathrm{solv}} \tag{1}$$

The first term in eq 1 accounts for the free energy change due to the condensation of n solvent molecules

$$\Delta G_{\mathrm{cond}} = -nRT \ln S \tag{2}$$

where S is the ratio of the partial pressure P of the condensing solvent vapor to its normal bulk vapor pressure P^0 at the system temperature T and R is the gas constant. The second term in eq

1 represents the work required for forming a finite-size droplet of radius r,

$$\Delta G_{\text{form}} = 4\pi N r^2 \sigma \tag{3}$$

where σ is the surface tension and N is Avogadro's number. The last term in eq 1 is the electrostatic stabilization energy of the ion by the condensing (solvent) dielectric or solvation free energy

$$\Delta G_{\text{solv}} = -\frac{q^2 N}{2}\left(1 - \frac{1}{\epsilon}\right)\left(\frac{1}{r_i} - \frac{1}{r}\right) \tag{4}$$

where ϵ is the solvent dielectric constant and q and r_i are the ion charge and radius, respectively. This solvation term is the finite-size cluster analogue of the Born continuum dielectric model[5,30,31] for ion solvation in liquids, and it naturally converges to the latter. This term has been recently rederived,[20,21] and it has been shown to represent cluster ion solvation free energies adequately, at least for large cluster sizes.[20]

In the LD model, the volume of the finite-size droplet is related to the number of solvent molecules n in the cluster by

$$n = \frac{4\pi}{3}(r^3 - r_i^{\,3})\frac{\rho N}{M} \tag{5}$$

where M and ρ are the molecular weight and bulk density of the solvent, respectively. The entropy of formation of a cluster is just the negative of the derivative of the free energy with respect to temperature, and the cluster enthalpy is then[32]

$$\Delta H_n = \Delta G_n + T\left(\frac{\partial \Delta G_n}{\partial T}\right)_P \tag{6}$$

where the temperature dependence of the free energy ΔG_n is explicitly introduced via that of the normal bulk solvent vapor pressure P^0, surface tension σ, dielectric constant ϵ, and bulk density ρ. The various components of the cluster enthalpy, i.e., the condensation, formation, and solvation enthalpies, are obtained by applying eq 6 to the corresponding components of the free energy. The necessary data, i.e., the solvent vapor pressure, surface tension, dielectric constant, and bulk density, as well as their temperature coefficients, have been tabulated by Castleman and co-workers.[12]

B. Applications of the Liquid Drop Model. One of the main prototype systems that we investigate here is the sodium ion–water cluster. First, the LD model was found to work reasonably well, for certain properties, for clusters containing water (though not necessarily for other solvents).[12] Second, there is reliable experimental data for the $Na^+(H_2O)_n$ system,[6] and it has therefore been the focus of a number of theoretical and computational studies.[8,9] Finally, the (spherical) LD formalism that we adopt for the ion–water clusters should be most appropriate for small, charge-concentrated, nonpolarizable cations, such as Na^+. For example, the use of a model where the ion is located inside a spherical solvent droplet may be more questionable for clusters of water and the larger halide ions, since there is increasing experimental[16,23] and theoretical[9,10] evidence that halide ions, except for fluoride,[33] tend to sit on the surface of small water clusters, a feature inconsistent with the model. We will introduce and test a slightly modified LD model—where the ion resides at the surface of the solvent droplet—to investigate $I^-(H_2O)_n$ cluster properties toward the end of this article. Although our focus is on water clusters, acetonitrile will also be considered in section III.C.

TABLE 1: Solvent Parameters Used in the LD Model

parameter[a]	water	acetonitrile
T (K)	313.15	293.15
M (g mol^{-1})	18.015	41.05
σ (erg cm^{-2})	69.56	29.10
$(\partial\sigma/\partial T)_{P=1}$ (erg cm^{-2} K^{-1})	−0.1635	−0.132
ϵ	73.15	37.67
$(\partial\epsilon/\partial T)_{P=1}$ (K^{-1})	−0.385	−0.200
ρ (g cm^{-3})	0.99224	0.782
$(\partial\rho/\partial T)_{P=1}$ (g cm^{-3} K^{-1})	−0.00038	−0.0011
ln P^0 (atm)	−2.62	−2.381
d ln P^0/dT (atm K^{-1})	0.053	0.0477

[a] Taken from ref 12.

We chose a cavity (or ionic) radius of 1.67 Å for the sodium ion in water. With this prescription, the Born solvation model[5,30] reproduces the experimental bulk liquid Na^+ hydration free energy, −98 kcal/mol at 298 K.[3−5] It is worth pointing out that there are discrepancies in the bulk liquid ion solvation free energies reported by various sources, since these numbers are extracted in pairs (for a cation and an anion) from properties of electrolyte solutions and since there is some ambiguity in the partitioning of the salt solvation free energy into the individual ion contributions. In earlier work,[34] we used the value −89.6 kcal/mol for the hydration free energy of sodium,[35] but we here use[36] the value −98 kcal/mol, which is encountered more often in the literature, together with a value for the hydration enthalpy of −106 kcal/mol.[3−5] The value of −106 kcal/mol is also in better agreement with absolute bulk solvation enthalpies determined with a model making use of small cluster properties,[15] which makes this choice even more appropriate in the context of the present work. Similarly, the ionic radius for iodide in water is set to 2.77 Å, which yields a Born hydration free energy in close agreement with the experimental value of −59 kcal/mol.[3−5] The ionic radii of sodium and iodide in acetonitrile are slightly larger, with values 1.72 and 2.94 Å, respectively, for which the Born solvation model reproduces experimental solvation free energies (−94 and −55 kcal/mol, respectively). Finally, the parameters for the solvent properties and their temperature dependence are those used in the earlier work of Castleman and co-workers[12] for liquid water at 313 K and acetonitrile at 293 K and are listed in Table 1. All cluster thermodynamic properties calculated in this work with the LD model are for a standard-state pressure $P = 1$ atm.

The stepwise cluster enthalpies and free energies calculated for $Na^+(H_2O)_n$ with the LD model are displayed in Figure 1. Inspection of Figure 1 reveals that the LD model predictions are in reasonable agreement with experimental thermodynamic data[6] even for the very small clusters and in similar agreement with the results of MD simulations for small cluster sizes[9] and our own Monte Carlo (MC) simulations for intermediate-size clusters (results of the latter simulations are not shown for small cluster sizes, since they coincide with the MD results). The simulations will be discussed later in greater detail. Let us now focus on the cluster thermodynamic properties predicted by the LD model for our prototype $Na^+(H_2O)_n$ clusters.

