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The Cluster−Continuum Model for the Calculation of the Solvation Free Energy of Ionic Species

Josefredo R. Pliego, Jr.* and José M. Riveros*

Instituto de Química, Universidade de São Paulo, CEP 05508-900 São Paulo, SP, Brazil

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A hybrid approach using a combination of explicit solvent molecules and the isodensity polarizable continuum model (IPCM) method is proposed for the calculation of the solvation thermodynamic properties of ions. This model, denominated cluster−continuum, has been applied to the calculation of the solvation free energy of 14 univalent ions, mainly organic species, and compared with the results obtained with the IPCM, polarizable continuum solvation model (PCM), and SM5.42R continuum methods. The average error in our calculated solvation free energies with respect to experimental data is 8.7 kcal mol^{-1}. However, the great merit of our model resides in the homogeneous treatment for different ions, resulting in a standard deviation of only 2.9 kcal mol^{-1} for the average error. Our results suggest that the cluster−continuum model must be superior to the IPCM, PCM, and SM5.42R methods for studying chemical reactions in the liquid phase, because these continuum methods present a standard deviation of ∼8 kcal mol^{-1} for the average error for the species studied in this work. The model can also be used to calculate the solvation entropy of ions. Predicted solvation entropies for five ionic species are in good agreement with available experimental data.

Introduction

Solvation phenomena are known to play a key role in a wide variety of chemical processes. For the particular case of ionic systems, solvent effects can have a dramatic influence on the rate and equilibrium of chemical reactions. As a consequence, theoretical modeling of liquid-phase chemical reactions must include the solvent for quantitative, or even qualitative, predictions of chemical behavior. To attain this objective, it is essential to develop theoretical protocols with the capability of calculating accurate values of solvation free energies.

In the past 20 years, considerable theoretical effort has been devoted to the development of methods for calculating the solvation free energy of neutral and ionic species. Liquid simulations are regarded as the most accurate approach to this problem because solvent molecules are explicitly included and good accuracy can be obtained with the help of an adequate intermolecular potential.[1−24] Continuum-based or implicit solvation models constitute attractive alternatives, and their easy and practical utilization makes these methods the most widely used approaches today.[25−39] Among these models, we can single out the polarizable continuum solvation model (PCM)[30,33,38,39] and its isodensity-based variations (IPCM and SCIPCM)[29] and the SMx solvation models of Cramer and Truhlar.[26,27,31,34] These methods consider the solvent as a dielectric continuum and the solute as a molecule imbedded in a cavity in the continuum. Differences among these methods range from the definition of the cavity to how the solute dielectric continuum interaction is considered. Additional contributions to the solvation free energy such as cavitation and dispersion−repulsion terms are also included by these different approaches. Nevertheless, these relatively simple treatments of the solvent have their drawbacks. The definition of cavity or solute−solvent boundary is not unique, and there is no consensus about the best choice. Furthermore, solvent molecules in the first coordination shell that may account for strong and specific solute−solvent interactions are not considered in a continuum model. The continuum approach is also based on the assumption of linear response, which is not always correct.[40,41] Finally, continuum behavior is not observed at small distances from the solute molecule. It has indeed been shown[3] that in aqueous solution the screening of charged ions predicted by the polarizable continuum is only correct beyond 7 Å.

An approach that improves part of the continuum deficiency consists of adding explicitly some solvent molecules to interact with the solute. This supermolecule is then embedded in the dielectric continuum. Such a method has been used by several authors[42−50] under different denominations: discrete-continuum,[42,49] supermolecule-reaction-field,[44] and semicontinuum.[41] While these ideas have been explored a number of times, the actual calculation of the solvation free energy is performed by using different procedures. Yet, regardless of how the explicit solvent and continuum models are combined, the calculation methodology must be based on sound theoretical grounds. Thus, two questions must be specifically addressed once the model is established: (a) how to calculate correctly the solvation free energy using this model or other relevant thermodynamic properties; (b) how many explicit solvent molecules should be included. In this work, we present a theoretical approach for a hybrid model and define a criterion for the choice of the number of solvent molecules to be explicitly included. We refer to this approach as the cluster−continuum model.

We first outline the theoretical foundations of our method and then proceed to illustrate its applications for several univalent ions. We believe that a detailed study of the performance of this approach will prove useful for studying chemical reactions in the liquid phase and be capable of providing accurate results. The present model evolves from our

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* To whom correspondence should be addressed. Address: Instituto de Química, University of São Paulo, Caixa Postal 26077, São Paulo, Brazil, CEP 05513-970. Phone/fax: 55-11-3818-3888. E-mail for J.M.R.: jmrnigra@iq.usp.br. E-mail for J.R.P.: josef@iq.usp.br.

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recent interest in the energetics of gas-phase OH^- cluster ions[1b] and a new method for obtaining accurate free energies of solvation.[1a]

The Cluster−Continuum Model

The cluster−continuum model introduced in this work and aimed at calculating the solvation free energy of ions is based on two premises: (1) the cluster is considered to be a rigid species having harmonic vibrational motion, and the energetics associated with its formation are determined from ab initio calculations; (2) the solvation free energies of the cluster and of the solvent molecules are then determined by a continuum model. The isodensity polarizable continuum model (IPCM) method has been chosen to model the second part even though this may not necessarily be the most accurate approach. However, IPCM can be conveniently applied to any system and its definition of cavity appears to be the most realistic one from our point of view.

