$$\theta = \frac{x_i V_i / (\epsilon_i + 2)}{\sum\limits_{i=1}^{2} [x_i V_i / (\epsilon_i + 2)]} \qquad (22)$$

An alternative possibility to calculate ϵ^E would be to evaluate it from the known dielectric constant theories and converting them into mixing rules; but their number is large starting with the original one by Mossotti and Clausius. It was thus decided to use only those models that are based on spherical cavity introducing no correlation factors. This narrowed our choice to only three equations given by Debye,[56] Onsager,[57] and Kirkwood.[58] Suitable computer programs were written for each equation and least-squares fittings were performed by using eq 13. The estimated standard errors and the smoothing constants of eq 13 have been evaluated for ϵ^E by using the dielectric mixing rules and eq 13.

In order to obtain further evidence to support the formation of 1:1 complexes in solution as shown by the isorefractive point in Figure 10, the total molar polarization, P_m, for mixture has been calculated by using the Kirkwood–Frohlich equation[54]

$$P_m = (\epsilon_m - n^2)(2\epsilon_m - n_m^2) V_m / 9\epsilon_m \qquad (23)$$

Thus, if long-chain alkanes have molecular ordering in their pure states, it is possible to use P_m values calculated from Kirkwood–

Frohlich equation as an approximate measure of molecular orientations of n-alkanes in the presence of bromoform. The calculated value of P_m from eq 23 at $x_1 \simeq 0.5$ is around 17 ± 1 cm^3/mol proving the existence of 1:1 weak molecular complexes as evidenced by maxima or minima of several excess properties in addition to the isorefractive point shown in Figure 10.

Conclusions

In the present paper we have attempted to study a number of excess thermodynamic functions based on the results of densities, viscosities, refractive indices, sound velocities, and dielectric constants of the mixtures of n-alkanes with bromoform. To the best of our knowledge these mixtures have not been studied previously in the literature. It is realized that for a prediction of the thermodynamic behavior of mixtures of n-alkanes with a nearly spherical molecule such as bromoform, it is necessary to have accurate data on thermodynamic excess functions. Further, the results of this study indicate the destruction or creation of order in n-alkanes and that there is a systematic variation of thermodynamic excess properties with the chain length of n-alkane molecules.

Registry No. TMP, 540-84-1; tetralin, 119-64-2; bromoform, 75-25-2; n-hexane, 110-54-3; n-heptane, 142-82-5; n-octane, 111-65-9; n-nonane, 111-84-2; n-decane, 124-18-5; n-dodecane, 112-40-3; n-tetradecane, 629-59-4; n-hexadecane, 544-76-3.

Supplementary Material Available: Tables IV–X, listing values of least-squares estimations of the various quantities, viz., V^E, η^E, ΔG^{*E}, k_S^E, k_T^E, $k_T^E(F)$, R^E, and ϵ^E (10 pages). Ordering information is given on any current masthead page.

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New Developments in the Continuum Representation of Solvent Effects

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New developments in the continuum representation of solvent effects are presented. General expressions for the Helmholtz free energy of an arbitrary discrete charge distribution placed in spherical and spheroidal (oblate and prolate) cavities and surrounded by multiple dielectric layers are derived. The solute–solvent interaction energy is accounted for by using the multipole expansion. This dielectric partition permits the modeling of nonlinear dielectric effects (NLDE). These results are incorporated into quantum mechanical formalisms at the CNDO/2 level, giving origin to prolate spheroidal (PS) generalized Born formula (GBF), PS modified GBF, and PS self-consistent multilayered reaction field with overlap schemes. Some of these schemes incorporate nonsphericity, NLDE, or both. The Miertus and Kysel parametrization of the solute–solvent interaction is generalized. The electrostatic contributions to some selected thermodynamic properties are presented. The integrative value of this work is shown through the recuperation of the spherical cases and of some expressions presented by Abe and Abrahams.

I. Introduction

Continuum models are widely used to deal with solvent effects.[1-5] Their simplicity makes them suitable for a number of applications, especially for large molecules. These models are based on considering the solute molecule inside an empty cavity surrounded by a polarizable continuous dielectric medium. The

potential acting on the solute is found by using reaction field theory[6] and then incorporated into quantum-mechanical formalisms.

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The first work in this area considered a point charge in the center of a spherical cavity surrounded by a dielectric medium characterized by the macroscopic permittivity of the solvent.[1] Its application (Born formula, BF) to ionic solvation showed a systematic overestimation when compared with experimental data.[7] This was due to the nonconsideration of three main factors: the solute's higher multipoles, the real shape of the molecules, and the nonlinear dielectric effects (NLDE; i.e., dielectric saturation and electrostrictive phenomena).

In subsequent works, the solute's higher multipoles were included by introducing the permanent and induced dipole moments[2] or the multipole expansion for a nonpolarizable[8] and a polarizable[9] molecule.

The nonsphericity of molecules was modeled by employing spheroidal cavities,[10-13] polyhedrical cavities,[14] cavities of an arbitrary shape,[15,16] or a set of interlocking spheres to represent the solute.[4,17]

NLDE are important because the main contributions to the electrostatic free energy of solvation come from the inner solvation shells.[18-20] Attempts to model these phenomena have considered the continuum as partitioned in concentric shells with different dielectric constants.[8,13,21-24] Also, modifications of the BF have been proposed[19,20,22,25] that are based on theoretical[26-30] and empirical[31] expressions taking into account the radial dependence of the medium's permittivity. However, the complexity of the theoretical problem and the relative lack of experimental data relating dielectric constants with high electric fields preclude the obtention of a realistic distance-dependent function. For this reason, the partition of the continuum is still the best way to predict solvation energies.[19-23]

Hereafter, we shall concentrate our attention on the methods incorporating solvent effects into the self-consistent field scheme via the generalized Born formula (GBF).[32] GBF considers each atom as a charged conducting sphere immersed in the continuum.[32,33] The total solvation free energy is computed by summing the atomic contributions appearing as Born-like terms. This approach is called the self-consistent reaction field (SCRF). Because the spheres are considered not to be in contact, there is an overestimation of the solvation free energy,[34] like in classical calculations. An improvement of this model employs an empirical function, f, taking into account the interlocking of spheres (desolvation process).[35-37] This leads to the modified generalized

