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Solvation energy of ions and dipoles in a finite number of solvent shells

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Abstract. The contributions of a polar solvent in thermodynamic equilibrium to the solvation free energy of a dipole and of an ion are estimated analytically as functions of distance within the framework of the mean-spherical approximation theory and compared to the analogous results derived from simple electrostatical arguments. For equal-sized solute and solvent molecules, accumulating 90% of the total energy in media of moderate polarity involves ~ 1 and ~ 7 solvent shells for dipole and ion solvation, respectively. For solvents characterized by high values of ϵ only upper bounds for the energy relevant to the solvent range can be stated. Relative to the continuum picture, the MSA calculation predicts an increase of the coupling range by $\sim 50\%$, without a significant dependence on the dielectric constant ϵ .

1. Introduction

The solvation free energy E associated with a dipole or an ion in an equilibrium polar fluid is an important quantity as regards processes which involve the motion or redistribution of charge. Examples are solvent effects on emission and absorption spectra of chromophores [1–4], electron transfer reactions [5], ion solvation [6], chemical reactions in fluid media [2], and charge transport phenomena in dielectric materials [7, 8]. Within the classical approach, this Born energy is a simple function of the static dielectric constant ϵ and refers to a dipolar or ionic hard-sphere solute embedded in a dielectric continuum. Calculations of the quantity E , especially $E(\epsilon)$, are crucial for quantifying the Stokes shifts of chromophoric solute molecules following their electronic excitation [9, 10]. Provided that a substantial change in the dipole moment μ occurs upon excitation, a polar medium will give rise to solvation dynamics on time-scales of the orientational dielectric relaxation. Recent detailed studies of these effects have unambiguously demonstrated that the simple continuum model for characterizing the solvent is inappropriate [10–16]. An attractive alternative is the mean-spherical approximation (MSA) theory, which relates the solvation free energy of hard-sphere dipoles or ions of solute diameter D to a solvent consisting of hard-sphere dipoles with diameter d and leading to a dielectric constant ϵ [17, 18]. The results of this liquid theory have proven to yield satisfactory coincidence with experimental data for the ϵ -dependence of inhomogeneous optical lineshapes as well as for the impact of the dielectric relaxation function $\epsilon^*(\omega)$ on time-resolved Stokes-shift dynamics [10–16].

In the context of the above solvation processes, it is often desirable to have an estimate on the number of solvent shells responsible for the bulk of the solvation free energy. Due to the different radial decay behaviours of the electric fields, this extent of the relevant amount of solvent around the solute is expected to differ for dipolar and ionic solvation.

Because $E(\varepsilon)$ in the continuum limit disregards any solvent structure, its range of coupling to the solvent must remain ε -invariant. However, the MSA formalism involves the solvent structure in terms of $E(\varepsilon, D, d)$, where D and d represent the solute and solvent molecular diameters, respectively. As a consequence, the relevant coupling ranges emerging from the MSA can be expected to depend on the dielectric constant ε , and, secondly, to differ from the continuum results.

The scope of the present work is to obtain estimates on the solvation free energy E as a function of the number of solvent shells surrounding the solute for the dipolar and the ionic case. We begin with simple electrostatical arguments in favour of the limited spatial extent of the free energies of solvation in a disordered dielectric continuum. In the following, after stating the solution from the MSA for $E(\varepsilon, D, d)$, it will be shown how a cut-off diameter $x \geq D$ for the solvent can be included in the formalism. Since the MSA yields solutions only for the infinitely extended solvent, screening effects of the inner solvent shell have to be disregarded, so this method tends to result in upper bounds for the spatial coupling ranges. Results are obtained for the dipole and ion solvation energies in media of various polarities and compared to the continuum limit analogue.