C. Convergence of Cluster Properties to Bulk. It is seen in Figure 1 that the stepwise thermodynamic properties indeed seem to reach a plateau value for $n \approx 5-10$, as observed in earlier work.[12] But what is striking is that the convergence to the bulk limit predicted by the model is rather slow and certainly not as fast as might be suggested by earlier analyses.[12] For example, even for $n = 100$, the stepwise cluster enthalpy $\Delta H_{n-1,n} = \Delta H_n - \Delta H_{n-1}$ is only 90% of the asymptotic limit of −10.5 kcal/mol predicted by the LD model with the set of parameters used here. (The latter asymptotic value is incidentally

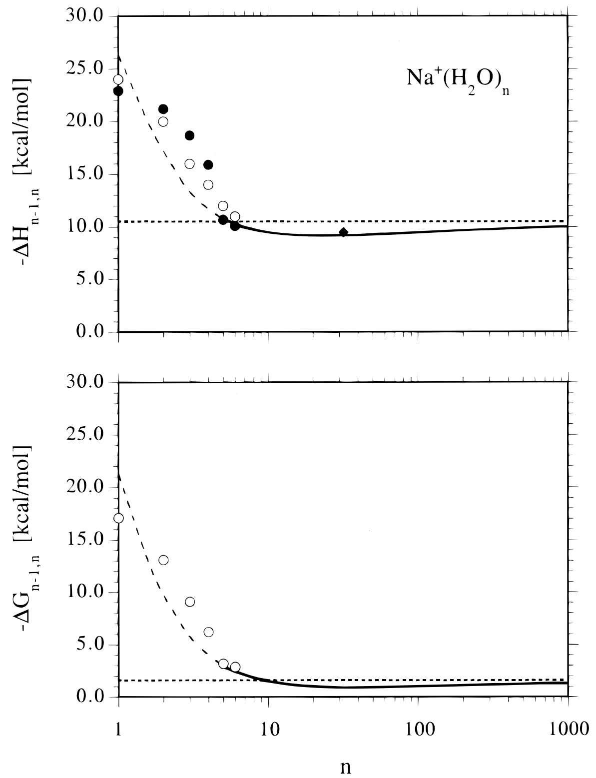

Figure 1. Stepwise $Na^+(H_2O)_n$ cluster enthalpies $\Delta H_{n,n-1}$ and free energies $\Delta G_{n,n-1}$ calculated with the LD model as a function of cluster size n at 313 K (solid and dashed lines are used to represent the LD model predictions for the very smallest clusters, where the model is supposed to breakdown, as discussed in the text; the same procedure will be used in the following figures). The dotted line represents the bulk limit predicted by the LD model. Also shown are the experimental data of ref 6 at 313 K (○), the stepwise cluster enthalpies calculated at 298 K by MD simulations in ref 9 (●), and those computed in this work (◆) by MC simulations (see text).

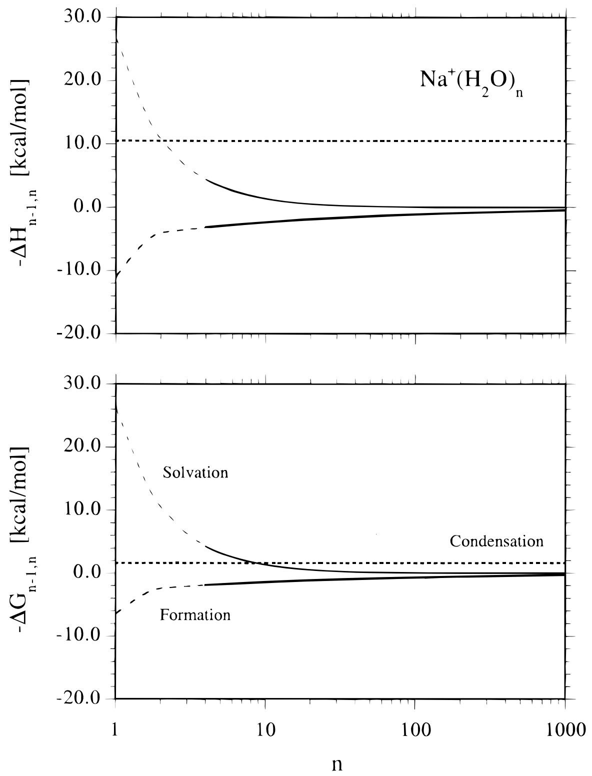

Figure 2. Formation, condensation, and solvation components of the stepwise $Na^+(H_2O)_n$ cluster enthalpies $\Delta H_{n,n-1}$ and free energies $\Delta G_{n,n-1}$ calculated with the LD model as a function of cluster size n at 313 K.

very close to the negative of the actual experimental heat of vaporization of water, which is 10.5 kcal/mol at 298 K).[32] The various components of the stepwise thermodynamic properties of the $Na^+(H_2O)_n$ clusters predicted by the LD model shown in Figure 2 help in the understanding of convergence issues. What is remarkable is that the major component of the total cluster thermodynamic properties (not shown here, but they can easily be obtained by adding the corresponding stepwise properties displayed in Figures 1 and 2) for the small clusters is the solvation part. This indicates that the comparison of the previous work[1,11] of the total cluster thermodynamic properties to the bulk ion solvation property is only meaningful for the very small clusters, where the condensation and formation components of the total cluster thermodynamic properties almost cancel each other. This cancellation only holds for the very small clusters, but by the time one reaches the cluster size $n = 5$, ion solvation only accounts for $\sim^2/_3$ of the cluster enthalpy, and thus, comparing the latter property to the bulk solvation enthalpy, which are about equal for $n = 5$, could mislead one to conclude that the cluster enthalpies or the ion solvation process converge rapidly to the bulk limit.

For the larger clusters ($n \geq 15-20$), the solvation and formation components are of similar magnitude and opposite sign, as shown in Figure 2, so that the cluster enthalpy is mainly due to the condensation component, and the stepwise enthalpy naturally converges to the (negative of the) water heat of vaporization.[37] Basically, the condensation enthalpy and free energy vary linearly with respect to cluster size n, and thus, the stepwise properties are constant and equal the bulk limit value. Therefore, the deviation of the thermodynamic properties from the bulk limit in Figure 1 can be attributed to the sum of the formation and solvation components, which is small for the larger clusters ($n \geq 15-20$) but nonzero (it accounts for ~10% or more of the total cluster thermodynamic properties). Because the convergence of the total cluster thermodynamic properties to bulk depends on that of both the formation and solvation components of the property, in fact little information can be extracted regarding ion solvation in clusters from inspection of the stepwise cluster thermodynamic properties (e.g., both formation and solvation components could be very slow to converge to their respective bulk limit, but because their contributions are of similar magnitude and opposite sign, the overall total cluster thermodynamic property could converge faster to the bulk limit than both of the individual components). Accordingly, we now turn our attention to the ion solvation component of the total cluster thermodynamic properties.

From the above, it should be noted that a very important feature of the LD model is that it allows a natural partitioning of the total cluster thermodynamic properties into various contributions. The solvation component of the thermodynamic properties of $Na^+(H_2O)_n$ clusters is shown in Figure 3. As mentioned earlier, the solvation component, not the total cluster free energy, is evidently the thermodynamic property of choice to consider when connecting cluster solvation properties to the bulk liquid limit (in which the condensation and formation contributions to the thermodynamic properties are absent).