The gas-phase and solution chemical potentials of a species X can be, respectively, written as

$$\mu_{\mathrm{g}}(\mathrm{X}) = \mu^*_{\mathrm{g}}(\mathrm{X}) + RT\ln[\mathrm{X}_{(\mathrm{g})}] \quad (1)$$

$$\mu_{\mathrm{sol}}(\mathrm{X}) = \mu^*_{\mathrm{g}}(\mathrm{X}) + \Delta G^*_{\mathrm{solv}}(\mathrm{X}) + RT\ln[\mathrm{X}_{(\mathrm{sol})}] \quad (2)$$

Here, the standard state (*) for both phases refers to 1 mol L^{-1}. They can easily be transformed to a 1 atm standard state (°) through

$$\mu^*_{\mathrm{g}}(\mathrm{X}) = \mu^\circ_{\mathrm{g}}(\mathrm{X}) + RT\ln[\tilde{R}T] \quad (3)$$

where $\tilde{R} = 0.082\,053\ \mathrm{K}^{-1}$. The term $\Delta G^*_{\mathrm{solv}}(\mathrm{X})$ is the solvation free energy defined by Bein-Naim[51] and is associated with the 1 mol L^{-1} (g) → 1 mol L^{-1} (sol) process. Thus, for an ion $A^{\pm}$ (cation or anion), solvation is represented by eq 4

$$\mathrm{A}^{\pm}_{(\mathrm{g})} \rightarrow \mathrm{A}^{\pm}_{(\mathrm{sol})} \qquad \Delta G^*_{\mathrm{solv}}(\mathrm{A}^{\pm}) \quad (4)$$

and by the equilibrium relationship (eq 5)

$$e^{-\Delta G^*_{\mathrm{solv}}(\mathbf{A}\pm)/(RT)} = \frac{[\mathrm{A}^{\pm}_{(\mathrm{sol})}]}{[\mathrm{A}^{\pm}_{(\mathrm{g})}]} \quad (5)$$

In the cluster−continuum model, we consider a process in which ion $A^{\pm}$ first interacts with n solvent molecules S to form a cluster, $A^{\pm}(S)_n$, and this cluster is then solvated by the bulk solvent to yield $A^{\pm}(S)_{n(\mathrm{sol})}$. The formal process can be represented by eq 6 where clustering occurs with nS solvent molecules initially solvated by the overall solvent.

$$\mathrm{A}^{\pm}_{(\mathrm{g})} + n\mathrm{S}_{(\mathrm{sol})} \rightarrow \mathrm{A}^{\pm}(\mathrm{S})_{n\,(\mathrm{sol})} \qquad \Delta G^*_{\mathrm{R}} \quad (6)$$

The corresponding free energy for process 6 can then be written in terms of the chemical potentials for the different gas-phase species and the solvation energies of the n solvent molecules and of the cluster itself:

$$\Delta G^*_{\mathrm{R}} = \mu^*_{\mathrm{g}}(\mathrm{A}^{\pm}(\mathrm{S})_n) + \Delta G^*_{\mathrm{solv}}(\mathrm{A}^{\pm}(\mathrm{S})_n) - \mu^*_{\mathrm{g}}(\mathrm{A}^{\pm}) - n\mu^*_{\mathrm{g}}(\mathrm{S}) - n\Delta G^*_{\mathrm{solv}}(\mathrm{S}) \quad (7)$$

or

$$\Delta G^*_{\mathrm{R}} = \Delta G^*_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_n) + \Delta G^*_{\mathrm{solv}}(\mathrm{A}^{\pm}(\mathrm{S})_n) - n\Delta G^*_{\mathrm{solv}}(\mathrm{S}) \quad (8)$$

Here, $\Delta G^*_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_n)$ stands for the clustering free energy (1 mol L^{-1} standard state) in the gas phase and

$$\Delta G^*_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_n) = \mu^*_{\mathrm{g}}(\mathrm{A}^{\pm}(\mathrm{S})_n) - \mu^*_{\mathrm{g}}(\mathrm{A}^{\pm}) - n\mu^*_{\mathrm{g}}(\mathrm{S}) \quad (9)$$

The free energy of process 6 corresponds then to the equilibrium

$$e^{-\Delta G^*_{\mathrm{R}}/(RT)} = \frac{[\mathrm{A}^{\pm}(\mathrm{S})_{n\,(\mathrm{sol})}]}{[\mathrm{A}^{\pm}_{(\mathrm{g})}][\mathrm{S}_{(\mathrm{sol})}]^n} \quad (10)$$

Comparison of eq 10 with eq 5 leads to relationship 11

$$e^{-\Delta G^*_{\mathrm{solv}}(\mathbf{A}\pm)/(RT)} = [\mathrm{S}_{(\mathrm{sol})}]^n\, e^{-\Delta G^*_{\mathrm{R}}/(RT)} \quad (11)$$

which can be also be written as

$$\Delta G^*_{\mathrm{solv}}(\mathrm{A}^{\pm}) = \Delta G^*_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_n) + \Delta G^*_{\mathrm{solv}}(\mathrm{A}^{\pm}(\mathrm{S})_n) - n\Delta G^*_{\mathrm{solv}}(\mathrm{S}) - nRT\ln[\mathrm{S}_{(\mathrm{sol})}] \quad (12)$$

According to eq 12, the solvation free energy of $A^{\pm}$ in the cluster−continuum model can be obtained from the clustering free energy, the solvation free energy of the cluster, and the solvation free energy and concentration of the solvent.