2. Method and results

2.1. Simple electrostatics

According to basic electrostatics [19], the electric field \mathbf{E} of a point-sized particle with charge q_1 and dipole moment $\boldsymbol{\mu}_1$ is

$$\mathbf{E}(\mathbf{r}) = q_1 \mathbf{r}_0 r^{-2} - \boldsymbol{\mu}_1 r^{-3} + 3(\boldsymbol{\mu}_1 \cdot \mathbf{r}_0) \mathbf{r}_0 r^{-3} \quad (1)$$

where the particle 1 is assumed to be positioned at the origin and with $\mathbf{r} = r \mathbf{r}_0$. Being interested only in the radial dependence of the interaction energies w , we restrict the following consideration to the equatorial plane with respect to $\boldsymbol{\mu}_1$, i.e. to the cases where $\boldsymbol{\mu}_1 \cdot \mathbf{r}_0 = 0$. The interaction energy of a dipole possessing a permanent moment $\boldsymbol{\mu}_2$ with the field $\mathbf{E}(\mathbf{r})$ is given by $w = -\boldsymbol{\mu}_2 \cdot \mathbf{E}(\mathbf{r})$. For the case of a central dipole we thus obtain $w_{\mu-\mu} \sim (\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2) r^{-3}$, and for the central-charge case $w_{q-\mu} \sim q_1 (\boldsymbol{\mu}_2 \cdot \mathbf{r}_0) r^{-2}$.

The goal of this section is to obtain a simple approach to the relevant spatial range for the solvation energy of a dipole or an ion embedded in an equilibrium polar fluid, i.e. in a continuum-like environment of dipoles. In order to obtain the interaction energy related to a central dipole in a solvent shell of radius r of solvent dipoles, the ensemble average $\langle w_{\text{dip}} \rangle$ has to be taken. At a certain distance r from the central dipole the number N of solvent dipoles increases as r^2 , i.e. as the surface area of a sphere with radius r . As outlined above, the radial dependence of a dipole field varies as r^{-3} . For an equilibrium configuration we have $\langle w_{\text{dip}} \rangle = -N \mu E \langle \cos \theta \rangle$, with $\langle \cos \theta \rangle$ being the ensemble average as regards the various orientations of dipoles with respect to the field of the central dipole. For non-interacting dipoles the Boltzmann distribution leads to $\langle \cos \theta \rangle = \mu E / 3kT$ and thus $\langle w_{\text{dip}} \rangle = -N \mu^2 E^2 (3kT)^{-1}$, with $N \sim r^2$ and $E \sim r^{-3}$. Therefore, the total distance dependence leads to $\langle w_{\text{dip}} \rangle \sim r^{-4}$ for a solute dipole centred in a spherical shell of radius r of equilibrium solvent dipoles. For the situation of a charge or ion in the centre the field varies as $E \sim r^{-2}$, so $\langle w_{\text{ion}} \rangle \sim r^{-2}$. If screening effects are ignored, i.e. for solvents of little polarity, integration from the solute radius $r = D/2$ up to the distance $r = x$ of the above results for $\langle w \rangle$ yields the energy $\langle W \rangle = \int \langle w \rangle dr$ related to the entire solvent within the radius x . For the radial dependence the results for $\langle W \rangle$ are $\langle W_{\text{dip}} \rangle \sim x^{-3}$ and $\langle W_{\text{ion}} \rangle \sim x^{-1}$.

As is obvious from the above, the fast convergence of $\langle W \rangle$ with x is intimately linked to

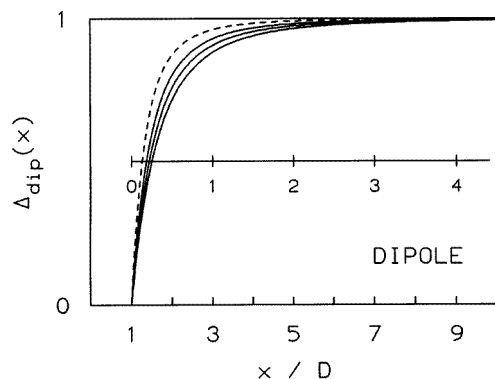


Figure 1. The normalized free energy of solvation, $\Delta_{\text{dip}}(x)$, for a dipole in a polar fluid is plotted as a function of the solvent cut-off x in units of the solute diameter D . In the order from the upper to the lower lines, the curves refer to the continuum limit $d = 0$ (dashed line), and to the MSA with $d = D$ (solid lines) for dielectric constants $\epsilon - 1 = 100, 10,$ and 1 . The inner scale counts solvent shells.

