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Molecular Dynamics Study of Aqueous Electrolyte Solutions Near a Structured Sphere

by

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Abstract

Molecular dynamics studies of water and ions around a charged small compact globular object are described. The hypothetical molecular ion C_{60}^{---} is used as the globular model. It is found that the cesium cation is in physical contact on the spherical surface much of the time with an incomplete hydration shell. The chloride ion spends part of the time in a solvent-separated adsorption configuration and part of the time in the diffuse region. No adsorption of the sodium ion onto the spherical surface is observed.

1 Introduction

This communication describes the first molecular dynamics study of water and ions around a charged small compact globular object about 1 nm in diameter and includes accurate and efficient treatment of all electrostatic interactions. The goal of this work is to gain some basic understanding of the organization of water and ions in electric double layers around 'spherical' objects since this is relevant, albeit on a somewhat larger scale, to the microscopic environment around small colloid particles, compact proteins and polyelectrolytes. In previous studies the Poisson-Boltzmann equation for large spherical ions has been studied analytically by calculating the singlet and pair correlation function using the Ornstein-Zernike equation, as for example in the work of Henderson and coworkers [1, 2, 3, 4]. In the present article, we choose the C_{60} molecule as the prototype 'structured sphere' because it possesses a computationally manageable size and has a characterized set of interaction parameters based on a considerable number of molecular dynamics simulations [5, 6, 7, 8, 9]. This paper is not meant to be a study of actual C_{60} ions in solution.

So far, computer simulations of electrochemical double layers have been mainly performed for aqueous electrolyte solutions near flat structureless surfaces [10, 11, 12, 13, 14, 15] and flat atomically structured surfaces [16, 17, 18, 19]. From a computational point of view, flat surfaces can be thought to be spheres with infinitely large radius so that one anticipates some common features between the two types of systems. In particular the first peak in the radial distribution function of a large sphere goes over into the density probability function in the coordinate z measured along the surface normal. Likewise a contact ion pair goes over into contact adsorption (also called specific adsorption) on the flat electrode surface, though in the case of metals the electrostatic image interactions differ. Because of the surface curvature changes, one also anticipates some features that differ in each case.

2 Molecular Dynamics Method

Constant (N, V, T) molecular dynamics simulations are carried out for two dilute aqueous solutions. The first is composed of 502 ST2 water molecules [20], four sodium cations, two chloride anions, and one C_{60} molecule on which each C atom carries the charge $-e/30$ so that the total on the molecular ion is $-2e$. The second is composed of 506 ST2 water molecules, two cesium cations, and one C_{60}^{--} molecular ion. For both the cases, the simulation cell has the dimensions of $2.5054 \times 2.5054 \times 2.5054$ nm^3, and periodic boundary conditions in three orthogonal directions are used. Each simulation lasts 1 ns, with the first 200 ps being used to equilibrate the system. Detailed description of the simulation method was given in previous papers [11, 12, 13, 14, 15].

Before proceeding, we remind the reader that C_{60} or buckminsterfullerene [21] is a soccer ball-like molecule with 60 carbon atoms sitting on the vertices of a truncated icosahedron. Each carbon atom interacts with the atoms comprising the solution components through Lennard-Jones potentials and a Coulomb potential. The ion-ion, ion-carbon, and water-carbon interactions are similarly modeled. The Lennard-Jones parameters of the carbon atom are taken from Steele's work on graphite [22]. The ion-water interactions are modeled by the 12-6 Lennard-Jones function between the ion and the oxygen atom of the water and the Coulomb potentials among charged sites. The Lennard-Jones parameters of the ions are taken from Heinzinger's results [23].

3 Adsorption and Hydration

The adsorption of the ions onto the structured sphere is partially described by the radial distribution functions (RDFs), $g_{\mathrm{H_2OC60}}$, g_{NaC60}, g_{ClC60}, and g_{CsC60}. If there is adsorption onto specific sites like the hollow site of a six membered ring then simple radial distributions based on the assumed spherical symmetry will not be adequate. However they clearly represent a good starting point for initial discussions. As shown in Fig. 1, there is a distinct first hydration shell surrounding the structured sphere with its highest local density ~ 0.65 nm away from the center of mass of C_{60} and the minimum around 0.74 nm which gives a coordination number of ~ 38 for the system containing sodium and chloride ions and ~ 39 for the system containing cesium ions. The two RDFs for water are remarkably similar especially when we realize that, as will be discussed later, the RDF for Cs^+ ion shows one ion to be contact adsorbed.

