Supporting Information

Generic mechanism for pattern formation in the solvation shells of buckminsterfullerene

Sanwardhini Pantawane\textsuperscript{a,c} Dibyendu Bandyopadhyay\textsuperscript{b}, and Niharendu Choudhury\textsuperscript{a,d,*}
\textsuperscript{a}Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400 085, India.
\textsuperscript{b}Heavy water Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.
\textsuperscript{d}Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India.

\textsuperscript{*}To whom correspondence should be addressed. Email: nihcho@barc.gov.in, niharc2007@gmail.com, niharc2002@yahoo.com

\textsuperscript{c}Present Address: Department of Physics, UM-DAE Centre for Excellence in Basic Sciences, University of Mumbai, Kalina Campus, Mumbai 400098, India
Simulation Models & Methods

The interaction potentials $U_{vv}(r)$ between two CG water molecules and $U_{uv}(r)$ between a C atom of the $C_{60}$ and a CG water molecule are shown below. The red line in Figure S1 b is the solute-solvent potential with $\lambda=0$, which corresponds to purely repulsive fullerene-water interaction and the blue line with $\lambda=1$ in the same figure is the solute-solvent potential when the interaction potential between the carbon atom of $C_{60}$ and the CG water is Lennard-Jones type (c.f. Eq. 2).

![Figure S1: Plots of (a) solvent-solvent and (b) solute-solvent potentials for the $C_{60}$-CG water system. The solute-solvent potential is between a carbon atom of the $C_{60}$ and a CG water molecule. The red line in the lower panel represents repulsive $C_{60}$-water interaction i.e. for (cf. Eq.(2) with $\lambda=0$) and the black line is for attractive $C_{60}$-water interaction (cf. Eq.(2) with $\lambda=1$).](image-url)
After the equilibration of a cubic solvent box of a particular density $\rho^*$ at a particular temperature $T^*$, the C$_{60}$ molecule was inserted at the middle of the box. All the solvent molecules overlapping with the carbon atoms of C$_{60}$ were removed. The C$_{60}$ molecule is rigid and has been held fixed at the middle of the box. The composite C$_{60}$-solvent system was equilibrated in the same way as mentioned above. Finally, a production run of $10^7$ steps were performed. Trajectories are stored at an interval of 20 steps for post processing.

RESULTS

Dissection of the first hydration shell of C$_{60}$:

We dissect first solvation shell (for $\rho^*$=0.6) further into three layers: front, middle and end, each of width 0.24 Å. The ADFs for these three layers are shown in Figure S2. It is observed that the front layer follows the same pattern as that observed in Figure 1 (main text). In this layer all the 5- and 6-memberd rings are occupied (Figure S2a) with the pattern at the hexagonal faces is triangular in shape; where as in the second layer (Figure S2b) additional solvent particles are accumulated on both the hexagonal and pentagonal faces. In the end layer however all the centers of the hexagonal faces are unoccupied (Figure S2c) and it is due to the excluded volume effect of the particles present in the previous (middle) layer.
Figure S2: The ADFs for local density of solvent particles in different regions of the first solvation shell of C_{60} at a bulk solvent density \( \rho^* = 0.6 \). The solvation shell is defined by a spherical shell around C_{60} with a radius extending up to first minimum in the C_{60}-solvent \( g(r) \) (cf. Figure 2c main text). The solvation layer is divided into three zones, front, middle and end layer depending on its position with respect to C_{60} surface. The front layer is the closest to the C_{60} surface. The ADFs in the (a) front layer, (b) middle layer and (c) end layer. The 60 carbon atoms of C_{60} are shown as black dots.
As expected the front layer is very similar to that observed in Figure 1 (main text). The middle layer has a particular pattern and the pattern in the end layer is complementary to that of the middle. It is observed that the number of particles in the front layer for \( \rho^* = 0.6 \) is around 32, the same as the number of faces on the \( C_{60} \) surface indicating that on an average each face is occupied by one solvent particle. Any additional number of solvent particles is sitting slightly away from the \( C_{60} \) center and these additional particles, which are available at higher solvent densities, are responsible for making the pattern different from that for the low density case. Comparing Figures S2a, b and c it is evident that the pattern observed in these three sub-layers of the first solvation shell is a result of complementary filling of spaces. The solvent particles at the end layer are occupying only those positions where there were no particles in the middle layer and vice versa.

![Graph showing the average number of solvent particles](image)

**Figure S3:** The average number \( <N> \) of solvent particles in a spherical shell of inner and outer radii \( r^* = 2.5 \) and 3.5 respectively around the \( C_{60} \) molecule as a function of bulk solvent density.
The average number of solvent particles in the spherical shell region between the first and the second peaks of the C\textsubscript{60}-solvent RDF are shown in Figure S3. It shows that up to the solvent density 0.16, there is almost no solvent particle between the conventional first and second solvation layers. At higher densities however the value of <N> increases. The large <N> values at \( \rho^* = 0.6 \) and above is due to the development of a new peak at \( r^* = 3.0 \) in the C\textsubscript{60}-solvent \( g(r) \) (cf. Figure 2c main text).