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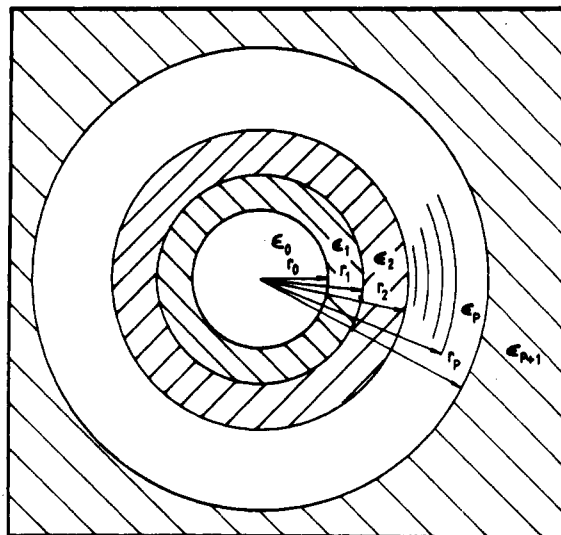
Figure 1.

Born formula (MGBF). Additionally, formal expressions for this process were given by Constanciel.[5] These models will be referred to as self-consistent reaction field with overlap (SCRF/O). The last amelioration consists in modeling NLDE effects.[6,38] This is done by the explicit inclusion of the first solvation layer through the use of a local dielectric constant.[17,34,39] This model is called self-consistent local reaction field with overlap (SCLRF/O).

All the above representations were developed for a solute composed of spherical atoms. Consequently, a natural extension can be undertaken by considering the solute molecule as a set of interlocking prolate spheroidal atoms to account for the deformation of the atomic electronic densities when a molecule is formed.

In a previous article we presented the reaction field potential and the Helmholtz free energy of an arbitrary discrete charge distribution in prolate and oblate spheroidal cavities embedded in two and three concentric dielectric continua, considering the complete multipolar expansion.[13]

This paper is organized as follows: In the Classical Aspects section, we shall consider the solvation free energy for spherical and spheroidal molecules. The full multipole expansion will be used, and the NLDE will be accounted for by means of a multilayer partition of the medium. In the Quantum Aspects section, we present the derivation of a new modified generalized Born formula for multiple layers and its incorporation to the CNDO/2 framework. Here, the solute is treated quantically and the solvent classically.

Also we derive the prolate spheroidal Fock Hamiltonians and their generalization for any number of solvation layers. The formalism is presented for all the models mentioned above at the CNDO/2 level of calculation. Finally, we present equations permitting the computation of the electrostatic contributions to some thermodynamic properties.

II. Classical Aspects

The problem of finding the reaction potential, V^R, for a discrete charge distribution within a cavity surrounded by one and two concentric dielectric continua of the same symmetry was solved for the spherical[8] and spheroidal (prolate and oblate) cases.[13,40] The general procedure used here to obtain the Helmholtz free energy of a discrete charge distribution surrounded by any number of layers follows the one employed by Beveridge et al.[8] Essentially, it consists in solving Laplace's equation in the appropriate co-

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ordinate system.[8,13,40] The potential in the different regions is formulated by separate and related through-boundary conditions ensuring its continuity and the continuity of the normal component of the dielectric displacement vector across the limiting surfaces. These restrictions provide a system of equations for the potential coefficients. Their resolution leads to expressions for them. Finally, starting from the cavity's potential, V^R is obtained.

The work necessary to introduce the charge distribution reversibly and isothermically into the previously cavitated solvent (insertion energy) is the Helmholtz free energy, A, that can be calculated for a discrete charge distribution as[8,13,40]

$$A = \frac{1}{2} \sum_{k=1}^{M} q_k V^R(\vec{r}_k) \tag{1}$$

where q_k is the net charge of particle k located at $\vec{r}_k$, the summation being over all the charges.

In the following, we deal with the case of a discrete charge distribution in a spherical cavity surrounded by three, four, and five dielectrics (Figure 1). Given that the mathematical work and the resulting expressions are similar to those appearing in the two-dielectric case,[8] we shall present here only the results. However, we must stress that we carried out a full verification of our work by fusing consecutively two neighborhood shells, until the recuperation of the expressions presented in ref 8. These equations permitted us to obtain, for the first time, general expressions for the reaction potential and the Helmholtz free energy for any number of layers.

For p spherical layers (Figure 1), we have found the following expression for the generalized Helmholtz free energy:

$$A = (1/2\epsilon_0) \sum_{n=0}^{\infty} \left[\frac{(n+1)(1-\epsilon_{r_0}^{(p)})}{(n+1)\epsilon_{r_0}^{(p)} + n} \right] \frac{Q_n^2}{r_0^{2n+1}}$$

$$+ (1/2\epsilon_0) \sum_{n=0}^{\infty} \sum_{i=1}^{p} \left[\frac{(n+1)(1-\epsilon_r^{(p-i)})}{(n+1)\epsilon_r^{(p-i)} + n} \right] \times$$

$$\prod_{j=1}^{i} \left[1 - \frac{n(1-\epsilon_r^{(p-i+j)})}{(n+1)\epsilon_r^{(p-i+j)} + n} \right] \frac{Q_n^2}{r_i^{2n+1}} \tag{2}$$

with the following definitions:

$$\epsilon_{r_x}^{(0)} = \epsilon_{x+1}/\epsilon_x \tag{3}$$

$$\epsilon_{r_x}^{(1)} =$$
$$\epsilon_{r_x}^{(0)} \left[1 + (1 - \epsilon_{r_x}^{(0)}) \frac{(n+1)(1-\epsilon_{r_{x+1}}^{(p-x-1)})}{(n+1)\epsilon_{r_{x+1}}^{(p-x-1)} + n} \left[\frac{r_x}{r_{x+1}} \right]^{2n+1} \right]^{-1} \tag{4}$$