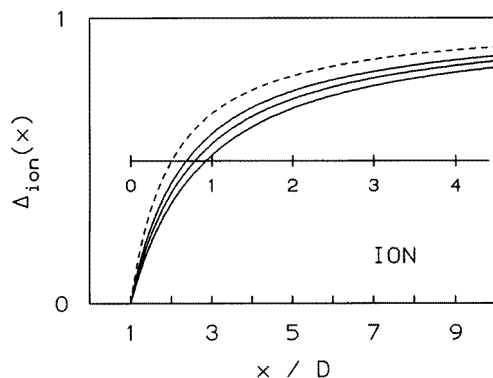


Figure 2. The normalized free energy of solvation, $\Delta_{\text{ion}}(x)$, for an ion in a polar fluid is plotted as a function of the solvent cut-off x in units of the solute diameter D . In the order from the upper to the lower lines, the curves refer to the continuum limit $d = 0$ (dashed line), and to the MSA with $d = D$ (solid lines) for dielectric constants $\epsilon - 1 = 100, 10,$ and 1 . The inner scale counts solvent shells.

the assumption of an equilibrium fluid-like solvent, such that the radial decay of E enters as E^2 ($\sim E \langle \cos \theta \rangle$) in the final result. For a crystalline counterpart structure of solvent dipoles ($\cos \theta$) will not decrease with r as does E , which leads to relatively excessive coupling ranges as regards the interaction energy. The interaction energies calculated above quantify the work required to assemble the solvent around the central particle, dipole or ion, which is equivalent to the work related to placing the particle into the equilibrium solvent. $\langle W \rangle$ at $x \rightarrow \infty$ is therefore a measure for the free energy of solvation in the case of non-interacting solvent dipoles and disregarding the effects of field screening by intermediate solvent shells. The graphs for $\langle W_{\text{dip}} \rangle \sim x^{-3}$ and $\langle W_{\text{ion}} \rangle \sim x^{-1}$ are included as dashed lines in figures 1 and 2, respectively, after normalization to $\langle W \rangle = 0$ at $x = D/2$ and to $\langle W \rangle = 1$ for $x \rightarrow \infty$.

2.2. MSA solutions

The model under study consists of a solute represented by a hard sphere of diameter D and solvent molecules represented by point dipoles centred in hard spheres of diameter d . Depending on the case of interest, indexed ‘dip’ or ‘ion’, the solute contains either a point dipole of moment μ or a charge of amount q . For this model of a spatially infinite solvent, the MSA integral equation has been solved to yield [17, 18]

$$E_{\text{dip}}(D) = [\beta\mu^2/4\pi\epsilon_0 D^3]\alpha_{\text{dip}}(\epsilon, D, d) \quad (2a)$$

$$\alpha_{\text{dip}}(\epsilon, D, d) = \frac{8(\epsilon - 1)}{2uR^3\rho^3 + 2\epsilon[1 + R(1 - 2u)]^3 + [1 + R\rho]^3} \quad (2b)$$

$$\rho = (1 - u)/(1 - 2u) \quad u = 3\xi/(1 + 4\xi) \quad (2c)$$

where β , R , and ξ are given by

$$\beta \equiv (k_B T)^{-1} \quad R = d/D \quad (3a)$$

$$\xi = \frac{1}{2}[1 - 9[4 + f^{1/3} + f^{-1/3}]^{-1}] \quad (3b)$$

$$f = 1 + 54\epsilon^{1/2}[1 - [1 + 1/(27\epsilon^{1/2})]^{1/2}]. \quad (3c)$$

The analogue for the ionic case reads

$$E_{\text{ion}}(D) = [\beta q^2/4\pi\epsilon_0 D]\alpha_{\text{ion}}(\epsilon, D, d) \quad (4a)$$

$$\alpha_{\text{ion}}(\epsilon, D, d) = [1 - 1/\epsilon] \left[1 + R \frac{1 - 2\xi}{1 + 4\xi} \right]^{-1} \quad (4b)$$

where β , R , and ξ are again given by equation (3). SI units are employed in the r.h.s. of equations (2a) and (4a). In the continuum limit, which is obtained for $d = 0$, the classical results $E_{\text{dip}}(D) = (\beta\mu^2/4\pi\epsilon_0 D^3)8(\epsilon - 1)/(2\epsilon + 1)$ and $E_{\text{ion}}(D) = (\beta q^2/4\pi\epsilon_0 D)(1 - 1/\epsilon)$ are restored by equations (2) and (4), respectively.