Use of 1 atm as Standard State for the Clustering and Vaporization Free Energies. Equation 12 can be rewritten in terms of more familiar data, i.e., the clustering free energy using the 1 atm standard state ($\Delta G^\circ_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_n)$) and the vaporization free energy of the solvent $\Delta G_{\mathrm{vap}}(\mathrm{S})$. For the clustering process, eqs 3 and 9 lead to

$$\Delta G^*_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_n) = \Delta G^\circ_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_n) - nRT\ln(\tilde{R}T) \quad (13)$$

The vaporization free energy is defined by

$$\Delta G_{\mathrm{vap}}(\mathrm{S}) = \mu^\circ_{\mathrm{g}}(\mathrm{S}) - \mu_{\mathrm{sol}}(\mathrm{S}) \quad (14)$$

or, alternatively, as

$$\Delta G_{\mathrm{vap}}(\mathrm{S}) = \mu^\circ_{\mathrm{g}}(\mathrm{S}) - (\mu^*_{\mathrm{g}}(\mathrm{S}) + \Delta G^*_{\mathrm{solv}}(\mathrm{S}) + RT\ln[\mathrm{S}_{(\mathrm{sol})}]) \quad (15)$$

Use of eq 3 then yields

$$\Delta G_{\mathrm{vap}}(\mathrm{S}) = -\Delta G^*_{\mathrm{solv}}(\mathrm{S}) - RT\ln[\tilde{R}T] - RT\ln[\mathrm{S}_{(\mathrm{sol})}] \quad (16)$$

The combination of eqs 12, 13, and 16 finally results in

$$\Delta G^*_{\mathrm{solv}}(\mathrm{A}^{\pm}) = \Delta G^\circ_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_n) + \Delta G^*_{\mathrm{solv}}(\mathrm{A}^{\pm}(\mathrm{S})_n) + n\Delta G_{\mathrm{vap}}(\mathrm{S}) \quad (17)$$

In summary, eq 17 shows that the solvation free energy of the $A^{\pm}$ ion in the cluster−continuum model can be calculated from the gas-phase clustering free energy at 1 atm, the solvation free energy of the cluster, and the vaporization free energy of the solvent. It is important to notice the fact that two very distinct thermodynamics properties such as the solvation and vaporization free energies of the solvent molecules are related by eq 16.

Number of Explicit Solvent Molecules and the Variational Principle. Once the number of solvent molecules to be included in the cluster has been defined, eq 12 or 17 can be used to determine the solvation free energy of the ion. But how is the number of solvent molecules in the cluster to be determined? The answer to this question lies in eq 17. If each term is calculated exactly, this equation leads to the solvation free energy of the $A^{\pm}$ ion for any value of n. When n is small, the value of $\Delta G^{\circ}_{\mathrm{clust}}(A^{\pm}(S)_n)$ can be obtained from ab initio calculations with a high level of accuracy. In the gas phase, these small clusters will be relatively *rigid*. By comparison, interaction of the cluster with solvent molecules in solution can give rise to a weak potential of mean force for ion−solvent interaction inside the cluster and consequently confer high mobility to some of the solvent molecules. This feature is not properly described by the theoretical approach that considers the cluster as *rigid*. As a result, it is likely that the final solvation free energy would be too positive even if we calculate exactly the solvation free energy of the *rigid* $A^{\pm}(S)_n$ cluster. On the other hand, if n corresponds to the number of solvent molecules that are strongly bound to the central ion, then the solvation free energy calculated by eq 17 using an exact solvation free energy for the *rigid* $A^{\pm}(S)_n$ cluster will be close to the real solvation free energy of the $A^{\pm}$ ion. Because the $\Delta G^{*}_{\mathrm{solv}}(A^{\pm}(S)_n)$ term is calculated by a continuum model that ignores strong specific interactions, the clustering free energy will contribute to give a good description of the first solvation shell and addition of the first solvent molecules should decrease the solvation free energy. As n increases, the *stepwise clustering enthalpy* will become less negative with a corresponding increase of the *stepwise clustering free energy*. At the same time, the solvation free energy of the cluster will also increase. Thus, a minimum in the $\Delta G^{*}_{\mathrm{solv}}(A^{\pm})$ as a function of n will occur. The n that minimizes $\Delta G^{*}_{\mathrm{solv}}(A^{\pm})$ is the ideal number of explicit solvent molecules, and the solvation free energy for this value of n would be the best calculated value for this property based on the cluster−continuum model. Thus, a variational principle can be established for the choice of the number of solvent molecules, i.e., the value of n that produces the lowest solvation free energy.

Extension of the Theory to the Enthalpy and Entropy of Solvation. Standard thermodynamic relationships can be used to derive the enthalpy and entropy of solvation within the cluster−continuum model from eqs 16 and 17. For the enthalpy,

$$\Delta H^{*}_{\mathrm{solv}}(A^{\pm}) = -T^2 \frac{\partial}{\partial T}\left(\frac{\Delta G^{*}_{\mathrm{solv}}(A^{\pm})}{T}\right) \tag{18}$$

$$\Delta H^{*}_{\mathrm{solv}}(A^{\pm}) = \Delta H^{\circ}_{\mathrm{clust}}(A^{\pm}(S)_n) + \Delta H^{*}_{\mathrm{solv}}(A^{\pm}(S)_n) + n\Delta H_{\mathrm{vap}}(S) \tag{19}$$

and similarly for the vaporization enthalpy,

$$\Delta H_{\mathrm{vap}}(S) = -\Delta H^{*}_{\mathrm{solv}}(S) + RT \tag{20}$$

It should be noted that $\Delta H^{*}_{\mathrm{solv}}(S) \approx \Delta G^{*}_{\mathrm{solv}}(S)$ in our model.

The solvation entropy can be obtained from

$$\Delta S^{*}_{\mathrm{solv}}(A^{\pm}) = -\frac{\partial \Delta G^{*}_{\mathrm{solv}}(A^{\pm})}{\partial T} \tag{21}$$

$$\Delta S^{*}_{\mathrm{solv}}(A^{\pm}) = \Delta S^{\circ}_{\mathrm{clust}}(A^{\pm}(S)_n) + \Delta S^{*}_{\mathrm{solv}}(A^{\pm}(S)_n) + n\Delta S_{\mathrm{vap}}(S) \tag{22}$$

and

$$\Delta S_{\mathrm{vap}}(S) = R\ln(\tilde{R}T) + R + R\ln[S] \tag{23}$$

under the approximation that

$$\Delta S^{*}_{\mathrm{solv}}(S) \approx 0 \tag{24}$$

While the clustering enthalpy and entropy can be determined from ab initio calculations, the continuum IPCM model only yields the solvation free energy of the cluster. To evaluate the enthalpy and entropy of solvation, the Born model can be used by assuming an effective cavity radius that yields the same solvation free energy as the IPCM model. Then, by considering this radius as fixed and by taking into account the variation of the dielectric constant as a function of temperature, we can obtain the enthalpy and entropy of solvation of the cluster.