The ion-C_{60} radial distribution functions indicate that the Cs^+ ion makes a contact pair whereas, in contrast, the smaller ions Na^+ and Cl^- do not and appear in diffuse regions only. We discuss the cesium cation RDF first. In Figure 1 the bottom curve shows that the RDF for Cs^+ consists of a sharp peak at approximately 0.7 nm followed by a broad diffuse region devoid of structure. The Cs^+ peak is consistent with a contact adsorbed ion because its position relative to the first water peak is equal to half the difference in the Lennard-Jones radii for water oxygen ($\sigma = 0.310$ nm) and cesium ($\sigma = 0.392$ nm). This strong adsorption tendency is not unexpected because there is a Coulombic attraction between the Cs^+ cation and C_{60}^- anion and the large size of the cation means a weaker hydration energy and unfavorable mixing entropy [24].

The RDF for chloride ion-C_{60} is broad and diffuse with the hint of a wide maximum near 0.85 nm and a weak minimum at approximately 1.05 nm. The distance of closest approach is approximately 0.65 nm, indicating that the anion occasionally touches the surface of C_{60} but does not form a stable contact pair. The broad peak in g_{ClC60} lying between the first and second peaks in the water-C_{60} RDF, g_{H_2OC60}, could be explained by some small tendency to take part in solvent-separated adsorption on the sphere. The solvent-induced interaction is attractive for the two like ions [25]. If we assume the chloride ions, whose distance from the center of mass of C_{60} is less than 1.05 nm where a weak minimum in g_{ClC60} is found, as solvent-separated adsorbing species, then the probability for such configurations would be about 26%.

The radial distribution function for the sodium cation-C_{60} in Figure 1 shows no probability for an approach closer than approximately 0.75 nm. At this point the C_{60} anion and Na^+ cation are separated by one water molecule. At the position of the first weak maximum in g_{NaC60} at approximately 0.9 nm the separation is equivalent to two water molecules. We conclude therefore that although the Coulomb interaction between the sodium ion and the C_{60} ion is attractive, the probability for observing a solvent-separated adsorption of the cation onto the anion is very small, since the cation is fully hydrated and the sodium-water interaction is very strong. By comparing the adsorption behavior of Na^+ with that of Cl^-, it is clear that the size of the ion plays a critical role in the adsorption process. Theories and many experimental results have shown that larger ionic size corresponds to a more negative entropy change and a less negative enthalpy change when the ion is transfered from nonpolar solvent to the aqueous environment [26]. In other words, large ions behave hydrophobically [27] and have a stronger tendency to be excluded from the solution.

Figure 2 describes the hydration structure of the ions through the ion-O and ion-H radial distribution functions. The central pair of plots for Na-H and Na-O in Figure 2, shows the sodium ion to be most strongly hydrated with distinct first and second shells. The hydration structures of the sodium cation and the chloride anion are not significantly perturbed by the C_{60} molecular ion and are very similar to the ions in the bulk NaCl solution [28]. On the other hand, the hydration shell of the cesium ion is not always complete and the average hydration number reduces from 8.3 in the absence of the C_{60} [28] to 7.5 in the presence of the C_{60}. The values for the first peaks of g_{CsO} and g_{CsH}, 3.4 and 2.2, in Figure 2 are much smaller than their values in the bulk solutions, that is, 4.7 and ~ 5 [28]. This significant decrease of the peak values for the Cs-O and Cs-H radial distribution functions is a consequence of the contact adsorption of the cation onto the C_{60} ion as discussed above in connection with the RDFs plotted in Figure 1.

In Figure 2 the first peak of g_{ClH} is shifted by ~ 0.1 nm, about the O-H bond length, compared with g_{ClO}. This suggests that the water molecules nearest to the anion have a preferred orientation with one O-H bond pointing directly towards the anion. For the sodium cation, the first peak of g_{NaH} is about 0.06 nm farther than the first peak of g_{NaO}. This shift corresponds to the configuration where one lone pair of the ST2 water points directly at the cation.

These conclusions concerning the orientation of water molecules in the hydration shells of the ions are confirmed by the curves in Figure 3. Here we plot the average orientations of the water molecules as functions of the distance between the oxygen atom of the water and the given ion. To measure the molecular orientation, we introduce the variable θ, which is the angle between the water dipole and the ion-O connecting line. If one O-H bond vector of the water molecule lies exactly on the line connecting the oxygen atom to the ion ($\theta = 125.25°$) or if one lone pair vector points directly towards the ion ($\theta = 54.75°$), then the average $< \cos\theta >$ would be ± 0.58. As indicated by the first two curves (from the top) in Figure 3, the water molecules surrounding C_{60} tend to be oriented with their dipoles pointing towards the center of the negatively charged sphere. Within the first hydration shell for Na^+ and Cl^-, the average $< \cos\theta >$ remains approximately constant, ~ 0.65 for sodium cation and ~ -0.6 for the chloride anion. For purposes of comparison, we note that in a bulk solution simulation without the C_{60} molecular-ion, Heinzinger and Vogel [28] found that the mean values of $\cos\theta$ are 0.69 for Na^+ and -0.65 for Cl^-. These values are slightly larger than the values obtained in this work. The orientational ordering of the water molecules surrounding the cesium ion is severely disturbed by the oppositely charged C_{60} molecular ion. If the C_{60} ion were absent, these dipoles would have their orientations similar to those of the water molecules around the Na^+ cation (the third curve in Fig.3).