The asymptotic limit for the solvation enthalpy of Na^+ predicted by the LD model is −101 kcal/mol at 313 K, which is slightly less in magnitude than the experimental number, −106 kcal/mol.[3−5] This could be corrected for by using a smaller ionic radius for the sodium ion, but this could only be done at the expense of the solvation free energy, which is the basis of our

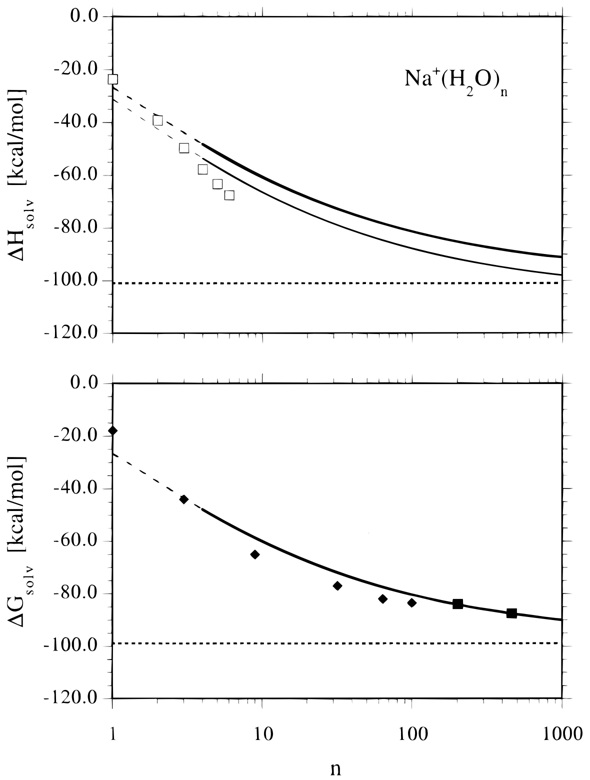

Figure 3. Solvation component of the $Na^+(H_2O)_n$ cluster enthalpies and free energies calculated with the LD model as a function of cluster size n at 313 K (thick line). The dotted line represents the bulk limit predicted by the LD model. Also shown are the DS model predictions at 313 K (thin line; note that the solvation free energy curve coincides with the LD model results), the cluster solvation enthalpies extracted from experimental data with the model of ref 15 (□), the cluster solvation free energies extracted from the 298 K MD simulation results of ref 41 (■), and those computed in this work (◆) by MC simulations (see text).

current prescription for choosing ionic radii.[38] Regardless of this, what is manifest in Figure 3 is that the cluster solvation enthalpy and free energy are very slow to converge to the bulk limit predicted by the LD model; e.g., the cluster solvation free energy is only 80 and 90% of the bulk values for cluster sizes of 100 and 1000, respectively. This finding is consistent with previous observations,[18,20,21] and it is evidently due to the very long-range nature of the ion−solvent electrostatic interactions; i.e., in the bulk liquid, solvent molecules even far from the ion significantly contribute to the ion solvation thermodynamic properties.

III. Range of Applicability of the Liquid Drop Model

In this section, we assess the general applicability of the LD model for predicting reliable cluster ion thermodynamic properties by comparing the model predictions to experimental data and computer simulation results. We also compare the LD model predictions for ion solvation thermodynamics to those of a recently proposed cluster solvation model known as dielectric sphere (DS) theory,[15,16] and we make a straightforward connection between both models. Finally, we will introduce a surface ion LD model, primarily to investigate clusters of water and the larger halide ions, and will discuss the limitations of the LD model in general. Acetonitrile clusters will also be briefly considered.

A. Comparison with Experimental and Computer Simulation Data. As mentioned in section II.B, inspection of Figure 1 reveals that the LD model predictions are in quite reasonable agreement with experimental thermodynamic data,[6] surprisingly even for the very small $Na^+(H_2O)_n$ clusters. Let us now turn our attention to the ion solvation component of the total cluster thermodynamic properties. Shown in the top panel of Figure 3 are the cluster solvation enthalpies extracted from experimental cluster enthalpies,[6] following Coe[15] and others,[37] by subtracting the total enthalpy for forming the pure water cluster $\Delta H[(H_2O)_n]$ from the total ion−water cluster enthalpies $\Delta H[Na^+(H_2O)_n]$:

$$\Delta H_{solv} = \Delta H[Na^+(H_2O)_n] - \Delta H[(H_2O)_n] \tag{7}$$

In this context, we used the recently parametrized $\Delta H[(H_2O)_n]$ expression of Coe.[15] The resulting "experimental" cluster solvation enthalpies are in reasonable, yet not perfect, agreement with the LD model predictions. (The trend observed in the small clusters might indicate that the cluster solvation enthalpies do converge to the bulk limit faster than predicted by the LD model, but this feature may depend on the parameters chosen for the water cluster enthalpy in eq 7, for which little experimental data is known.)[15]

The LD model predictions for the solvation free energy of $Na^+(H_2O)_n$ clusters are compared to the results of MD and MC simulations in the bottom panel of Figure 3. As already discussed in section II.B and shown in Figure 1, the stepwise cluster enthalpies calculated by us with MC simulations and by Jorgensen and co-workers with MD simulations[9] agree fairly well with experimental data for the very small clusters, which inspires some confidence in the reliability of the computer simulation results for intermediate-size clusters for which experimental data are not available.[39] For these, the computer simulation results in fact agree fairly well with the LD model predictions.

All simulations above employ the TIP3P model potential[40] for water and parameters for the sodium ion−water interactions derived by Aqvist[41] in order to reproduce the experimental ion bulk solvation free energy.[3−5] The TIP3P model is a simple yet quite reasonable water model, which has been parametrized in part to reproduce the experimental heat of vaporization of water.[42] The simulated stepwise enthalpies eventually converge to the TIP3P water heat of vaporization, i.e., −10.45 kcal/mol, but it should be noted that the statistical uncertainty in the simulated stepwise cluster enthalpies is known to increase with cluster size as one starts subtracting larger and larger numbers from one another. Finally, the simulations were performed at 298 K, while the experimental numbers and the LD model calculations correspond to a temperature of 313 K, but we do not expect this slight temperature difference to be an issue in comparing the various sets of data. As a further note on our MC simulations, we also made use of statistical perturbation theory[41,43,44] to calculate the solvation free energy of the sodium ion in water clusters. Basically, small free energy differences were calculated by the acceptance ratio method[44] between states representing a gradually annihilated ion,[43] and they were summed together to yield the ion solvation free energy.[45] Samples of 10^5−10^6 configurations, depending on the cluster size, were collected following equilibration for about half the number of configurations in the sample of collected data.[46]

Finally, large "cluster" solvation free energies have been extracted from the results of MD simulations of sodium ion solvation in bulk liquid water[41] and are displayed in the bottom panel of Figure 3. The simulations were performed with the surface constraint all-atom solvent (SCAAS) model,[47] in which the solvent is represented as an isolated sphere surrounding the solute. To account for proper boundary conditions, the surface layer of the solvent sphere is subject to constraints so that the density and angular orientations of the solvent molecules are representative of the bulk liquid. A Born (continuum dielectric) correction term[5,30] is then added to the calculated free energy in order to account for the (infinite) medium surrounding the sphere. The simulations reproduced the experimental sodium ion bulk solvation free energy very well (actually, the solute−solvent interaction parameters were adjusted to do so). We extracted “cluster” solvation free energies by removing the Born correction term, which is nonnegligible (−15 and −11 kcal/mol for clusters containing 202 and 460 waters, respectively), from the reported calculated bulk solvation free energy. The resulting “cluster” solvation free energies may be considered as an upper bound to the true cluster solvation free energies because of the surface constraints of the SCAAS model that would not be present in true cluster simulations. Nevertheless, it is seen in Figure 3 that the values extracted from the simulation results agree very well with the LD model predictions.

