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Hydration energies of C_{60} and C_{70} fullerenes – A novel Monte Carlo simulation study

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Abstract

The hydration energies of C_{60} and C_{70} are estimated at temperatures ranging from 20 to 90 °C by incorporating the cavity formation energies and van der Waals contributions. The structural parameters of the fullerenes are deduced using the optimized geometries from Gaussian 03 version while those pertaining to water are obtained from the TIP4P model. The cut-off radii pertaining to the sphere of influence of fullerenes with water are incorporated using a simple Monte Carlo simulation methodology and the entropy changes involved in the hydration are also evaluated.

Keywords: Fullerenes; Hydration; Scaled particle theory; Monte Carlo simulation; Gaussian 03

1. Introduction

The aqueous solutions of fullerenes have interesting implications in diverse fields such as medicinal chemistry [1], environmental science [2], development of non-linear optical devices [1,3], etc. However, the extent of solubility of C_{60} in water is inadequate; consequently several strategies have been investigated in order to enhance the solubility. Among them, mention may be made of the following: (i) encapsulation in spherical cavities [4,5], (ii) use of co-solvents to prepare suspensions [6] and (iii) functionalization of fullerenes [7,8]. Recently, the plausibility of obtaining aqueous solutions of C_{60} and C_{70} without employing stabilizers and chemical modification strategies has also been pointed out [9,10]. While these improvizations are valuable in expanding the scope and applicability of fullerenes, it is of interest to comprehend the influence of temperature on their hydration energies so that further insights regarding the hydration of fullerenes can be formulated.

In this article, we report the estimation of hydration free energies as well as the corresponding entropy changes for C_{60} and C_{70} by employing the classical scaled particle theory in conjunction with a simple Monte Carlo simulation technique. A novel feature of the formalism consists in incorporating the structural parameters of the solutes (C_{60} and C_{70}) using their optimized structures deduced from the Gaussian 03 as well as in introducing temperature-dependent parameters of the constituent species wherever necessary.

2. Methodology of estimating hydration free energies of C_{60} and C_{70}

The hydration free energy (ΔG_{hyd}) may be represented in a general manner as [11]

$$\Delta G_{\text{hyd}} = \Delta G_{\text{cav}} + \Delta G_{\text{vdW}} + \Delta G_{\text{ele}} \tag{1}$$

wherein the terms represent the cavity formation energy, electrostatic interaction and van der Waals contribution, respectively. On account of the neutral nature of C_{60}, the electrostatic contributions arising from partial atomic charges of carbon atoms may be neglected thus yielding

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$$\Delta G_{\text{hyd}} = \Delta G_{\text{cav}} + \Delta G_{\text{vdW}}. \tag{2}$$

The cavity formation energy ΔG_{cav} denotes the energy required for creating a suitable cavity that encloses a given solute. The concept of cavity formation is very useful as it provides a measure of the repulsive energies involved during the hydration process. Consequently, various innovative approaches have been formulated for estimating ΔG_{cav} such as (i) test-particle insertion method using molecular dynamics [12]; (ii) inclusion of shapes of solutes (cf. rigid chains) [13]; (iii) free energy perturbation methods for cavity–solvent interactions [14] and (iv) information theory model for predicting the origin of entropy convergence [15]. A comparison of different methods also has been carried out [16]. Since our objective here consists in obtaining a preliminary estimate for the influence of temperature on hydration, we employ the scaled particle theory for deducing ΔG_{cav}.

2.1. Cavity formation energy from the Scaled Particle Theory

A convenient expression arising from the scaled particle theory for cavity formation energy of solutes is as follows [17]:

$$\Delta G_{\text{cav}} = RT\left[K_0 + K_1\left(\frac{\sigma_{\text{cav}}}{\sigma_{\text{wat}}}\right) + K_2\left(\frac{\sigma_{\text{cav}}}{\sigma_{\text{wat}}}\right)^2 + K_3\left(\frac{\sigma_{\text{cav}}}{\sigma_{\text{wat}}}\right)^3\right] \tag{3}$$

wherein $K_0 = -\ln(1-\xi)$, $K_1 = \frac{3\xi}{1-\xi}$, $K_2 = \frac{K_1}{2}(K_1+2)$ and $K_3 = \frac{\xi P v}{RT}$, v being the molar volume of the solvent (water) while $\xi = \frac{\pi\sigma_{\text{wat}}^3 N_{\text{A}}}{6v}$. N_{A} denotes the Avogadro number, σ_{wat} is the diameter of water, P denotes the hydrostatic pressure (equal to one atmosphere) and R is the universal gas constant, T being the absolute temperature. In the above equation, the cavity formation energy is dictated by the molar volume of the solvent as well as the sizes of the solute and solvent.