Consider now the role of the solute diameter D within this hard-sphere model. Since the solute cavity is assumed to carry zero polarizability, the only effect of increasing D from $D_1 \rightarrow D_2$ is to replace the polar medium in the range $D_1 - D_2$ by vacuum, i.e. by $\epsilon = 1$. $E(x)$ is thus the contribution from solvent molecules outside the diameter $x \geq D$ felt by the solute of diameter D , in the *absence* of the first $(x/D - 1)/2$ solvent shells. This absence suppresses the shielding of the electric field by the inner $(x/D - 1)/2$ solvent shells, actually characterized by a dielectric constant ϵ instead of 1. For small values of ϵ , $E(x) = E'(x)$, where $E'(x)$ reflects the contribution to E of the solvent outside x in the *presence* of the inner shells. Larger values of ϵ lead to $E'(x) < E(x)$, so $E(x)$ can be regarded as an upper limit in this case. We can now quantify the complement of $E(x)$ related to the solvent within the range $D - x$ by $E(D) - E(x)$, where $E(x)$ stands for $E_{\text{dip}}(x)$ or $E_{\text{ion}}(x)$, whichever is appropriate. Being interested in the spatial dependence only, we further normalize the result and define $\Delta(x) = [E(D) - E(x)]/E(D)$, i.e.

$$\Delta_{\text{dip}}(x) = 1 - E_{\text{dip}}(x)/E_{\text{dip}}(D) \quad x \geq D \quad (5a)$$

$$\Delta_{\text{ion}}(x) = 1 - E_{\text{ion}}(x)/E_{\text{ion}}(D) \quad x \geq D. \quad (5b)$$

In the continuum limit, $d = 0$, the functions $\Delta(x)$ no longer depend on ϵ and reduce to the simple expressions $\Delta_{\text{dip}}(x) = 1 - (x/D)^{-3}$ and $\Delta_{\text{ion}}(x) = 1 - (x/D)^{-1}$. The calculated results of equation (5), $\Delta_{\text{dip}}(x)$ and $\Delta_{\text{ion}}(x)$, are shown graphically in figures 1 and 2, respectively, for the range $1 \leq x/D \leq 10$ and for the case $d = D$ using the values $\epsilon - 1 = 1, 10$, and 100, and for the continuum model $d = 0$. Note that for the dipole case in figure 1, $\Delta_{\text{dip}}(x) \approx 1$ for $x = 3D$ already, and that $x/D = 3$ refers to *one* solvent shell only as indicated by the inner scale of figure 1.

3. Discussion

The equilibrium solvent modelled within the framework of the MSA is composed of interacting dipoles. In the continuum limit, $d = 0$, the MSA approach yields identical results for the spatial scale effects on the solvation energy, as does the initial approach based on simple electrostatical arguments. Therefore, disregarding the interaction among solvent dipoles in the continuum limit appears to be irrelevant in the present context. A limitation inherent in both methods of calculation is the necessity of disregarding the effect of the field of the central particle at some distance being decreased by the screening due to the presence of the intermediate solvent. In reality, outer solvent shells will therefore contribute less to the solvation energy than expected on the basis of the above results.

Table 1. The solvent cut-off diameter $x_{90\%}$ (in units of the solute diameter D) for which 90% of the solvation energy is preserved. The values of x/D are calculated for dipolar and ionic solvation in materials of various polarities in terms of $\varepsilon - 1$. The results for $0 \leq \varepsilon - 1 \leq \infty$ are obtained using the MSA equations (1)–(3) assuming $d = D$. The continuum limit at $d = 0$ is independent of ε .