4 Conclusions

The first layer of water is oriented with its dipole pointing towards the center of the 'spherical' doubly charged C_{60} anion. The cesium cation is in physical contact on the spherical surface about 10% of the time. The smaller ions occupy extensive diffuse layers around the C_{60} molecular ion. No adsorption of the sodium ion onto the spherical surface is observed. Its distance of closest approach is one water molecule, with a separation of two or more water molecules more likely. The chloride ion appears to spend part of the time in a solvent-separated adsorption configuration and part of the time in the diffusion region. The hydration structures of the sodium cation and the chloride anion are not significantly perturbed by the presence of the C_{60} molecule. The hydration shell of the cesium ion is incomplete and the orientations of the water molecules around Cs^+ are severely disturbed by the surface of C_{60}.

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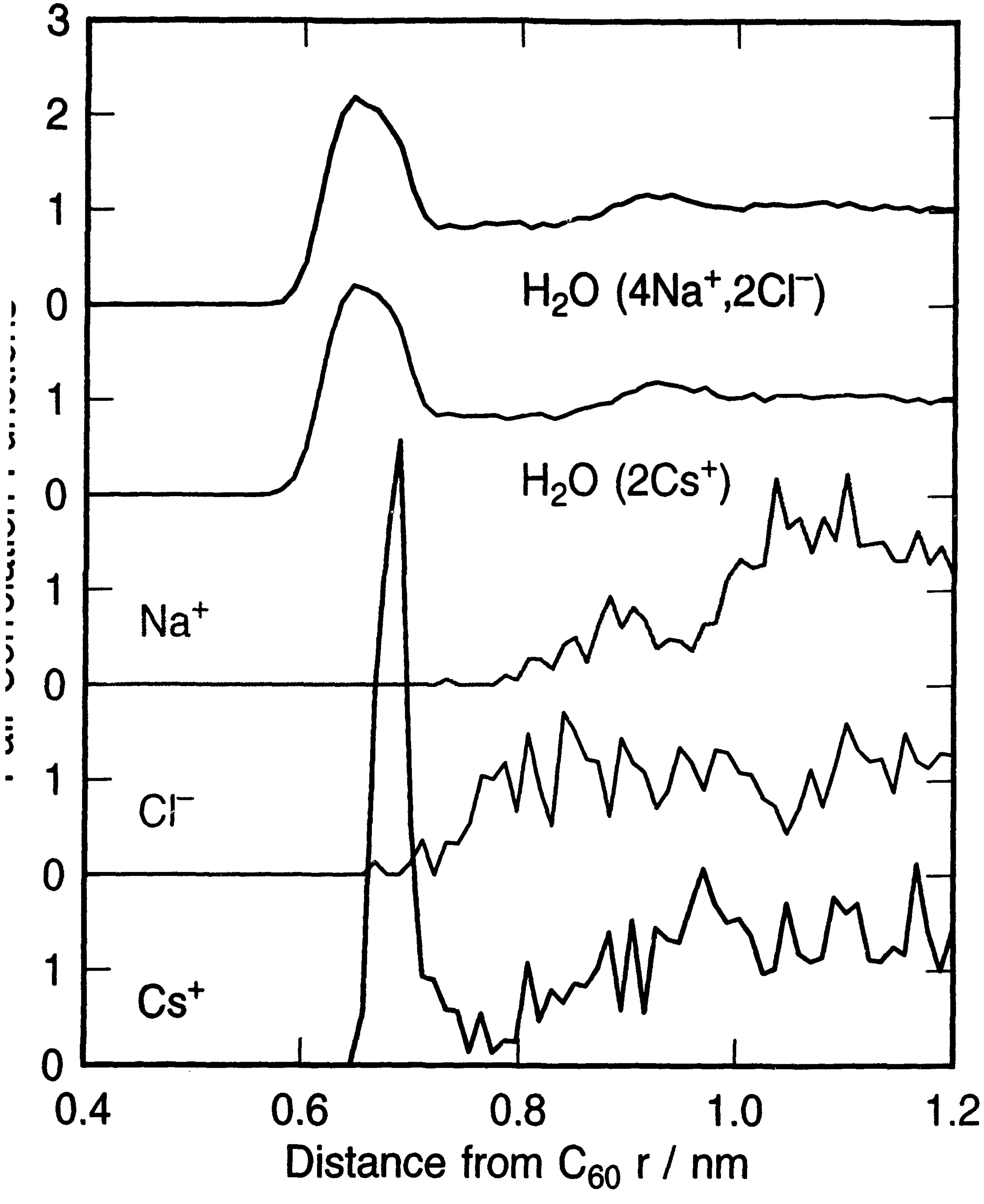
Figure Captions