The Born model states that

$$\Delta G^{*}_{\mathrm{solv}} = -\frac{1}{4\pi\epsilon_0}\frac{q^2}{2R}\left(1 - \frac{1}{\epsilon}\right) \tag{25}$$

From this, the enthalpy can be obtained as

$$\Delta H^{*}_{\mathrm{solv}} = -T^2 \frac{\partial}{\partial T}\left(\frac{\Delta G^{*}_{\mathrm{solv}}}{T}\right) = -\frac{1}{4\pi\epsilon_0}\frac{q^2}{2R}\left(1 - \frac{1}{\epsilon} - \frac{T}{\epsilon}\frac{\partial \ln \epsilon}{\partial T}\right) \tag{26}$$

$$\Delta H^{*}_{\mathrm{solv}} = \Delta G^{*}_{\mathrm{solv}}\left(1 - \frac{T}{\epsilon - 1}\frac{\partial \ln \epsilon}{\partial T}\right) \tag{27}$$

and the entropy as

$$\Delta S^{*}_{\mathrm{solv}} = -\frac{\partial \Delta G^{*}_{\mathrm{solv}}}{\partial T} = \frac{1}{4\pi\epsilon_0}\frac{q^2}{2R}\left(\frac{1}{\epsilon}\frac{\partial \ln \epsilon}{\partial T}\right) \tag{28}$$

$$\Delta S^{*}_{\mathrm{solv}} = -\Delta G^{*}_{\mathrm{solv}}\left(\frac{1}{\epsilon - 1}\frac{\partial \ln \epsilon}{\partial T}\right) \tag{29}$$

Equations 27 and 29 provide a simple relationship for calculating the electrostatic contribution to the enthalpy and entropy of solvation of the cluster that only requires knowledge of the variation of the dielectric constant with temperature.

Ab Initio Calculations

Equilibrium structures were obtained by full geometry optimization at the Hartree−Fock (HF) level using the 6-31+G(d,p) basis set. Single point energy calculations were then performed at the MP2 level using the 6-31+G(d,p) and 6-311+G(2df,2p) basis sets. The stationary points were confirmed to be minima by analysis of the harmonic frequencies, which were also used in the calculation of the thermodynamic properties of clustering.

For comparison purposes, the solvation free energy of several ions was calculated by the following methods: the isodensity surface polarizable continuum model (IPCM)[29] using the MP2/6-31+G(d,p) wave function, an isodensity of 0.0004, and a dielectric constant of 78.0; the polarizable continuum model (PCM)[30] as implemented in GAMESS using the HF/6-31+G(d,p) wave function and including only electrostatic contributions; the SM5.42R/HF/6-31G* solvation model[26] available in GAMESOL 2.2.4. In the meantime, the cluster−continuum model was applied to the calculation of solvation free energies using the IPCM method.

All gas-phase ab initio calculations as well as the IPCM calculations were done with the GAUSSIAN 94 program system.[52] The PCM calculations were done with the GAMESS program,[53] and the SM5.42R method was carried out using the GAMESOL program.[54]

Anharmonic Correction to Some Vibrational Levels. The harmonic approximation was used for all cases with the exception of the $Cl^{-}(H_2O)_2$ cluster. For this species, the

TABLE 1: Calculated Thermodynamic Data for Gas-Phase Clustering Processes[a]

cluster	MP2/6-31+G(d,p)	MP2/6-311+G(2df,2p)	ΔZPE	Δ*E*	Δ*H*°	Δ*S*°	Δ*G*°
$OH^-(H_2O)_2$	−51.44	−50.37	4.74	−45.63	−47.28	−48.26	−32.89
$OH^-(H_2O)_3$	−71.63	−70.07	7.71	−62.36	−64.75	−75.52	−42.21
$OH^-(H_2O)_4$	−89.76	−87.43	11.25	−76.18	−79.48	−111.08	−46.36
$CH_3O^-(H_2O)_3$	−68.27	−65.31	8.31	−57.00	−58.73	−78.37	−35.36
$CH_3CH_2O^-(H_2O)_3$	−65.56	−62.92	8.27	−54.65	−56.35	−80.86	−32.24
$PhO^-(H_2O)_3$	−51.03	−48.09	7.96	−40.13	−41.78	−82.82	−17.09
$HCOO^-(H_2O)_2$	−35.08	−33.84	4.73	−29.11	−29.95	−50.44	−14.91
$HCOO^-(H_2O)_3$	−48.66	−46.99	6.63	−40.36	−41.32	−73.18	−19.50
$NH_2^-(H_2O)_2$	−50.61	−48.12	5.52	−42.60	−44.45	−52.34	−28.84
$CH_3NH^-(H_2O)_2$	−50.53	−47.99	5.13	−42.86	−44.14	−53.37	−28.22
$Cl^-(H_2O)$	−14.70	−14.62	1.37	−13.25	−13.97	−18.03	−8.60
$Cl^-(H_2O)_2$	−28.11	−27.69	2.78	−24.91	−25.50	−27.38	−17.34
$Cl^-(H_2O)_2$[b]					−26.15	−37.22	−15.05
$HS^-(H_2O)_2$	−29.06	−28.16	3.64	−24.52	−25.20	−38.55	−13.71
$CH_3S^-(H_2O)_2$	−30.25	−29.33	3.51	−25.82	−26.05	−37.20	−14.96
$CH_3S^-(H_2O)_3$	−45.02	−43.58	6.09	−37.49	−38.34	−68.27	−17.99
$H^+(H_2O)$	−172.56	−170.11	8.62	−161.49	−162.92	−24.83	−155.52
$H_3O^+(H_2O)_2$	−60.57	−58.22	4.39	−53.83	−55.48	−53.27	−39.60
$H_3O^+(H_2O)_3$	−81.56	−78.12	6.56	−71.56	−73.34	−79.36	−49.68
$H_3O^+(H_2O)_4$	−96.20	−91.61	8.47	−83.14	−85.20	−101.30	−55.00
$CH_3OH_2^+(H_2O)_2$	−52.74	−50.49	4.23	−46.26	−47.22	−54.45	−30.99
$CH_3CH_2OH_2^+(H_2O)_2$	−49.86	−47.49	4.36	−43.13	−43.99	−54.83	−27.64
$NH_4^+(H_2O)_2$	−39.99	−37.84	3.96	−33.88	−34.77	−42.04	−22.24
$NH_4^+(H_2O)_3$	−56.03	−52.75	5.70	−47.05	−48.06	−69.43	−27.36
$CH_3NH_3^+(H_2O)_2$	−36.93	−34.62	3.52	−31.10	−31.45	−42.08	−18.90
$CH_3NH_3^+(H_2O)_3$	−52.20	−48.72	5.13	−43.59	−43.95	−70.54	−22.92