$$\epsilon_{r_x}^{(y)} = \epsilon_{r_x}^{(y-1)} \left[1 + \right.$$

$$\frac{\epsilon_{r_x}^{(y-1)}}{\epsilon_{r_x}^{(0)}} (1 - \epsilon_{r_x}^{(0)}) \frac{(n+1)(1-\epsilon_{r_{x+y}}^{(p-x-y)})}{(n+1)\epsilon_{r_{x+y}}^{(p-x-y)} + n} \left[\frac{r_x}{r_{x+y}} \right]^{2n+1} \times$$

$$\left. \prod_{j=1}^{y-1} \left[1 - \frac{n(1-\epsilon_{r_{x+y-j}}^{(p-x-y+j)})}{(n+1)\epsilon_{r_{x+y-j}}^{(p-x-y+j)} + n} \right] \right]^{-1} \quad y > 1 \tag{5}$$

and the square of the multipole moments:[8]

$$Q_n^2 =$$
$$\sum_{k=1}^{M} \sum_{l=1}^{M} q_k q_l r_k^n r_l^n \sum_{m=-n}^{+n} \frac{(n-|m|)!}{(n+|m|)!} P_n^m(\cos\theta_k) P_n^m(\cos\theta_l) e^{-im(\phi_k-\phi_l)} \tag{6}$$

where the P_n^m's are the associated Legendre polynomials of the first kind.[40,41]

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In eqs 2 and 3, the ϵ_x's represent the permittivity of the dielectrics accordingly to Figure 1, and the r_x's are the radii of the surfaces limiting the dielectrics. The second term of eq 2 vanishes when $p = 0$ (i.e., when no layers are present), recuperating eq 15 of ref 8. The multilayer expression for the reaction potential can be easily obtained by using eqs 1 and 2.

On the other hand, the resolution of the case of a prolate spheroidal cavity was carried out for zero,[40] one, and two[13] layers. Using the same techniques of our earlier work,[13] we solved for the three-layer case. The verification of the results was carried out by fusing two adjacent layers in order to recuperate the inferior case and by considering the case in which the eccentricity of the ellipsoid tends to zero in order to recuperate the spherical case. The mathematical work is based on eqs 27-36 of ref 40. These results and those presented in refs 13 and 40 permit the following extrapolation to p layers:

$$A = (1/2\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \Gamma_{nm}(\epsilon_{\lambda_0}^{(p)}, \lambda_0) Q_{nm}^2 +$$

$$(1/2\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \sum_{i=1}^{p} \Gamma_{nm}(\epsilon_{\lambda_i}^{(p-i)}, \lambda_i) \times$$

$$\prod_{j=1}^{i} \left[1 + \Gamma_{nm}\left(\epsilon_{\lambda_{i-j}}^{(p+i-j)}, \lambda_{i-j}\right) \frac{\dot{P}_n^m(\lambda_{i-j})}{\dot{Q}_n^m(\lambda_{i-j})} \right] Q_{nm}^2 \tag{7}$$

where λ is one of the spheroidal coordinates defining prolate surfaces. Also, in eq 7 we have defined the following relative dielectric permittivities:

$$\epsilon_{\lambda_x}^{(0)} = \epsilon_{x+1}/\epsilon_x \tag{8}$$

$$\epsilon_{\lambda_x}^{(1)} = \epsilon_{\lambda_x}^{(0)} \left[1 + (1 - \epsilon_{\lambda_x}^{(0)}) \Gamma_{nm}(\epsilon_{\lambda_{x+1}}^{(p-x-1)}, \lambda_{x+1}) \frac{P_n^m(\lambda_x)}{Q_n^m(\lambda_x)} \right]^{-1} \tag{9}$$

$$\epsilon_{\lambda_x}^{(y)} = \epsilon_{\lambda_x}^{(y-1)} \left[1 + \frac{\epsilon_{\lambda_x}^{(y-1)}}{\epsilon_{\lambda_x}^{(0)}} (1 - \right.$$

$$\epsilon_{\lambda_x}^{(0)}) \frac{P_n^m(\lambda_x)}{Q_n^m(\lambda_x)} \Gamma_{nm}\left(\epsilon_{\lambda_{x+y}}^{(p-x-y)}, \lambda_{x+y}\right) \prod_{j=1}^{y-1} \left[1 + \right.$$

$$\left. \left. \Gamma_{nm}\left(\epsilon_{\lambda_{x+y-j}}^{(p-x-y+j)}, \lambda_{x+y-j}\right) \frac{\dot{P}_n^m(\lambda_{x+y-j})}{\dot{Q}_n^m(\lambda_{x+y-j})} \right] \right]^{-1} \quad y > 1 \tag{10}$$

Here, the Q_n^m are the associated Legendre polynomials of the second kind,[40,41] the pointed functions representing their first derivative. The square of the ellipsoidal multipoles is[12,41]

$$Q_{nm}^2 = (2n + 1/d) \sum_{k=1}^{M} \sum_{l=1}^{M} (-1)^m q_k q_l \left[\frac{(n-|m|)!}{(n+|m|)!} \right] \times$$
$$P_n^m(\lambda_k) P_n^m(\mu_k) P_n^m(\lambda_l) P_n^m(\mu_l) e^{-im(\phi_k-\phi_l)} \tag{11}$$

where μ and ϕ are prolate spheroidal coordinates.

As in the spherical case, the ϵ_x's describe the relative medium's permittivity of the dielectrics, and the λ_i's, the surfaces limiting these regions.

The Γ_{nm} functions obtained in this work are

$$\Gamma_{nm}(\epsilon, \lambda) = \frac{1-\epsilon}{\epsilon} \left[\frac{P_n^m(\lambda)}{Q_n^m(\lambda)} - \frac{1}{\epsilon} \frac{\dot{P}_n^m(\lambda)}{\dot{Q}_n^m(\lambda)} \right]^{-1} \tag{12}$$

and can be considered as a generalization of the Γ quantity introduced by Abbot and Bolton[28] and employed by Beveridge et al.[40]

For the zero-layer case, the second term of the right side of eq 7 vanishes.

The resolution of this problem for the oblate case is similar to that for the prolate one with the only difference being that it is

necessary to work in the complex plane by replacing λ and d everywhere by $i\lambda$ and d/i, respectively.[40,41] The resulting equations are, therefore, eqs 7-12 including these changes.