Fig. 1 Radial distribution functions for water-C60 pair in the NaCl solution, water-C60 pair in the Cs solution, sodium-C60 pair, chloride-C60 pair, and cesium-C60 pair (from top to bottom).

Fig. 2 Hydration structure of the ions. The dotted curves are for ion-O radial distribution functions and the solid curves are for ion-H radial distribution functions.

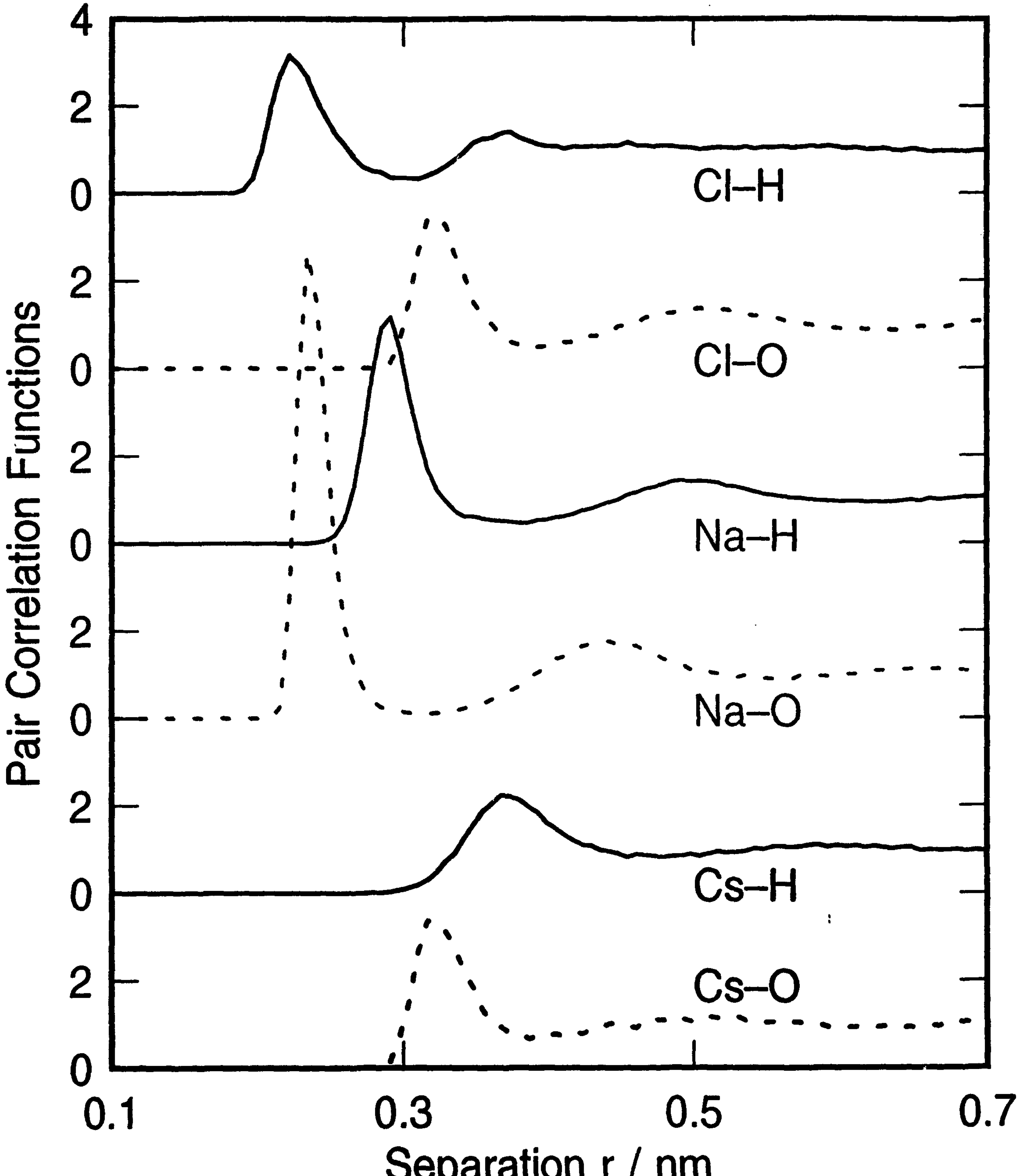
Fig. 3 Average $\cos\theta$ as a function of the distance between an ion and the oxygen atom. Curves from top to bottom represent the molecular orientations around C60 in the NaCl solution, around C60 in the Cs solution, Na^+, Cl^-, and Cs^+.