[a] Units of kcal mol^{-1} except for the entropy calculated in cal mol^{-1} K^{-1}. $T = 298.15$ K, $P = 1$ atm. Geometries obtained at the HF/6-31+G(d,p) level of theory. [b] Inclusion of anharmonic correction for the three lower vibrational modes.

calculations yield a very low harmonic vibrational frequency of only 2.7 cm^{-1}. We have therefore made a simple anharmonic correction for the three lower vibrational modes of this cluster by computing the energy levels through the formula

$$E_n = \left(n + \frac{1}{2}\right)A + \left(n + \frac{1}{2}\right)^2 B \qquad (30)$$

The *A* and *B* parameters were fitted to the two lower energy levels of each mode, which were determined through the vibrational self-consistent-field method (VSCF) of Gerber et al.[55] as recently implemented in GAMESS. Only diagonal elements of the potential were included to obtain the energy levels. Equation 30 was also used in the calculation of the vibrational partition function and thermodynamic properties.

Results and Discussion

The thermodynamic properties associated with the clustering process are presented in Table 1, and solvation free energies calculated by the cluster−continuum method are displayed in Table 2. Optimized structures for the clusters are shown in Figures 1−4. For the $OH^-(H_2O)_n$ species, the structures are available in a previous publication.[1b] The solvation free energy of the water molecules determined by the IPCM method is −5.40 kcal mol^{-1} leading to a vaporization free energy of 1.13 kcal mol^{-1} (see eq 16).

The solvation of the hydroxide ion is an important test case for the cluster−continuum model. In Table 2, calculated values for the solvation free energy of the hydroxide ion are listed for different numbers of water molecules included in the cluster. It is easily recognized that the solvation free energy reaches a minimum with three water molecules resulting in a solvation free energy of −92.1 kcal mol^{-1}. While the experimental value is −105.0 kcal mol^{-1}, it should be emphasized that the IPCM method only predicts a value −69.6 kcal mol^{-1}. Therefore, this initial result points out a substantial improvement in the theoretical solvation free energy with the cluster−continuum model.

For different ions, an adequate (ideal) number of solvent molecules in the cluster can be determined by the variational principle outlined in the previous section. This approach was applied to OH^-, $HCOO^-$, CH_3S^-, H_3O^+, and $CH_3NH_3^+$. For these univalent ions, the ideal number of solvent molecules is calculated to be either two or three.[56] On the basis of this fact and structural similarity, we have extended our calculation of solvation free energy to several other ions using a predefined number of solvent molecules. As an example, because OH^- ion has three water molecules in the ideal cluster, the same number was used for the CH_3O^-, $CH_3CH_2O^-$, and PhO^- ions. For the H_3O^+ ion, water molecules fill the three coordination sites. By analogy, we have used two water molecules for the $CH_3OH_2^+$ and $CH_3CH_2OH_2^+$ species to fill their two coordination sites.

The $Cl^-(H_2O)_2$ cluster is characterized by a set of very low harmonic frequencies: 2.7, 13.1, and 52.3 cm^{-1}. These vibrational modes are highly anharmonic and make an important contribution to the entropy. Thus, we have included anharmonic corrections as described above in the calculation of the thermodynamic properties. Thermodynamic data with and without anharmonic corrections are in shown Table 1. While the enthalpy is only slightly changed by 0.65 kcal mol^{-1} with these corrections, the entropy suffers an important correction of about 10 cal K^{-1} mol^{-1}. Consequently, the clustering free energy is increased by 2.3 kcal mol^{-1}.

The effect of explicit water molecules on the different ions studied in this work is variable. It is very important for the hydroxide ion and responsible for a decrease of 23 kcal mol^{-1} in the solvation free energy, while for the ammonium ion this effect amounts only to 1.8 kcal mol^{-1}. The nature of the continuum model used (IPCM) is in part responsible for this behavior because this model attributes to negatively charged species a larger volume than it attributes to positively charged ones, resulting in less solvation by the continuum. Inclusion of explicit solvent molecules seems to eliminate this problem. On the other hand, the solvation free energy of positively charged species such as H_3O^+, $CH_3OH_2^+$, and $CH_3CH_2OH_2^+$ is greatly

TABLE 2: Calculated Solvation Free Energy of Univalent Ions by the Cluster−Continuum Model[a]