B. Dielectric Sphere Theory. DS theory has been recently advanced[15,16,48] and used in cluster studies by Coe[15,16] and others.[48] In this model, the free energy of solvation of a cluster of size n is

$$\Delta G_{\mathrm{solv}} = \Delta G^{\infty}_{\mathrm{solv}} + \frac{q^2 N}{2 r_{\mathrm{s}}}\left(1 - \frac{1}{\epsilon}\right)(n + \xi)^{-1/3} \tag{8}$$

where $\Delta G^{\infty}_{\mathrm{solv}}$ is the bulk solvation free energy, r_{s} is the effective bulk radius of a solvent molecule, and ξ is the ratio of the ion effective volume to that of the solvent. For consistency with the LD model [see eq 5], we express this ratio as

$$\xi = \frac{4\pi}{3} r_{\mathrm{i}}^{\,3} / \frac{M}{\rho N} \tag{9}$$

In earlier work by Coe, the choice of an appropriate ξ was deemed too problematic and asymptotic continuum dielectric trends were considered instead.[16] For example, cluster ion solvation free energy data was plotted vs $n^{-1/3}$ and compared to the asymptotic slopes predicted by the DS theory [where ξ becomes negligible in eq 8]. A more quantitative treatment over the whole range of cluster sizes can be performed here with a choice of the ξ parameter guided by ingredients of the LD model, which, as we shall see presently, proves judicious.

The solvation enthalpy can be obtained as outlined in section II.A for the LD model and is given by[15,16]

$$\Delta H_{\mathrm{solv}} = \Delta H^{\infty}_{\mathrm{solv}} + \frac{q^2 N}{2 r_{\mathrm{s}}}\left[\left(1 - \frac{1}{\epsilon}\right)\left\{1 + \left(\frac{\partial\, 1\mathrm{n}\, r_{\mathrm{s}}}{\partial \ln T}\right)_P\right\} - \frac{1}{\epsilon}\left(\frac{\partial\, 1\mathrm{n}\, \epsilon}{\partial \ln T}\right)_P\right](n + \xi)^{-1/3} \tag{10}$$

where $\Delta H^{\infty}_{\mathrm{solv}}$ is the bulk solvation enthalpy. The DS model was recently developed[48,49] on the basis of continuum dielectric arguments similar to those used for the LD model; thus, it is not so surprising that both representations are absolutely equivalent if eqs 4 and 8 are related by the following expression

$$r^3 = r_{\mathrm{s}}^{\,3}(n + \xi) \tag{11}$$

[assuming $\Delta G^{\infty}_{\mathrm{solv}}$ in eq 8 can be represented by the Born expression for the bulk solvation free energy]. Upon substitution of the expression for ξ in eq 9 and that for r in eq 5, it is straightforward to show that eq 11 yields

$$\frac{4\pi}{3} r_{\mathrm{s}}^{\,3} = \frac{M}{\rho N} \tag{12}$$

which is precisely the definition of r_{s}, the effective bulk radius of a solvent molecule.

Displayed in Figure 3 are the DS model predictions for the solvation thermodynamic properties of our prototype $\mathrm{Na}^+(\mathrm{H_2O})_n$ clusters. In the present DS calculations, we have used the parameters derived independently by Coe for liquid water over a temperature range 273−373 K.[16] The r_{s} parameter of Coe at 313 K and that calculated with eq 12 and the parameters[12] for liquid water that we use in the LD model are almost the same (1.9315 vs 1.9310 Å, respectively). Thus, in light of the preceding discussion, it comes as no surprise that the cluster solvation free energies predicted by the LD model and DS theory are the same for all cluster sizes, as seen in the bottom panel of Figure 3 [note that the DS model curve coincides with the LD model one]. The apparent discrepancy between the cluster solvation enthalpies predicted by the LD and DS models in the top panel of Figure 3 arises from the use of the experimental bulk liquid solvation free energy for $H^{\infty}_{\mathrm{solv}}$ in eq 9, which is a few kcal/mol lower than that predicted by the LD model. If one were using the asymptotic value predicted by the LD model for $H^{\infty}_{\mathrm{solv}}$ in the DS model, then both models would actually predict indistinguishable cluster solvation enthalpies.[50]

C. Surface Ion Liquid Drop Model. As mentioned in section II.B, the LD model is most appropriate for cluster ions, such as $\mathrm{Na}^+(\mathrm{H_2O})_n$, where the ions sit in the interior of an approximately spherical solvent droplet, but it may break down for surface ion clusters such as clusters of water and the larger halide ions. To study the latter clusters, we introduce a *surface ion* LD model, in which the formation and condensation terms are the same as those for the interior ion model, but the volume of the finite-size droplet is now related to the number of solvent molecules n in the cluster by

$$n = \frac{4\pi}{3}\left(r^3 - \frac{r_i^{\,3}}{2}\right)\frac{\rho N}{M} \tag{13}$$

which is the analogue of eq 5 except that the ion sits at the surface of the spherical solvent droplet, and thus, only half of the ion volume is embedded in the droplet volume. The electrostatic stabilization energy of the ion at the surface of the dielectric is taken to be

$$\Delta G_{\mathrm{solv}} = -\frac{q^2 N}{2}\frac{\epsilon - 1}{\epsilon + 1}\left(\frac{1}{r_i} - \frac{1}{r}\right) + \frac{q^2 N}{2r}\frac{\epsilon - 1}{(\epsilon + 1)^2}\left(\frac{1}{2} - \ln\frac{r_i}{r}\right) + O\left(\frac{1}{r^2}\right) + O\left(\frac{\epsilon - 1}{(\epsilon + 1)^3}\right) \tag{14}$$

which was derived by Nitzan and co-workers earlier.[21] Before proceeding, a few comments are in order here about both the simplicity of the proposed model and a number of refinements that could be introduced to paint a more realistic picture of surface ion clusters. First, the solvent droplet may not be spherical and it could be modeled as, for example, ellipsoidal, but this would be at the expense of rather simple expressions for the thermodynamic properties. Second, the expressions for the cluster solvation free energy of a surface ion in eq 14 is a truncated series in both the (inverse of the) droplet radius and solvent dielectric constant. Thus, it is obvious that eq 14 will be most appropriate for highly polar solvents and rather large clusters. Once again, more refined expressions could be obtained here, especially for the smaller clusters, but as already mentioned