Now, if we consider only the charge contribution ($n = 0$) to the interaction energy (effective charge approximation) and start from eq 7 for the prolate case or if we take this contribution for $p = 0$ and 1 and work as in ref 13, we get

$$A_0 = \frac{q^2}{4d}\sum_{i=0}^{p}\left[\frac{1}{\epsilon_{i+1}} - \frac{1}{\epsilon_i}\right]\ln\left[\frac{\lambda_i + 1}{\lambda_i - 1}\right] \qquad (13)$$

where q_0 is the net charge of the distribution, λ_i defines the ith prolate surface limiting the ith and $(i + 1)$th dielectrics, and ϵ_{p+1} represents the bulk dielectric permittivity.

Noting that the eccentricity of the ellipsoid is $e_i = \lambda_i^{-1} = d/r_i$ and expanding the natural logarithm in a Taylor's series, we showed that[13]

$$A_0 = \frac{q_0^2}{2}\sum_{i=0}^{p}\left[\frac{1}{\epsilon_{i+1}} - \frac{1}{\epsilon_i}\right]\frac{K_i}{r_i} \qquad (14)$$

where we defined

$$K_i = 1 + \sum_{t=1}^{\infty}\frac{e_i^{2t}}{2t+1} \qquad (15)$$

By inserting eq 14 into eq 1, we get for the reaction potential

$$V^R = -q\sum_{i=0}^{p}\left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_{i+1}}\right]\frac{K_i}{r_i} \qquad (16)$$

The spherical limit is attained when all the eccentricities tend to zero, disappearing the summation on t in eq 15 and the K_i's in eqs 14 and 16. This limit case can be also recuperated from eq 2.

It is important to stress that K_0 is a convergent series expansion and that the number of terms to consider in a given case will depend on the convergence criterion imposed. By taking only the first term of eq 16, i.e., by considering the nonlayered case, we obtain

$$V^R = -\left[\frac{1}{\epsilon_0} - \frac{1}{\epsilon_1}\right]\frac{q}{r_0}K_0 \qquad (17)$$

which corresponds to the reaction potential for the spherical case multiplied by the factor K_0. Then, the K's can be considered as a corrective terms taking into account the loss of sphericity. When the spheroid tends to a sphere (i.e., $e_0 \rightarrow 0$), K_0 tends to the unity and V^R tends to the nonlayered spherical case described in ref 8.

III. Quantum Aspects

In the following, we shall present the main lines for the derivation of the Fock Hamiltonian in the framework of the MGBF for the nonlayered spheroidal case. The basis of this work can be found in refs 4, 17, 39, and 42.

In reaction field theory, the polarization of the solvent can be represented by a potential due to the creation at the surface $\lambda = \lambda_0$ of a fictitious polarization charge given by[35]

$$^0q^{pol} = -\alpha^0q \qquad (18)$$

where

$$\alpha^0 \equiv \left[\frac{1}{\epsilon_0} - \frac{1}{\epsilon_1}\right]K_0 \qquad (19)$$

Accordingly, the reaction potential acting on the particle can be expressed as

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(42) Constanciel, R. The effects of a polarizable environment represented by the generalized Born formula in Self Consistent quantum chemical calculations: application to the study of ambident reactions. In *Quantum Theory of Chemical Reactions*; Daudel, R., Pullman, A., Salem, L., Veillard, A., Eds.; D. Reidel: Dordrecht, 1981; Vol. II, pp 73-98.

$$V^R = {}^0q^{pol}/r_0 \qquad (20)$$

Within the framework of the GBF each atom B of the solute, having a net charge q_B, contributes to the total reaction field with the following Born-like term:

$$V^R_B = {}^0q^{pol}_B/r_0 \qquad (21)$$

where

$${}^0q^{pol}_B = -\alpha^0q_B \qquad (22)$$

In this case, the potential acting at point $\vec{r}_1$ due to the polarization charge distribution induced in the solvent can be expressed in an atomic orbital basis $\{\mu, \sigma, ...\}$ as[42]

$$V^{pol}(\vec{r}_1) = -\sum_B {}^0q^{pol}_B \int \frac{|\mu(\vec{r})|^2}{|\vec{r}_1 - \vec{r}|}d\vec{r} \qquad \mu \in B \qquad (23)$$

$$V^{pol}(P) = -\sum_B {}^0q^{pol}_B\Gamma^0_{AB} \qquad (24)$$

where P is the density matrix and Γ^0_{AB} are integrals representing the solute–solvent interaction. To get eq 24, we made the approximation that atomic eccentricities differ little from zero.

From eq 24 and within the zero differential overlap approximation, we get the following expression for the matrix elements of the solvent's reaction field operator:[42]

$$[V^{pol}]_{\mu\sigma} = -\delta_{\mu\sigma}\sum_B {}^0q^{pol}_B\Gamma_{AB}^0 \qquad (25)$$

$\delta_{\mu\sigma}$ being the Dirac δ function.

Up to now, the procedure we followed is totally analogous to that appearing in similar works, the only difference being the introduction of the nonsphericity factor, K_0.

To maintain the internal coherence of the model, the polarization charges must satisfy the condition[36]

$$\lim_{\epsilon \rightarrow \infty}({}^0q_B^{pol} + q_B) = 0 \qquad (26)$$

for all B.