$A^{\pm}(H_2O)_n$	ΔG°_{clust}	ΔG^{*}_{solv}	$n\Delta G_{vap}$	$\Delta G^{*}_{solv}(A^{\pm})$
OH^-		−69.64		−69.64
$OH^-(H_2O)_2$	−32.89	−58.74	2.26	−89.37
$OH^-(H_2O)_3$	−42.21	−54.26	3.39	−93.08
$OH^-(H_2O)_4$	−46.36	−50.12	4.52	−91.96
CH_3O^-		−64.18		−64.18
$CH_3O^-(H_2O)_3$	−35.36	−50.40	3.39	−82.37
$CH_3CH_2O^-$		−61.24		−61.24
$CH_3CH_2O^-(H_2O)_3$	−32.24	−48.81	3.39	−77.66
PhO^-		−52.96		−52.96
$PhO^-(H_2O)_3$	−17.09	−46.85	3.39	−60.55
$HCOO^-$		−60.81		−60.81
$HCOO^-(H_2O)_2$	−14.91	−51.12	2.26	−63.77
$HCOO^-(H_2O)_3$	−19.50	−45.10	3.39	−61.21
NH_2^-		−63.70		−63.70
$NH_2^-(H_2O)_2$	−28.84	−54.90	2.26	−81.48
CH_3NH^-		−60.31		−60.31
$CH_3NH^-(H_2O)_2$	−28.22	−52.87	2.26	−78.83
Cl^-		−61.80		−61.80
$Cl^-(H_2O)$	−8.60	−57.60	1.13	−65.07
$Cl^-(H_2O)_2$	−15.05	−55.15	2.26	−67.94
HS^-		−57.98		−57.98
$HS^-(H_2O)_2$	−13.71	−53.23	2.26	−64.68
CH_3S^-		−56.58		−56.58
$CH_3S^-(H_2O)_2$	−14.96	−51.17	2.26	−63.87
$CH_3S^-(H_2O)_3$	−17.99	−47.41	3.39	−62.01
H_3O^+		−88.77		−88.77
$H_3O^+(H_2O)_2$	−39.60	−62.59	2.26	−99.93
$H_3O^+(H_2O)_3$	−49.68	−55.58	3.39	−101.87
$H_3O^+(H_2O)_4$	−55.00	−51.61	4.52	−102.09
$CH_3OH_2^+$		−72.41		−72.41
$CH_3OH_2^+(H_2O)_2$	−30.99	−55.91	2.26	−84.64
$CH_3CH_2OH_2^+$		−66.48		−66.48
$CH_3CH_2OH_2^+(H_2O)_2$	−27.64	−50.33	2.26	−75.71
NH_4^+		−77.56		−77.56
$NH_4^+(H_2O)_2$	−22.24	−58.37	2.26	−78.35
$NH_4^+(H_2O)_3$	−27.36	−55.41	3.39	−79.38
$CH_3NH_3^+$		−68.83		−68.83
$CH_3NH_3^+(H_2O)_2$	−18.90	−56.05	2.26	−72.69
$CH_3NH_3^+(H_2O)_3$	−22.92	−52.22	3.39	−71.75

[a] The thermodynamic data for clustering were obtained at the MP2/6-311+G(2df,2p)//HF/6-31+G(d,p) level of theory. Units of kcal mol^{-1} and $T = 298.15$ K. The IPCM model with a MP2/6-31+G(d,p) wave function was used for the continuum calculations. $\Delta G_{vap} = 1.13$ kcal mol^{-1}.

affected by the explicit water molecules, which are responsible for a decrease of 10 kcal mol^{-1} in the value of this property. In conclusion, the use of the cluster−continuum model has an important effect on the solvation free energy of both negative and positive species, although the effect is more pronounced for negatively charged ions.

Comparison with Experimental Data and with Continuum Models. The solvation free energies calculated by the cluster−continuum and by the standard continuum methods as well as a comparison with the experimental data are shown in Table 3. These experimental data were taken from a very recent compilation by Pliego and Riveros[57] based on a standard proton solvation free energy of −264.0 kcal mol^{-1} as reported by Tissandier et al.[58] The errors with respect to the experimental data are indicated in parentheses, while the overall average error and the standard deviation for each method are listed at the bottom of the table.

The cluster−continuum model yields an average error of 8.7 kcal mol^{-1} and a standard deviation of 2.9 kcal mol^{-1} for the solvation free energy. By comparison, the SM5.42R method yields an average error of only 2.5 kcal mol^{-1} but a standard deviation of 8.2 kcal mol^{-1}. The other two continuum models, PCM and IPCM, reveal average errors of 10.0 and 19.2 kcal mol^{-1}, respectively, and standard deviations similar to the SM5.42R method of approximately 8 kcal mol^{-1}. These results point out that the cluster−continuum model is more stable, treating the ions with similar accuracy. On the other hand, an error of almost 10 kcal mol^{-1} in the absolute value of the solvation free energy is admittedly high and may limit the applicability of this model for studying liquid-phase chemical reactions. Nevertheless, for reactions in solution involving an ion and a neutral species, the relevant parameter is the standard deviation because the difference in solvation free energies determines the activation free energy in solution. Thus, a small standard deviation implies a small error in the activation free

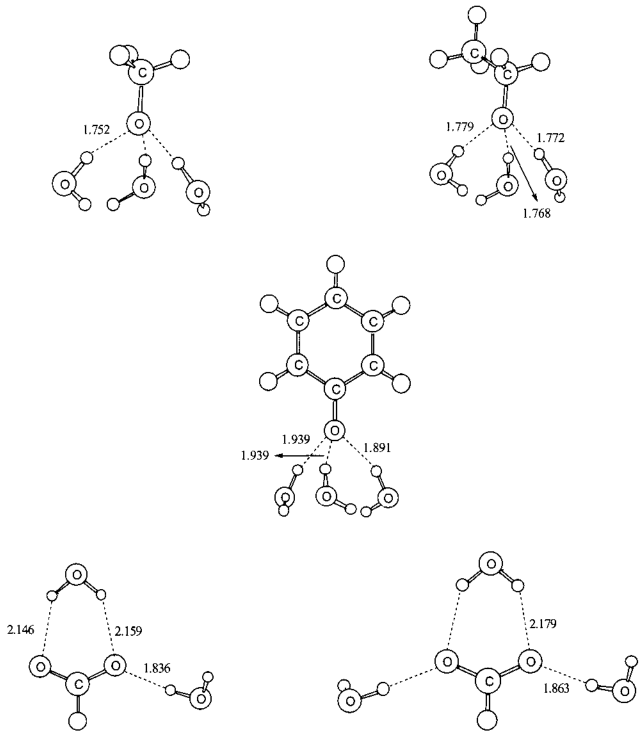

Figure 1. Optimized geometries for the $MeO^-(H_2O)_3$, $EtO^-(H_2O)_3$, $PhO^-(H_2O)_3$, $HCOO^-(H_2O)_2$, and $HCOO^-(H_2O)_3$ clusters.