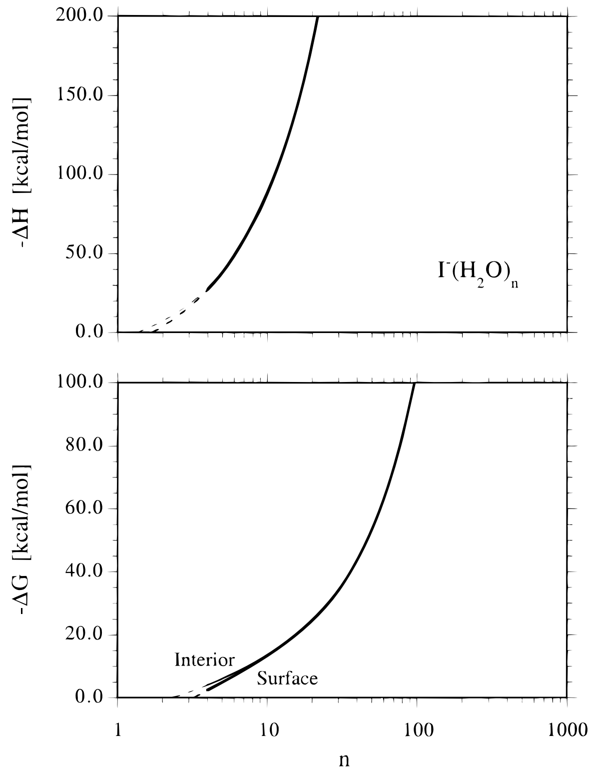

Figure 4. Total $I^-(H_2O)_n$ cluster enthalpies ΔH and free energies ΔG calculated with the surface ion LD model (thick line) and the interior ion LD model (thin line) as a function of cluster size n at 313 K.

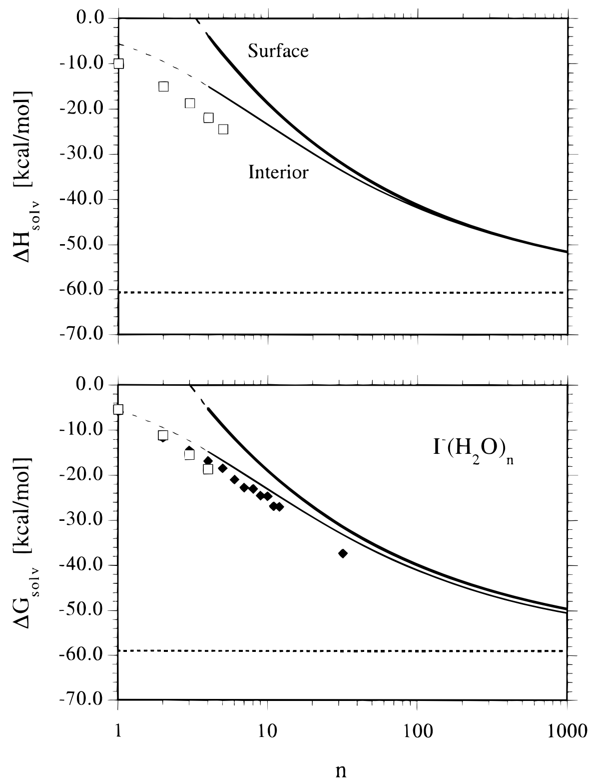

Figure 5. Solvation component of the $I^-(H_2O)_n$ cluster enthalpies and free energies calculated with the surface ion LD model (thick line) and the interior ion LD model (thin line) as a function of cluster size n at 313 K. The dotted line represents the bulk limit predicted by the (interior ion) LD model. Also shown are the solvation free energies calculated at 298 K by MC simulations (◆) in this work (see text) and the cluster solvation properties extracted from experimental data with the model of refs 15−16 (□).

in section II.A, we do not expect the LD model to perform well for very small clusters [even though it surprisingly does for Na^+-$(H_2O)_n$ clusters!], and for simplicity, we restrict our investigation of the LD models to clusters containing more than just a few solvent molecules.

The total thermodynamic properties obtained with the surface ion and interior ion LD models for $I^-(H_2O)_n$ clusters are shown in Figure 4. The cluster thermodynamic properties predicted by the surface ion and interior ion LD models are very similar (the properties predicted by the surface ion model are slightly larger in magnitude than those predicted by the interior ion for clusters of size $n > 12$, but the difference between the properties is too small to be considered quantitative). As a result, surface ion structures are thermodynamically slightly favored, or at least equally probable to interior structures, and the cluster thermodynamic properties are fairly insensitive to the exact location of the ion in the cluster. It should be noted that the *strictly interior*/*central* or *strictly surface* configurations assumed in the models are extreme, limiting cases of cluster structures in which the ion is located exactly at the center or at the surface of a solvent spherical droplet, respectively. Computer simulations of larger halide ion−water clusters[9] have shown that, at room temperature, the ion is *predominantly* at the surface of the cluster, but it may still be surrounded by a much larger number of solvent molecules than assumed in our simple-minded surface ion model; in other words, the ion does not just sit on the surface of a spherical pure water droplet, and a number of solvent molecules surround/solvate the ion even though the ion solvation shell is not complete, and one side of the cluster ion is somewhat open. The more realistic cluster ion structures observed in computer simulations are thus somewhat intermediate to the limiting cluster configurations assumed in the simple interior and surface ion LD models. The fact that *strictly* surface ion cluster structures are predicted to be very likely but equally probable compared to *strictly* interior/central structures is consistent with the *predominantly* surface cluster structures observed in computer simulations[9,10] and inferred from experiments.[16,23] We have also determined that very similar agreement is obtained between the cluster thermodynamic properties of ion−water clusters calculated with the interior ion and surface ion models for other large halides such as bromide, although the agreement becomes poorer, as expected, for chloride. In contrast, it is worth pointing out (but it is not shown here) that the LD models correctly predict the interior ion structure to be thermodynamically more stable for $Na^+(H_2O)_n$ clusters.