2.2. van der Waals energies pertaining to C_{60} fullerene–water system

It is customary [18] to employ the Lennard-Jones potential for estimating the van der Waals contributions whereby

$$\Delta G_{\text{vdW}} = \sum_{i=1}^{m} \sum_{j=1 \text{ or } j=i+1}^{n} \mu(r_{ij}), \tag{4a}$$

$$\mu(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]. \tag{4b}$$

In Eq. (4a), μ_{ij} denotes the effective Lennard-Jones potential energy between i and j whose parametric dependence on the well-depth parameter (σ_{ij}) and the pair-wise interaction energy (ε_{ij}) is provided by Eq. (4b). Furthermore, the summation indices i and j refer, respectively, to the interacting components. The values for m and n are dictated by the type of van der Waals interaction being considered viz carbon–carbon, carbon–water, water–water, etc.

In the present formalism, one C_{60} (or C_{70}) molecule is surrounded by a large number of water molecules and hence the van der Waals energy is composed of (i) carbon–carbon non-bonded intra-molecular interactions $\Delta G_{\text{vdW}}(\text{I})$; (ii) carbon–water interactions within the sphere of influence $\Delta G_{\text{vdW}}(\text{II})$ and short range water–water interactions $\Delta G_{\text{vdW}}(\text{III})$.

Using Eq. (4), the Lennard-Jones contribution pertaining to carbon–carbon non-bonded interaction within the molecule is given by

$$\mu(r_{\text{c–c}}) = 4\varepsilon_{\text{c–c}}\left[\left(\frac{\sigma_{\text{c–c}}}{r_{\text{c–c}}}\right)^{12} - \left(\frac{\sigma_{\text{c–c}}}{r_{\text{c–c}}}\right)^{6}\right]. \tag{5}$$

In the above equation, $\varepsilon_{\text{c–c}}$ and $\sigma_{\text{c–c}}$ are the Lennard-Jones parameters pertaining to non-bonded carbon atoms within the C_{60} (or C_{70}) while $r_{\text{c–c}}$ denotes the distance between two carbon atoms obtained from the atomic coordinates of C_{60} (or C_{70}). Analogously, the carbon–water term is given by

$$\mu(r_{\text{c–w}}) = 4\varepsilon_{\text{c–w}}\left[\left(\frac{\sigma_{\text{c–w}}}{r_{\text{c–w}}}\right)^{12} - \left(\frac{\sigma_{\text{c–w}}}{r_{\text{c–w}}}\right)^{6}\right] \tag{6}$$

wherein the parameters $\varepsilon_{\text{c–w}}$ and $\sigma_{\text{c–w}}$ pertain to water–carbon interactions. These values are deduced from Lorenz–Berthelot mixing rules [20] using the values of $\varepsilon_{\text{w–w}}$ and $\sigma_{\text{w–w}}$ from TIP4P water model [19].

$$\varepsilon_{\text{c–w}} = \sqrt{\varepsilon_{\text{c–c}}\varepsilon_{\text{w–w}}} \quad \text{and} \quad \sigma_{\text{c–w}} = \frac{\sigma_{\text{c–c}} + \sigma_{\text{w–w}}}{2}. \tag{7}$$

However, the distance $r_{\text{c–w}}$ appearing in Eq. (6) requires a new method of estimation in view of the peculiar structure of fullerenes. The expression for $\mu(r_{\text{w–w}})$ is analogous to Eq. (5) *mutatis mutandis*. Having formulated the Lennard-Jones terms, the appropriate van der Waals energies follow after proper identification of m and n in Eq. (4a) and Table 1 provides the values of these. Scheme 1 gives a qualitative description of the methodology employed here.

Table 1
Interpretation of the summation indices m and n pertaining to each van der Waals energy contribution

Interaction term	Representation	Significance of m in Eq. (4a)	Significance of n in Eq. (4a)	Remarks
Carbon–carbon	$\Delta G_{\text{vdW}}(\text{I})$	Number of carbon atoms	Number of carbon atoms	$m = n$ (j varies from $i+1$ to n)
Carbon–water	$\Delta G_{\text{vdW}}(\text{II})$	Number of carbon atoms	Number of water molecules	$m \neq n$ (j varies from 1 to n)
Water–water	$\Delta G_{\text{vdW}}(\text{III})$	Number of water molecules	Number of water molecules	$m = n$ (j varies from $i+1$ to n)