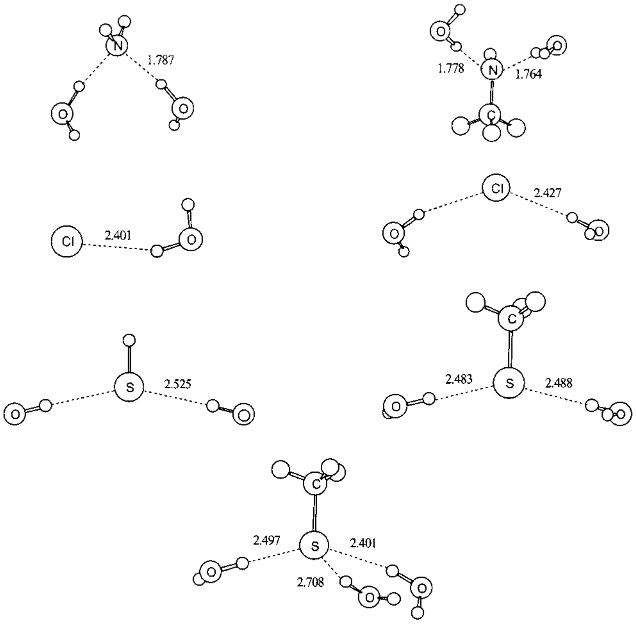

Figure 2. Optimized geometries for the $NH_2^-(H_2O)_2$, $CH_3NH_2^-(H_2O)_2$, $Cl^-(H_2O)$, $Cl^-(H_2O)_2$, $HS^-(H_2O)_2$, $CH_3S^-(H_2O)_2$, and $CH_3S^-(H_2O)_3$ clusters.

TABLE 3: Comparison between Methods of Calculation for the Solvation Free Energy ($\Delta G^*_{\mathrm{solv}}$) of Univalent Ions[a]

$A^{\pm}$	experimental	cluster−cont	SM5.42R	PCM	IPCM
OH^-	−105.0	−93.08(11.9)	−108.96(−4.0)	−92.14(12.9)	−69.64(35.4)
CH_3O^-	−94.0	−82.37(11.6)	−86.79(7.2)	−79.98(14.0)	−64.18(29.8)
$CH_3CH_2O^-$	−91.0	−77.66(13.3)	−81.87(9.1)	−76.70(14.3)	−61.24(29.8)
PhO^-	−68.6	−60.55(8.1)	−64.59(4.0)	−63.78(4.8)	−52.96(15.6)
$HCOO^-$	−74.6	−63.77(10.8)	−75.22(−0.6)	−72.41(2.2)	−60.81(13.8)
NH_2^-	−91.8	−81.48(10.3)	−89.30(2.5)	−85.44(6.4)	−63.70(28.1)
Cl^-	−74.7	−67.94(6.8)	−77.05(−2.4)	−72.70(2.0)	−61.80(12.9)
HS^-	−70.7	−64.68(6.0)	−84.37(−13.7)	−71.04(−0.3)	−57.98(12.7)
CH_3S^-	−72.6	−63.87(8.7)	−78.97(−6.4)	−69.27(3.3)	−56.58(16.0)
H_3O^+	−110.4	−101.87(8.5)	−92.51(17.9)	−83.64(26.8)	−88.77(21.6)
$CH_3OH_2^+$	−90.8	−84.64(6.2)	−79.82(11.0)	−71.16(19.6)	−72.41(18.4)
$CH_3CH_2OH_2^+$	−86.9	−75.71(11.2)	−74.04(12.9)	−66.12(20.8)	−66.48(20.4)
NH_4^+	−84.9	−79.38(5.5)	−87.03(−2.1)	−77.42(7.5)	−77.56(7.3)
$CH_3NH_3^+$	−75.2	−72.69(2.5)	−76.03(−0.8)	−69.17(6.0)	−68.83(6.4)
average error		8.7	2.5	10.0	19.2
standard dev		2.9	8.2	7.9	8.5

[a] Units of kcal mol^{-1}. The values in parentheses are the deviation from experimental data.

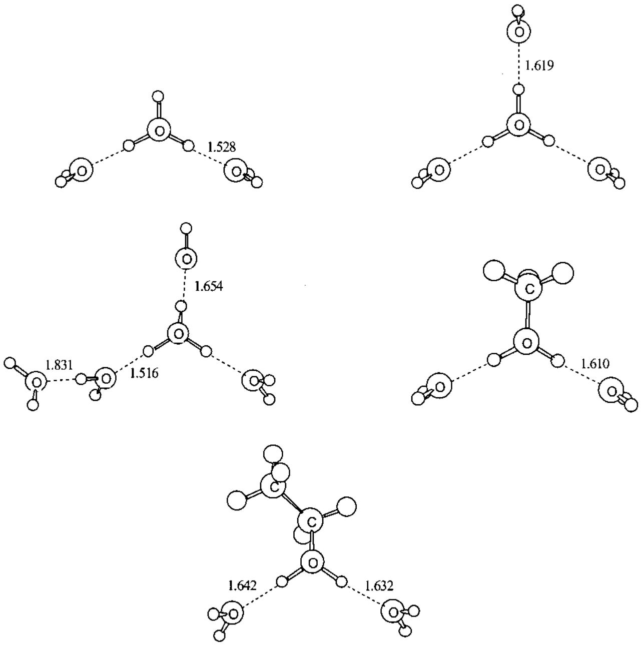

Figure 3. Optimized geometries for the $H_3O^+(H_2O)_2$, $H_3O^+(H_2O)_3$, $H_3O^+(H_2O)_4$, $CH_3OH_2^+(H_2O)_2$, and $CH_3CH_2OH_2^+(H_2O)_2$ clusters.