The fact that the total cluster thermodynamic properties are similar for both the surface ion and interior ion models for $I^-(H_2O)_n$ clusters may be puzzling at this stage, since placing the ion at the surface of the solvent droplet certainly results in a loss of ion solvation energy, as shown in Figure 5, but this can be traced back to the competition between the relative magnitudes of the ion solvation and droplet formation components of the total cluster thermodynamic properties. When the ion is placed at the surface of the solvent droplet, the (negative) ion solvation enthalpy and free energy decrease in magnitude (see Figure 5), but the (positive) droplet formation thermodynamic properties also decrease, as the solvent droplet radius decreases [see eq 13 and Figure 6] to a similar extent. As a result, the total cluster enthalpies and free energies are similar in magnitude with both models. One may actually make a parallel between this feature of the LD model and the molecular picture of the larger halide ion−water clusters, where the

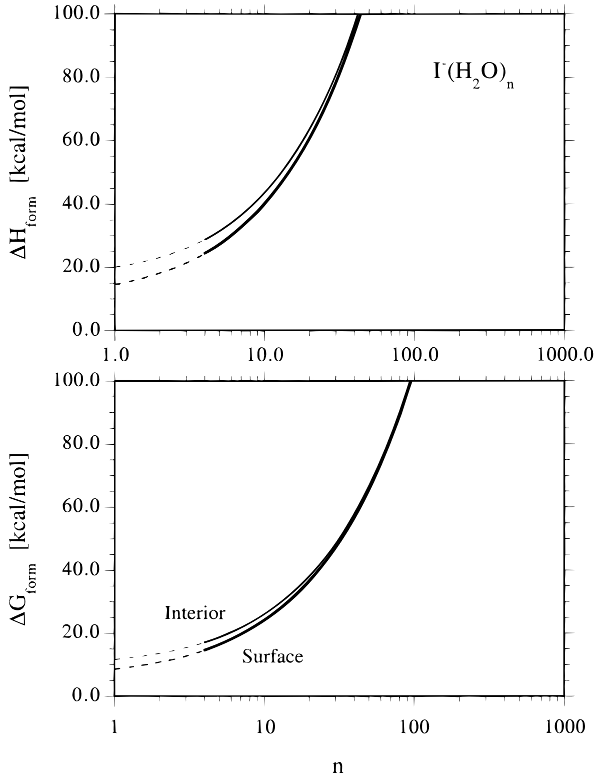

Figure 6. Formation component of the $I^-(H_2O)_n$ cluster enthalpies and free energies calculated with the surface ion LD model (thick line) and the interior ion LD model (thin line) as a function of cluster size n at 313 K.

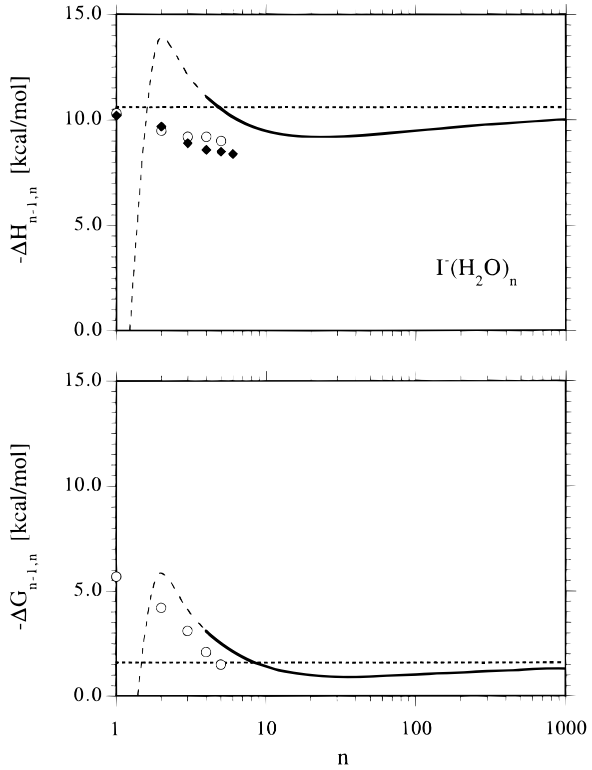

Figure 7. Stepwise $I^-(H_2O)_n$ cluster enthalpies $\Delta H_{n,n-1}$ and free energies $\Delta G_{n,n-1}$ calculated with the surface ion LD model as a function of cluster size n at 313 K (solid line). The dotted line represents the bulk limit predicted by the LD model. Also shown are the experimental data of ref 55 at 313 K (○) and the stepwise cluster enthalpies calculated at 298 K by MC simulations (◆) in this work (see text).

predominant surface character is commonly attributed[51] to a competition between the ability of water to hydrogen-bond to itself and the propensity of the ion to disrupt the water network and maximize its degree of solvation, or more generally the competition between the relative strengths of the solvent−solvent and solute−solvent interactions. In the LD model, the hydrogen-bonding ability of the solvent is obviously not explicitly taken into account, but in the model some stabilization energy due to solvation is lost when placing the ion at the surface of the cluster, while the droplet formation thermodynamic cost is reduced (to a similar or greater extent), which amounts to saying that a larger ion is thermodynamically more likely to sit at the surface of the cluster to avoid a large change in the size of the solvent droplet. On the other hand, smaller, less spatially disruptive ions such as sodium are more likely to exhibit interior cluster structures,[52] and the LD model accounts for this via the type of competition just described.

The difference between the cluster thermodynamic properties predicted by the interior ion and surface ion LD models is largest for the small cluster sizes, for which the applicability of the models is questionable, but tends to disappear quite rapidly with increasing cluster size. This latter finding is certainly consistent with the earlier observation by Nitzan and co-workers[21] that cluster ion solvation free energies were fairly insensitive to the actual location of the solute ion in the cluster—whether it is located primarily at the surface or the center of the cluster—over the range of cluster sizes 24−60 that they investigated with continuum dielectric models.

The stepwise thermodynamic properties obtained with the surface ion LD model for $I^-(H_2O)_n$ clusters are shown in Figure 7, along with experimental data and computer simulation results. The computer simulation results for $I^-(H_2O)_n$ clusters displayed in Figures 5 and 7 agree fairly well with experimental data for the very small clusters, and thus, we may consider the computer simulation results for intermediate-size clusters as quite reliable. In contrast to what was observed with $Na^+(H_2O)_n$ clusters, the predictions of none of the LD models agree with experimental data for the very small $I^-(H_2O)_n$ clusters. However, for the larger clusters, both the trends seen in experimental data and the results of computer simulations seem to agree reasonably well with the LD model predictions.[53]

It is a little puzzling that numerically the solvation free energies from computer simulations agree best with the predictions of the interior ion solvation model (cf. Figure 5), at least for smaller clusters, whereas the surface solvation state is undoubtedly thermodynamically preferred for $I^-(H_2O)_n$ clusters,[9,10,16,23] and indeed, we have argued above that LD models indicate such surface structures. This behavior may be either fortuitous or due to the limitations, discussed earlier, of eq 14 for describing surface ion solvation over a given range of (small) cluster sizes that we have chosen not to investigate in great detail here. It is worth pointing out that the surface ion solvation model employed here may thus underestimate the solvation component of the cluster thermodynamic properties, and with a refined surface ion solvation model, the surface character of the larger halide ion−water clusters would presumably be found to be even more predominant than predicted by the present LD models.