Physically, eq 26 means that in highly polarizable solvents the charge loses its capacity to interact electrostatically with other charges because of the screening produced by the solvent's polarization. Condition 26 is satisfied by the spherical case but not for that studied here. This can be shown by introducing eqs 19 and 20 into eq 26. To surmount this problem, we adopted the procedure of Constanciel and Contreras,[35] i.e., we considered that the polarization charges can be partitioned into the following two contributions:

$${}^0q^{pol}_B = {}^0q^{pol,a}_B + {}^0q^{pol,b}_B \qquad (27)$$

with the definitions

$${}^0q^{pol,a}_B = -[1/\epsilon_0 - 1/\epsilon_1](1 - K_0^B)q_B \qquad (28)$$

$${}^0q^{pol,b}_B = -[1/\epsilon_0 - 1/\epsilon_1]K_0^Bq_B \qquad (29)$$

It is easy to demonstrate that these polarization charges fulfill eq 26. In addition, it is necessary to redefine the reaction potential as

$$[V^{pol}]_{\mu\sigma} = -\delta_{\mu\sigma}\sum_B({}^0q^{pol,a}_B\Gamma^{0,a}_{AB} - {}^0q^{pol,b}_B\Gamma^{0,b}_{AB}) \qquad (30)$$

where the new solute–solvent interaction integrals are given by

$$\Gamma^{0,a}_{AB} = (1 - K^A_0)\Gamma^0_{AB} \qquad (31)$$

$$\Gamma^{0,b}_{AB} = K^A_0\Gamma^0_{AB} \qquad (32)$$

Inserting eqs 28, 29, 31, and 32 into eq 30, we get for the reaction field potential

$$[V^{pol}]_{\mu\sigma} = \delta_{\mu\sigma}[1/\epsilon_0 - 1/\epsilon_1]\sum_B\beta^0_{AB}q_B\Gamma^0_{AB} \qquad (33)$$

with

$$\beta^0_{AB} = 1 - (K^0_A + K^0_B - 2K^0_AK^0_B) \qquad (34)$$

The corresponding Fock Hamiltonian is

$$[F_e]_{\mu\sigma} = [F_1]_{\mu\sigma} + [V^{pol}]_{\mu\sigma} \qquad (35)$$

where $[F_1]_{\mu\sigma}$ corresponds to the Fock Hamiltonian for the isolated system.

Introducing eq 33 into eq 35, we obtain

$$[F_e]_{\mu\sigma} = [F_1]_{\mu\sigma} + \delta_{\mu\sigma}\left[\frac{1}{\epsilon_0} - \frac{1}{\epsilon_1}\right]\sum_B \beta^0{}_{AB}q_B\Gamma^0{}_{AB} \qquad (36)$$

Equation 36 corresponds to the RF level of approximation. As mentioned above, the spherical analogue of eq 36 overestimates the solvation free energy, given that the atoms of the solute are implicitly considered as lying in separate cavities.[34]

Now, we shall allow for the steric inhibition to solvation due to the specific neighborhood of each atomic center of the solute (SCRF/O scheme). Even when the general formalism and its application to the spherical case is in the literature,[35,36,42,43] its application to the case treated here is not direct. For this reason we present in the following the main equations to solve this problem. The methodology consists in making allowance for an empirical corrective parameter characterizing the specific neighborhood effects on atom A.[36] However, if we operate in the same way as in ref 35, the condition of electroneutrality for the whole system is not satisfied. The solution consists in carrying out the following partition of the polarization charges, solute–solvent interaction integrals, and reaction potential:

$$^0q^{pol,a}{}_B = {}^0q^{pol,ac}{}_B + {}^0q^{pol,ad}{}_B,$$
$$^0q^{pol,b}{}_B = {}^0q^{pol,be}{}_B + {}^0q^{pol,bf}{}_B \qquad (37)$$

$$^0q^{pol,ac}{}_B = {}^0q^{pol,a}{}_B(1 - f_B), \qquad ^0q^{pol,ad}{}_B = {}^0q^{pol,a}{}_B f_B \qquad (38)$$

$$^0q^{pol,be}{}_B = {}^0q^{pol,b}{}_B(1 - f_B), \qquad ^0q^{pol,bf}{}_B = {}^0q^{pol,b}{}_B f_B \qquad (39)$$

$$\Gamma^{0,ac}{}_{AB} = \Gamma^{0,a}{}_{AB}(1 - f_A), \qquad \Gamma^{0,ad}{}_{AB} = \Gamma^{0,a}{}_{AB} f_A \qquad (40)$$

$$[V^{pol}]_{\mu\sigma} = -\delta_{\mu\sigma}\sum_B [^0q^{pol,ac}{}_B\Gamma^{0,ac}{}_{AB} + {}^0q^{pol,ad}{}_B\Gamma^{0,ad}{}_{AB} +$$
$$^0q^{pol,be}{}_B\Gamma^{0,be}{}_{AB} + {}^0q^{pol,bf}{}_B\Gamma^{0,bf}{}_{AB}] \qquad (41)$$

By introducing eqs 38–40 into eq 41 and carrying out a little algebra, we obtain the following expression for the reaction field operator with overlap:

$$[V^{pol}]_{\mu\sigma} = \delta_{\mu\sigma}[1/\epsilon_0 - 1/\epsilon_1]\sum_B \beta^0{}_{AB}(1 - F_{AB})q_B\Gamma^0{}_{AB} \qquad (42)$$

where we have defined

$$F_{AB} = f_A + f_B - 2f_{AB} \qquad (43)$$

In eq 42, the term containing F_{AB} has been interpreted as giving an account of a desolvation contribution to the reaction field potential.[37]

By using eqs 35 and 42, we get the following final form for the Fock operator:

$$[F_e]_{\mu\sigma} = [F_1]_{\mu\sigma} + \delta_{\mu\sigma}[1/\epsilon_0 - 1/\epsilon_1]\sum_B \beta^0{}_{AB}(1 - F_{AB})q_B\Gamma^0{}_{AB} \qquad (44)$$

Equation 44 corresponds to the prolate spheroidal self-consistent reaction field with overlap approach (SCRF/O).