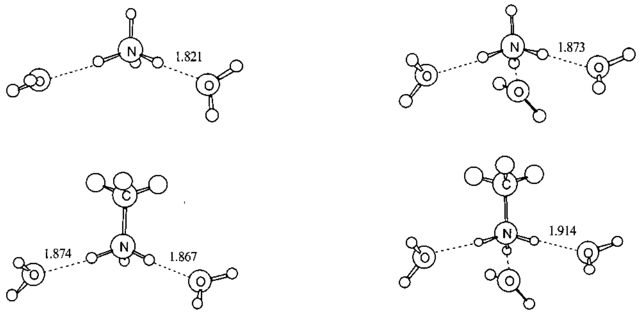

Figure 4. Optimized geometries for the $NH_4^+(H_2O)_2$, $NH_4^+(H_2O)_3$, $CH_3NH_3^+(H_2O)_2$, and $CH_3NH_3^+(H_2O)_3$ clusters.

energy. For these cases, the cluster−continuum model is the best theoretical approach among the four methods presented in Table 3 and provides a substantial improvement over the pure continuum models.

Another situation to consider is a chemical reaction involving a cation and an anion to form a neutral species. In this case, accurate values of solvation free energy are necessary. The SM5.42R method would apparently be the appropriate approach because of the smaller average error. However, the high standard deviation shown in Table 3 can lead to inaccurate results. An alternative approach to this problem is to correct the solvation free energy obtained by the cluster−continuum model by its average error. Thus, a corrected solvation free energy could be calculated from

$$\Delta G^*_{\mathrm{corrected}} = \Delta G^*_{\mathrm{clust-cont}} - 8.7\ \mathrm{kcal\ mol^{-1}} \qquad (31)$$

Given the smaller standard deviation for the values calculated with the cluster−continuum model, the use of this method in conjunction with eq 31 should lead to good values for the solvation free energy of univalent ions. An even better and more accurate approach could be used. Equation 31 is based on the average error of different functional groups. If we compare the error in the solvation free energy of similar species, we could predict very accurate solvation free energies from the known solvation free energy of a representative species. As an example, a corrected solvation free energy for the methoxide ion can be derived from the experimental solvation free of the hydroxide ion:

$$\Delta G_{\mathrm{corrected}}(\mathrm{MeO^-}) = \Delta G_{\mathrm{exp}}(\mathrm{OH^-}) + (\Delta G_{\mathrm{theor}}(\mathrm{MeO^-}) - \Delta G_{\mathrm{theor}}(\mathrm{OH^-})) \qquad (32)$$

Through the use of data from Table 3 and eq 32, a solvation free energy of −94.3 kcal mol^{-1} is predicted for the methoxide ion, in excellent agreement with the experimental value of −94.0 kcal mol^{-1}. For comparison purposes, eq 31 predicts −91.1 kcal mol^{-1}.

Entropy of Solvation. The transfer of ions from the gas phase to aqueous solution has an important effect on the entropy. Small and highly charged ions give rise to a very negative solvation entropy, while large univalent ions are characterized by small solvation entropies. One of the most important contributions to this property is the immobilization of the water molecules of the first solvation shell surrounding the ion. The cluster−continuum model can account for this effect through the clustering entropy term. We have tested the performance of our method to predict solvation entropies using eqs 22, 23, and 29. These results appear in Table 4. The experimental values, $\Delta S^{\circ}_{\mathrm{solv}}$, were taken from the work of Marcus[59] and converted to $\Delta S^*_{\mathrm{solv}}$ values by the equation

$$\Delta S^*_{\mathrm{solv}} = \Delta S^{\circ}_{\mathrm{solv}} + R\ln(\tilde{R}T) + R \qquad (33)$$

TABLE 4: Calculated Solvation Entropy (ΔS^*_{solv}) of Some Univalent Ions[a]

$A^{\pm}$	experimental	cluster−continuum
OH^-	−30.1[b]	−29.9
$HCOO^-$	−21.3[b]	−20.9
Cl^-	−9.6[c]	−7.9
HS^-	−15.8[b]	−9.1
NH_4^+	−18.4[c]	−23.8

[a] Units of cal K^{-1} mol^{-1}. T = 298.15 K. [b] Reference 59b. [c] Reference 59a.

The results in Table 4 show that the cluster−continuum model works well, especially for OH^- and HCO_2^- ions. For Cl^-, the error is only 1.7 cal K^{-1} mol^{-1}, while it is greater for NH_4^+ and HS^-. It is likely that anharmonic corrections could improve the ΔS^*_{solv} of the HS^- ion as they do for the Cl^- ion. The source of error in the ammonium ion is not so clear. However, the very low dependence of the solvation free energy on the number of solvent molecules in the respective cluster may be responsible for the poor agreement.

Conclusion

The cluster−continuum model provides a substantial improvement over the IPCM method in the prediction of solvation free energy of univalent ions. The main feature of our model relies on treating the different ions in a more homogeneous form, resulting in solvation free energies with similar deviation from experimental data. As a result, the cluster−continuum model should be superior to other continuum approaches such as the PCM and the SM5.42R methods in the study of chemical reactions in the liquid phase. Furthermore, our hybrid approach predicts reasonable values of solvation entropy that are not available through the pure continuum methods.

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