Finally, we have also applied the LD model to cluster ions with acetonitrile as the solvent, and results for $Na^+(CH_3CN)_n$ and $I^-(CH_3CN)_n$ clusters are displayed in Figures 8−10 along with available experimental data[54,55] for the very small clusters. It is remarkable that the LD models predict an interior structure to become thermodynamically more stable for $I^-(CH_3CN)_n$ clusters, as shown in Figure 9, in contrast to the water case and

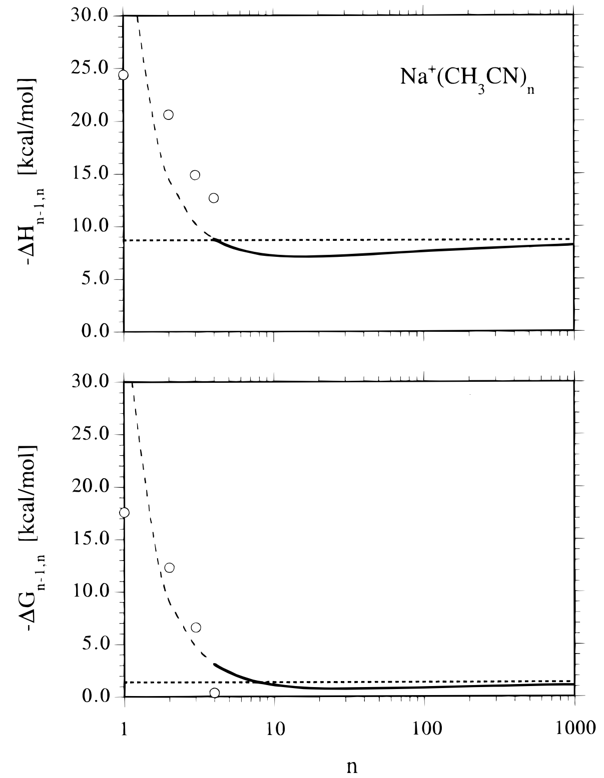

Figure 8. Stepwise $Na^+(CH_3CN)_n$ cluster enthalpies $\Delta H_{n,n-1}$ and free energies $\Delta G_{n,n-1}$, calculated with the LD model as a function of cluster size n at 293 K (solid line). The dotted line represents the bulk limit predicted by the LD model. Also shown are the experimental data of ref 54 at 298 K (○).

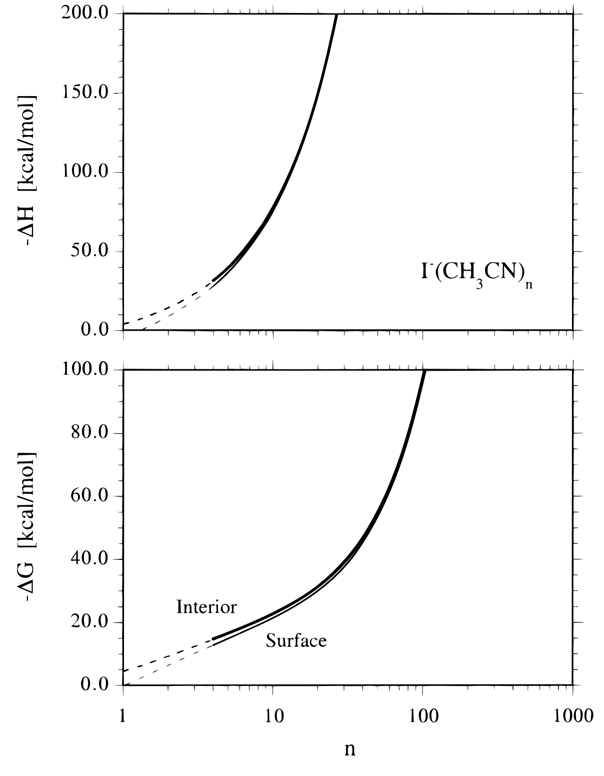

Figure 9. Total $I^-(CH_3CN)_n$ cluster enthalpies ΔH and free energies ΔG calculated with the interior ion LD model (thick line) and the surface ion LD model (thin line) as a function of cluster size n at 293 K.

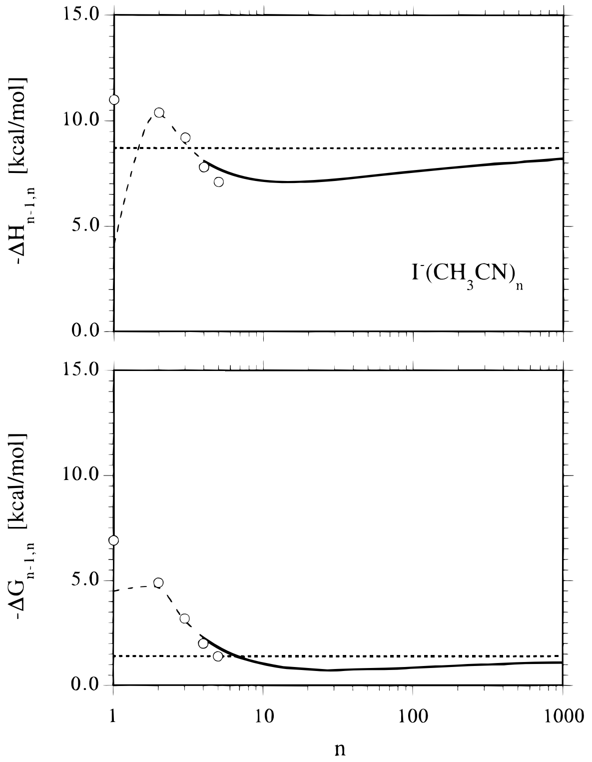

Figure 10. Stepwise $I^-(CH_3CN)_n$ cluster enthalpies $\Delta H_{n,n-1}$ and free energies $\Delta G_{n,n-1}$ calculated with the interior ion LD model as a function of cluster size n at 293 K (solid line). The dotted line represents the bulk limit predicted by the LD model. Also shown are the experimental data of ref 55 at 298 K (○).

in good agreement with the indications of recent computer simulations.[56] This behavior is evidently due to the fact that the loss of solvation resulting from moving the ion toward the surface of the solvent droplet is not totally compensated by the thermodynamic gain associated with forming a smaller solvent droplet for acetonitrile. In the context of the model, the latter is due to the fact that acetonitrile has a larger molecular volume than water, and thus, clusters of a given size have larger radii and the relative change in the formation thermodynamic properties associated with moving the ion to the surface is less pronounced for acetonitrile than it is for water. In other words, the size of the solute ion relative to that of the cluster ion plays a less significant role in reducing the formation thermodynamic properties from cluster interior states to surface states [see eqs 5 and 13] for acetonitrile. By analogy, in the molecular picture, the disruption of the solvent droplet structure caused by the presence of the ion is much less dramatic for acetonitrile than it is for water, since the presence of the ion at the center of the cluster ion does not involve breaking up a large number of strong hydrogen bonds as it is the case for water.[52,57]

The difference between the thermodynamic properties predicted by the strictly surface ion and strictly interior/central ion LD models for $I^-(CH_3CN)_n$ clusters, even though larger than for the water case, is still not very large. This finding is consistent with the fact that large anions solvated in large clusters of polar solvents are thought to be located if not at the cluster surface, then near the surface.[56] In the absence of reliable computer simulation data, we can only conclude from the stepwise cluster thermodynamic properties in Figures 8 and 10 that the LD model predictions agree with the experimental data trends to the same extent as they do with water as a solvent, and thus, the model may perform equally well and suffer from the same limitations with both solvents. Finally, the convergence of cluster ion thermodynamic properties to the bulk limit remains slow, regardless of the solvent.