Usually, the f_A parameter appearing in eq 43 is empirically expressed as[43]

$$f_A = \frac{1}{2}\sum_{B\neq A} S_{AB} \qquad (45)$$

where S_{AB} is the overlap integral between the $2s_A$ and $2s_B$ atomic orbitals of atoms A and B (1s for H atoms). Our experience with the spherical SCRF/O approach suggested that a better representation involves the square of S_{AB} in eq 45.[44] A further way

to compute the f_A's is through the hydration shell model.[45]

Proceeding in an analogous way, it is possible to obtain the following expressions for the matrix elements of the self-consistent multilocal reaction field with overlap (SCMLRF/O):

$$[F_e]_{\mu\sigma} = [F_1]_{\mu\sigma} + \delta_{\mu\sigma}\sum_{i=0}^{p}\left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_{i+1}}\right]\sum_B \beta^i{}_{AB}(1 - F_{AB})q_B\Gamma_{AB}{}^i \qquad (46)$$

In eq 46, the parameter $\beta^i{}_{AB}$ is analogous to that in eq 34, the only difference being that the coefficients K_A and K_B must be calculated by considering the eccentricities of the ith limiting surface of atoms A and B, respectively (see eq 34). The superscript i in the Γ_{AB}'s refers to the interaction integrals of the solute with the polarization charges located on the ith surface. They can be evaluated according to the parametrization suggested by Miertus and Kysel,[46] enlarged by Contreras,[34] and generalized here as follows:

(a) When the atomic orbitals belong to the same atom A, we make

$$\Gamma^0{}_{AA} = 1/r_A \qquad (47)$$

$$\Gamma^i{}_{AA} = \frac{\Gamma^0{}_{AA}}{1 + R_i\Gamma^0{}_{AA}} \qquad (48)$$

where r_A is the van der Waals radius of atom A and R_i is the thickness of the ith layer.

(b) When the AOs belong to different nucleus, we use

$$\Gamma^0{}_{AB} = \frac{1}{R_{AB} + r_B} \qquad (49)$$

$$\Gamma^i{}_{AB} = [R_{AB} + \frac{1}{2}\{(\Gamma^i{}_{AA})^{-1} + (\Gamma^i{}_{BB})^{-1}\}]^{-1} \qquad (50)$$

where R_{AB} is the internuclear distance between atoms A and B. Also, it is possible to use the $^0\Gamma_{AB}$ integrals directly provided by the CNDO/2 method as the electronic repulsion integrals.

IV. Thermodynamic Aspects

Here we shall present the general equations permitting the calculation of the electrostatic contributions to some selected thermodynamic properties. Starting from the relation for the Helmholtz free energy of the solute–solvent system (eq 1) and by using the reaction potential in the effective charge approximation for the multilayer case, we get the following expression:

$$A = \frac{1}{2}\sum_{i=0}^{p}\left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_{i+1}}\right]\sum_A\sum_B \beta^i{}_{AB}q_Aq_B(1 - F_{AB})\Gamma^i{}_{AB} \qquad (51)$$

Physically, this energy corresponds to the work required to transfer isothermically the solute from the gas phase to the previously cavitated solvent without changing the nuclear and electronic configurations (insertion energy).[40]

On the other hand, it has been demonstrated through statistical-thermodynamical arguments that the insertion energy can be assimilated to the electrostatic contribution to the solute's Helmholtz free energy of solvation, ΔA_s.[47] Now, if the charging process is carried out at constant pressure, ΔA_s is the electrostatic contribution to the Gibbs free energy of solvation, ΔG_s. Then

$$\Delta G_s = \frac{1}{2}\sum_{i=0}^{p}\left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_{i+1}}\right]\sum_A\sum_B \beta^i{}_{AB}(1 - F_{AB})q_Aq_B\Gamma_{AB}{}^i \qquad (52)$$

The electrostatic contribution to the solvation entropy can be found starting from

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$$\Delta S_s = -\left[\frac{\partial \Delta G_s}{\partial T}\right]_P =$$

$$-\frac{1}{2}\sum_{i=0}^{P}\sum_A\sum_B \beta^i{}_{AB}(1 - F_{AB})q_A q_B \Gamma_{AB}{}^i \frac{\partial}{\partial T}\left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_{i+1}}\right] \quad (53)$$

where T and P are, respectively, the absolute temperature and the pressure.

After taking the derivative and considering that the only temperature-dependent variables in ΔG_s are the dielectric constants, it is possible to find the general relation

$$\Delta S_s = \frac{1}{2T}\sum_{i=0}^{P}\left[\frac{1}{\epsilon_i}\left[\frac{\partial \ln \epsilon_i}{\partial \ln T}\right]_P - \right.$$

$$\left. \frac{1}{\epsilon_{i+1}}\left[\frac{\partial \ln \epsilon_{i+1}}{\partial \ln T}\right]_P\right]\sum_A\sum_B \beta^i{}_{AB}(1 - F_{AB})q_A q_B \Gamma^i{}_{AB} \quad (54)$$

Given that ϵ_0 does not depend on T, the first derivative for $l = 0$ vanishes in all the cases.

The solvation enthalpy can be easily obtained from eqs 52 and 54.

On the basis of the above relations, it is possible to compute the electrostatic contributions to other thermodynamical properties. For example, the electrostatic contribution to the partial molar volume is

$$\Delta V = \frac{N_0 P}{2}\sum_{i=0}^{P}\left[\frac{1}{\epsilon_i}\left[\frac{\partial \ln \epsilon_i}{\partial P}\right]_P - \frac{1}{\epsilon_{i+1}}\left[\frac{\partial \ln \epsilon_{i+1}}{\partial P}\right]_P\right]\sum_A\sum_B \beta^i{}_{AB}(1 -$$

$$F_{AB})q_A q_B \Gamma_{AB}{}^i \quad (55)$$

where N_0 is Avogadro's number.

The electrostatic contribution to the heat caloric capacities at constant pressure is

$$\Delta C_p = -\frac{1}{2}\sum_{i=0}^{P}\left[\frac{1}{\epsilon_i}\left[\left[\frac{\partial \ln \epsilon_i}{\partial \ln T}\right]_P^2 + \left[\frac{\partial \ln \epsilon_i}{\partial \ln T}\right]_P - \right.\right.$$

$$\left.\left[\frac{\partial^2 \ln \epsilon_i}{\partial \ln T^2}\right]_P\right] - \frac{1}{\epsilon_{i+1}}\left[\left[\frac{\partial \ln \epsilon_{i+1}}{\partial \ln T}\right]_P^2 + \left[\frac{\partial \ln \epsilon_{i+1}}{\partial \ln T}\right]_P - \right.$$

$$\left.\left.\left[\frac{\partial^2 \ln \epsilon_{i+1}}{\partial \ln T^2}\right]_P\right]\right]\sum_A\sum_B \beta^i{}_{AB}(1 - F_{AB})q_A q_B \Gamma^i{}_{AB} \quad (56)$$

V. Discussion

Equations 2 and 7 are, respectively, the general expressions for the helmholtz free energy of an arbitrary discrete charge distribution in spherical and prolate spheroidal cavities surrounded by p finite dielectric layers of the same symmetry and immersed in a continuum. In these equations, each term of the summations on n gives the contribution to the interaction energy coming from the nth-order multipoles. Thus, the terms with $n = 0$ are the multilayered spherical and ellipsoidal counterparts of the Born charging energy, and those with $n = 1$ the multilayered Onsager analogues.