$\varepsilon - 1$	$\rightarrow 0$	1	10	100	$\rightarrow \infty$	$d = 0$
Dipolar	3.31	3.21	2.90	2.61	2.40	2.16
Ionic	19.0	17.6	15.1	13.2	11.9	10.0

In order to demonstrate the extent of finite-size effects on the solvation free energy, table 1 compiles data for $x_{90\%}$ (in units of D) at which $\Delta(x) = 90\%$ of the total normalized energy $\Delta(\infty) = 1$ is accumulated from solvent contributions in the spatial range $D-x$. These results indicate that (i) no strong dependence on ε is found in the experimentally relevant range $2 \leq \varepsilon \leq 100$, (ii) the MSA results are $\approx 50\%$ in excess of the continuum values, and (iii) the diameter beyond which only 10% of the contribution to E is disregarded is ≈ 5 times higher for ionic solvation compared to the dipolar case. The number s of solvent shells related to these data is given by $s = (x/D - 1)/2$, and the number n of solvent molecules involved is $n = [(x/D)^3 - D^3]/d^3$. According to the above notions, $E(x)$ for $\varepsilon \gg 1$ serves as an upper limit for $E'(x)$, where $E'(x)$ designates the contribution of the solvent outside the diameter x to the solvation energy in the presence of solvent molecules within $D-x$. For a strongly polar system, $\varepsilon \gg 1$, the $x_{90\%}$ -data in table 1 should therefore be regarded as upper bounds for the solvent ranges relevant for 90% of the solvation energy. Within the point-dipole/hard-sphere model underlying the MSA, a strict lower bound for $x_{90\%}$ is $2D$, or in general $D + d$ for arbitrary $d \neq D$, because no solvent dipole resides within a sphere of diameter $D + d$ around the solute origin. Therefore, the real values $x_{90\%}/D$ for dipole solvation in solvents of strong polarity have only little uncertainty, e.g. $2 \leq x_{90\%}/D \leq 2.9$ for $\varepsilon - 1 = 10$.

The implications of these calculations are that the bulk (90%) of the solvation energy is dominated by ≈ 1 and ≈ 7 solvent shells for dipolar and ionic solvation, respectively, for solvents of moderate polarity. For media of higher polarity, the relevant number of solvent shells is decreased further. These values are $\approx 50\%$ in excess of what is expected on the basis of the continuum dielectric approach. It should be noted that the present results concur well with those obtained by Papazyan and Maroncelli [15, 16] employing detailed simulations of solvation in Brownian dipole lattices, where the contribution of distinct solvent shells to E in the presence of the remaining solvent is calculated.

In the light of the prediction that no more than ≈ 1 solvent shell entirely dictates the

solvation free energy in the dipolar case, it is not trivial that equation (2) as an input to statistical mechanical calculations leads to predictions of the inhomogeneous optical lineshapes of chromophores [9] which are strongly confirmed by experimental data [10]. As a consequence, it may be concluded that the dielectric properties in the immediate vicinity of a dipolar solute are not disturbed significantly by the presence of the solute molecule, provided that $D \approx d$. In contrast, ionic solutes can give rise to dielectric saturation [15] and electrostriction within the nearest-neighbour solvent molecules.

A further interesting implication of this strongly limited coupling range regarding the solvation energy of dipolar solutes concerns Stokes-shift dynamics experiments in liquids confined to mesopores of dielectrically inactive porous glasses. In this context, it follows that geometrical confinement of the liquid to pore diameters as small as $\approx D + 2d$ will have only little effect on the extent of the total Stokes shift $\Delta\nu = \nu(t = 0) - \nu(t = \infty)$. Recent experiments [20] on time-resolved solvation dynamics of the dipolar probe molecule quinoxaline in the supercooled solvent 2-methyltetrahydrofuran in porous sol-gel glasses with average pore sizes 2.5, 5.0, and 7.5 nm directly confirm these expectations. An analogous notion holds for empirical polarity scales based on solvatochromic effects, which are known to be governed mainly by electrostatical interactions [21]. According to the present results, a spectroscopically determined measure for the solvent polarity will refer only to the immediate vicinity of the chromophore, which might be especially important for mesoscopically heterogeneous materials.

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