IV. Concluding Remarks

The liquid drop (LD) model advocated in early work by Castleman and co-workers for studying ion-induced nucleation and cluster ion thermodynamic properties has been revisited. The model predictions agree reasonably well with both the trends in experimental data for small clusters and the results of MD and MC simulations with model potentials of intermediate-size clusters. The model predictions also agree surprisingly well with the experimental data for small $Na^+(H_2O)_n$ clusters. The stepwise cluster thermodynamic properties are found to converge slowly to the bulk limit, in contrast to earlier indications, and comparison of the total cluster thermodynamic properties to bulk ion solvation data was shown to be of little interest. On the other hand, the LD model allows a natural partitioning of the total cluster thermodynamic properties into various components, one of which is the solvation term that can be used to connect cluster solvation properties to the bulk limit. Ion solvation is indeed very long-range in nature, and consequently, the cluster solvation free energy only converges slowly to the bulk limit. The earlier observation that a few hundred solvent molecules account for only 80% or so of the bulk solvation free energy of small charged solutes in clusters[18] is not surprising in that respect. The present considerations indicate that valuable information for larger clusters (several hundreds of molecules) can sometimes be extracted from finite system MD simulations intended to account for bulk properties, as in section III.A; they also indicate that smaller simulation systems[58] containing single ions may have ion thermodynamics properties noticeably different from the bulk values.

Dielectric sphere (DS) theory was shown to be an absolutely equivalent alternative form to the long-proposed continuum dielectric expression employed in the LD model for describing ion solvation in clusters; calculations with both models and independent sets of parameters, which we proved to be consistent, indeed yielded indistinguishable solvation thermodynamic properties.

One of the main findings reported here is that the overall agreement of the dielectric model predictions with experimental trends and simulations inspires some confidence in the applicability and reliability of dielectric models for describing the cluster solvation thermodynamics of simple ions, as was found earlier for bulk liquid ion solvation.[59-61] Dielectric models are by no means restricted to simple interior ion clusters, and for example, we have made use of an earlier result for surface ion cluster solvation[21] to introduce a slightly modified LD model, where the ion resides at the solvent droplet surface. The resulting model successfully predicts that surface ion $I^-(H_2O)_n$ clusters are thermodynamically very likely and that large halide ions tend to be located, if not at the surface, then very close to the cluster surface in large clusters of polar solvent molecules, while smaller, less spatially disruptive ions such as sodium tend to exhibit interior cluster structures. Further, the model indicates that for acetonitrile, even a large ion such as I^- can adopt a favored interior cluster structure. We have also adapted the dielectric models to study the cluster solvation of ion pairs (or dipolar solutes), but our findings about, for example, the convergence of dipole cluster solvation to the bulk limit, which is naturally much faster than it is for simple ion cluster solvation, will be deferred to a later publication.[62]

Finally, the LD model as a whole seems, despite its simplicity, to be a rather powerful and reliable model for predicting cluster ion thermodynamic properties in general over a very wide range of cluster sizes and certainly for cluster sizes smaller than have been suggested before. Not surprisingly, the LD model may fail in most cases for the very smallest clusters, where the model is not so physically meaningful in the first place. The development of a molecular theory to replace the LD model would seem to be necessary here. Development of such a theory, which would also shed light on why the simple LD model works well into a size regime where it should fail, is left for the future.

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(39) It should be pointed out that computer simulations are performed by us and others for isolated clusters, whereas the actual experimental measurements do involve clusters of various size in thermodynamic equilibrium with the solvent vapor. The proper definition of the physical cluster has been a long-standing issue in investigations of nucleation and capillarity phenomena, but it is now generally agreed that thermodynamic properties computed for isolated clusters—the only practical approach at this point—give an adequate representation of the properties of clusters in equilibrium with the solvent vapor under realistic experimental conditions. See, for example, Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; Wiley: New York, 1998, p 569. Lee, J. K.; Barker, J. A.; Abraham, F. F. *J. Chem. Phys.* **1973**, *58*, 3166. Reiss, H.; Tabazadeh, A.; Talbot, J. *J. Chem. Phys.* **1990**, *92*, 1266. Weakliem, C. L.; Reiss, H. *J. Phys. Chem.* **1994**, *98*, 6408.

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(46) The random-walk Metropolis Monte Carlo method [e.g., ref 44] is employed here. A new configuration is generated by randomly translating one water molecule in all three Cartesian directions and rotating the water molecule around its Euler angles. The range for translational and rotational displacements is chosen to yield typical configuration acceptance ratios of ∼50%.

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(50) Alternatively, if one compares the cluster solvation enthalpies calculated with the DS model and displayed in the top panel of Figure 3 to the asymptotic limit predicted by the model (−106 kcal/mol), one still concludes that the cluster solvation enthalpy is slow to converge to the bulk limit.

(51) See, for example, ref 56.

(52) It should be noted that there is a competition between ion−solvent and solvent−solvent interactions even in the solvation free energy contribution ΔG_{solv}. In the macroscopic continuum view, the contribution of the former (the interaction free energy) is negative and equal in magnitude to twice the value of the latter positive contribution (the "self" free energy of the solvent). Clearly, a LD model does not do justice to the microscopic aspects of this competition.

(53) It should be noted that the "experimental" solvation free energies extracted from experimental cluster data by Coe[16] seem to be in better agreement with the predictions of the dielectric models than the solvation enthalpies extracted in a similar fashion—as outlined in section III.A—from experimental data,[55] but this may depend strongly on the parametrization of the thermodynamic properties for forming the neutral water clusters.

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(57) We note here that iodide ion clusters may behave differently and exhibit different structural properties, depending on the solvent, and this solvent dependence will prove to play an important role for NaI ion pairs in clusters [see ref 62].

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(59) See, for example, Rashin, A. A.; Honig, B. *J. Phys. Chem.* **1985**, *89*, 5588. Jayaram, B.; Fine, R.; Sharp, K.; Honig, B. *J. Phys. Chem.* **1989**, *93*, 4320.

(60) The very fact that continuum models predict at least the right trends for a variety of more complex solute properties in bulk solution [e.g., Morita, T.; Ladanyi, B. M.; Hynes, J. T. *J. Phys. Chem.* **1989**, *93*, 1386] is encouraging in that respect.

(61) It is interesting to note that the success of simple dielectric models in describing cluster ion solvation thermodynamic properties over a wide range of cluster sizes suggests that one could evaluate bulk solvation properties from cluster simulations using simple dielectric corrections, at least for simple ions. Cluster simulations do not require the use of periodic boundary conditions, the exact implementation of which remains to date controversial [Aqvist, J.; Hansson, T. *J. Phys. Chem. B* **1998**, *102*, 3837. Hummer, G.; Pratt, L. R.; Garcia, A. E.; Garde, S.; Berne, B. J.; Rick, S. W. *J. Phys. Chem. B* **1998**, *102*, 3841. Ashbaugh, H. S.; Sakane, S.; Wood, R. H. *J. Phys. Chem. B* **1998**, *102*, 3844].

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