The reaction field technique, in the form used here, does not show clearly the breakdown of A into contributions coming from each particular dielectric.[24] This problem arises from the fact that, in eqs 2 and 7, each term incorporates all the dielectric constants of the system through $\epsilon_{r_0}{}^{(p)}$ and $\epsilon_{\lambda_0}{}^{(p)}$, respectively. However, for any given number of layers, it is possible to fully expand and reorder A in order to find these contributions. Also, it is important to stress that for p layers, there are $\sum_{i=1}^{p+1} i$ values of $\epsilon_{r_0}{}^{(d)}$ or $\epsilon_{\lambda_0}{}^{(d)}$ ($p, c \geq 0$).

The multilayered prolate spheroidal Born charging energy is given by eqs 13 or 14. Here, each value of i represents the contribution to A_0 due to the polarization charges on the surface $\lambda = \lambda_i$. These contributions depend on the eccentricity of the limiting surface and on the permittivities of both dielectrics. As NLDE generates an approximately sigmoidal behavior of ϵ with λ or r for ionic solvation,[29] it is expected that the contributions

of the more external shells will be negligible.

From eq 14, it is easy to obtain the spherical Born charging energy in a multilayered medium (see eq 15). In this limit case and when no layer is present, eq 14 reduces to the Born equation.[1] When p takes the values 1 and 2, eq 16 becomes those of Abraham et al.[24]

Equation 36 is the Fock Hamiltonian in the SCRF approach within the CNDO/2 framework, permitting us to take into account solvent effects by the incorporation of a reaction field operator in the effective charge approximation. Also, it considers the nonsphericity of atoms in molecules, modeling them as prolate spheroids. In the limit case, i.e., when atoms become spherical, $K^0{}_B$ and β_{AB} tend to unity and eq 36 becomes the Fock Hamiltonian for the spherical SCRF.[32,35] Then, eq 36 is the first prolate spheroidal generalized Born's formula. As mentioned above, the β_{AB}'s give an account of the deviation from sphericity. Given that in nonspherical cavities $K_A > 1$, it follows that $\beta_{AB} > 1$, increasing the molecular energy and all the thermodynamical parameters.

In eq 36, the second term of the right side is the quantum operator of the total reaction potential, and each term i represents the contribution to the reaction potential acting on atom A of the solute, due to the virtual polarization charges induced by the entire solute in the surface $\lambda = \lambda_i$. Also, each term B of the summation is a contribution to the total reaction potential over atom A of the solute, due to all the polarization charges induced in the solvent by atom B.

Equation 44 is the Fock Hamiltonian in the SCRF/O level of approximation. Desolvation effects are modeled through the F_{AB}'s.[35,43] When atoms are not in contact, all the F_{AB}'s tend to zero and we recuperate the SCRF scheme of eq 36. If we consider spherical atoms, we also recuperate the spherical SCRF scheme.[32,35] Then, eq 44 is the first prolate spheroidal modified generalized Born's formula. The physical meaning of the terms appearing in eq 44 is similar to those in eq 36.

To model nonlinear dielectric effects, we have generalized our work by considering that all the solute's atoms are surrounded by multiple dielectric shells. This level of approximation is given by eq 46 and was called self-consistent multilayered reaction field with overlap (SCMLRF/O). In this scheme, if we consider no layers, we recuperate eq 44. On the other hand, the spherical limit of the monolayer case permits the recuperation of the local reaction field methodology previously published.[17,35] In eq 46, each term i of the summation represents the reaction potential on atom A due to the polarization charges lying on surface i.

It is interesting to notice that in the original RF framework, the α coefficients of the polarization charges (eq 18) depend only on the solvent's dielectric properties.[42] With the development of the RF/O scheme the α's become also dependent upon the overlapping factors[35] and, in the LRF/O method, on the solvent's partition.[17] In this work we have shown that the α's can be also dependent upon the cavity's geometry through the K's. This is logical given that all these parameters influence the electrical field acting on the solute.

With respect to the partition of the polarization charges (eqs 27 and 37), we shall not attempt to give a physical meaning because, as Constanciel pointed it out, this is only a mathematical artifact for maintaining the internal coherence of the model.[5]

Concerning the increasing effect of the solvation energetic due to the β's, in a previous article we showed that this is physically correct.[13] On the other hand, given that in the same system the spherical cavity induces a more major NLDE than the spheroidal one[13] and also that NLDEs have an effect opposite to that of the β's, there is a subtle equilibrium between these effects. Therefore, in the SCMLRF/O scheme it is important to select good values for the local dielectric constant.

Regarding the solute–solvent interaction integrals, they can be computed accordingly to the Miertus and Kysel parametrization,[46] generalized here for multiple surfaces.

A very interesting feature of the continuum models is that they permit the obtention of a complete picture of the thermodynamics of solvation and the incorporation of temperature-dependent effects.[34,47]

In the thermodynamics section we presented equations permitting the calculation of the electrostatic contributions to the solvation properties. They were obtained for the prolate spheroidal multilayer scheme with overlap. Other levels of approximation can be easily obtained.

The SCF procedure carries out the optimization of the solvation free energy. The other thermodynamical properties are computed at the end of the SCF cycle by using the density matrix. Since the classical formalism considered the insertion of the solute in a frozen nuclear configuration,[5] these expressions, including the Hamiltonians, can be used for relatively nonpolarizable solutes or for polarizable ones but immersed in a low-polarity medium. Also, to derive eqs 53–56, we considered in a first approach that the cavity's volume is not temperature or pressure dependent. Finally, the atomic eccentricities must be small.

The components of the solvent's polarization can be divided into atomic, electronic, and orientational ones. In a first approximation the atomic contribution can be neglected. In the inner solvation layers, especially the first one, the solvent molecules are strongly oriented by the solute's electrical field. Therefore, in this case it is possible to consider only the electronic component of the polarization. In the external layers, the solute's field is screened by the polarization charges, the solvent's molecules being less oriented. This effect is accentuated by the thermal agitation, generating the so-called orientational polarization. On the basis of the above considerations, it is possible to see that the derivatives of ϵ with T are important only in the external layers. Then, in a strong approximation, we may consider only the bulk contribution to ΔS_s. In this case, eq 54 reduces to

$$\Delta S_s = -\frac{1}{2}\frac{1}{\epsilon_{p+1}T}\left[\frac{\partial \ln \epsilon_{p+1}}{\partial \ln T}\right]_P \sum_A \sum_B \beta_{AB}q_A q_B(1 - F_{AB})\Gamma_{AB} \quad (57)$$

This limit case was published for the spherical case.[39] Its application to the study of the protonation of primary alkylamines in water showed an overestimation of ΔS_s. In light of the above discussion, it is expected that consideration of more layers will improve the results.

In an analogous way, pressure variations affect more strongly the most external layers. Then, in a first approach it is possible to consider in eq 55 only the bulk's contribution.

For the optimum values of ϵ, there are theories accounting for the radial dependence of the dielectric permittivities.[27–31] To our knowledge, no expression relating ϵ to λ has been published. However, as a first approach, it appears reasonable to change the radial symmetry of $\epsilon(r)$ for the ellipsoidal case simply by substituting λ for r. The border conditions for ϵ still hold, i.e., when $\lambda = \lambda_0$, $\epsilon = 1$ and when $\lambda = \infty$, $\epsilon = \epsilon_B$ (see, for example, Block and Walker's function in ref 27). Then, optimum values of ϵ can be found by averaging $\epsilon(\lambda)$ among the selected values of λ that determinate the layer thickness. It is important to stress that theoretical expressions for $\epsilon(r)$ have been developed considering ionic solvation. In neutral molecules, as the atomic net charges are small in relation to atomic ions, it is expected that NLDE be not very pronounced. This phenomenon also influences the derivatives of ϵ.

There are no homogeneous criteria for the best solvent's partition. As a working rule it seems logical to consider layers with a thickness given by the solvent's diameter. The number of shells to consider should be given by the distance at which NLDE are negligible. In water, this is accounted for in an approximate way by considering two layers plus the bulk region.[19,20,29]

There exist some empirical data about derivatives of ϵ with respect to P and T for the bulk dielectric and in the neighborhood of atomic ions.[7,48] An alternative way to compute thermodynamical properties is to restrict the calculations to one layer model using these experimental values or to consider the derivatives as adjustable parameters. More refined solutions to this problem will be given only when theories accounting for the behavior of $\epsilon(\lambda,T,P)$ appear.

In the actual state of research, it is difficult to provide a good methodology to calculate atomic eccentricities (and therefore, K^B_i and β^i_{AB}). Nevertheless, it appears reasonable to optimize these values in the framework of the SCRF/O methodology. After this procedure, we may use the models with layers because with the original values we may calculate the eccentricities of the layers. Other useful, but strong approximation, is to use the same eccentricity for all the atoms.

It is clear that for nonpolar molecules NLDE are not important and then the best election is to use the spherical or spheroidal nonlayered method (SCRF/O). This is also true for dipolar molecules and, apparently, for molecular monocharged ions such as acetate.[49] However, it is possible to expect that for highly dipolar molecules, such as zwitterions or multicharged species, NLDE become important. In this case, a bilayered method could be the correct tool.

The main contributions to the solvation energy are the electrostatic energy, the specific solute–solvent interaction energy, and the cavitation energy.[18,23,50] On the other hand, reaction field theory is restricted only to the evaluation of the electrostatic contribution. Thus, if specific solute–solvent effects are present, they should be taken into account by carrying out a mixture of continuum plus supermolecule calculations. If large molecules are considered, the cavitation energy becomes nonnegligible. This contribution can be evaluated through Monte Carlo simulations,[51] by scaled particle theory,[52] or by experimental procedures.[53,54]

Regarding quantum chemical calculations incorporating the spheroidal multilayered model, these can be done for approximately spheroidal charged solutes, as in Rivail's work,[12] i.e., by inserting the entire solute in a single cavity. The parameters d and ϵ can be computed as in refs 11, 12, and 55.

In this last part, it is necessary to stress the integrative value of the formalisms above presented. Effectively, when we apply appropriate border conditions to the formulas developed here, they are reduced to various expressions that appeared in the literature recently. We give a further example. If the dielectric layers become of infinitesimal thickness, we get for the spherical case

$$A_0 = \frac{q_0^2}{2}\int_{r_0}^{\infty}\frac{d\epsilon^{-1}(r)}{r} = \frac{q_0^2}{2}\int_{r_0}^{\infty}\frac{d\epsilon(r)}{\epsilon^2(r)r} \quad (58)$$

Now, if we introduce into eq 58 Block and Walker's function,[27] we get

$$A_0 = \frac{q_0^2}{2r_0}\left[\frac{1}{\ln \epsilon_B} - \frac{1}{\epsilon_B \ln \epsilon_B} - 1\right] \quad (59)$$

where ϵ_B is the bulk's dielectric permittivity. Equation 59 corresponds to a modified Born's formula due to Abe.[25]

A similar treatment for the spheroidal case leads to the new modified Born's formula:

$$A_0 = -\frac{q_0^2}{2d}\sum_{t=0}^{\infty}\frac{(2t)!}{(\lambda_0 \ln \epsilon_B)^{2t+1}}\left[\frac{1}{\epsilon_B} - \sum_{k=0}^{2t+1}\frac{(-1)^k}{k!}(\ln \epsilon_B)^k\right] \quad (60)$$

This equation incorporates both the nonsphericity of molecular ions and the nonlinear dielectric effects. In the limit case when $e_0 \rightarrow 0$, and remembering that $e_0 = \lambda_0^{-1} = d/r_0$, eq 60 transforms into Abe's modified Born formula (eq 59).

In future works, we shall present numerical applications of these methodologies.

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