F1

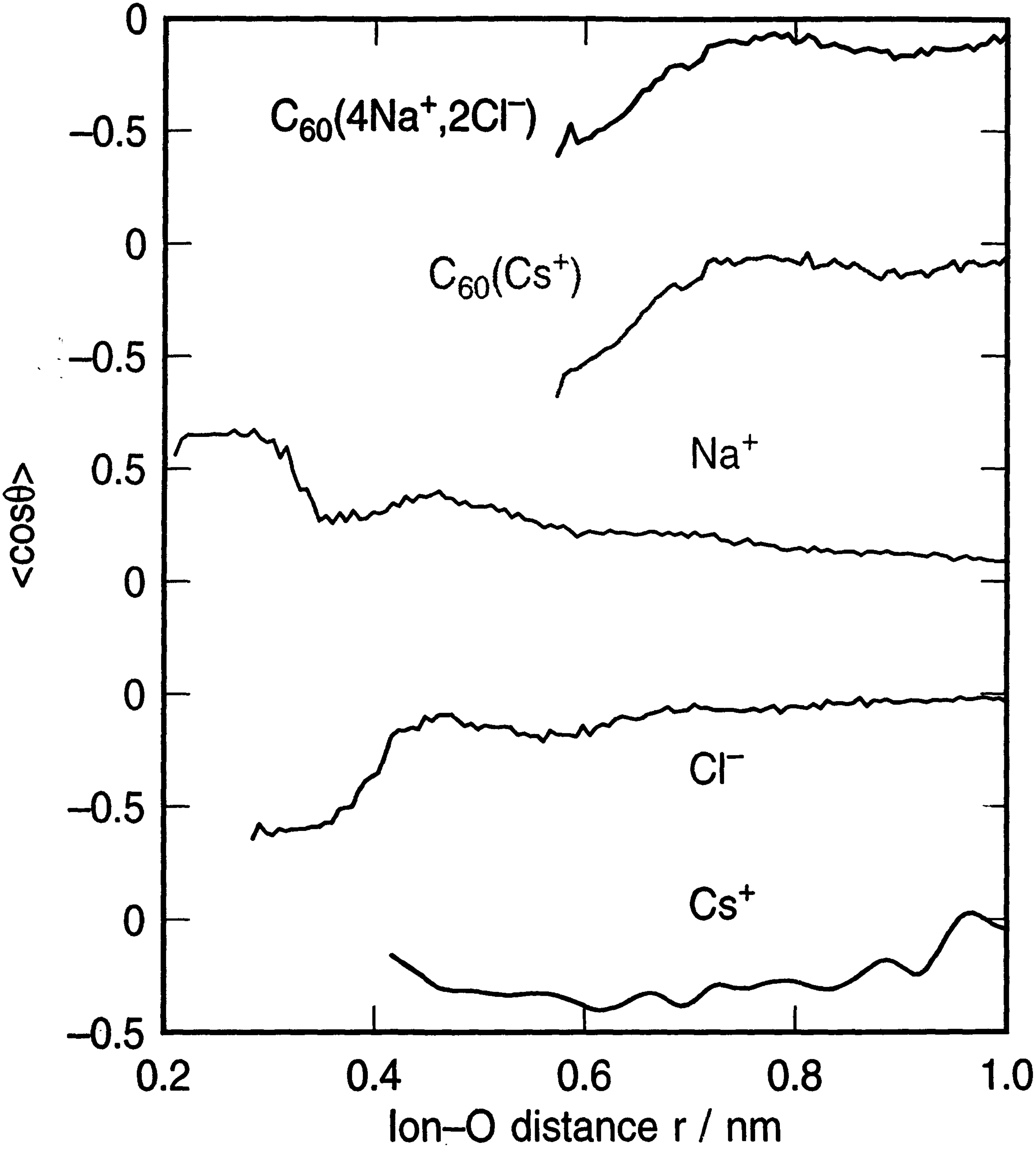


3
2
1
0
1
0
1
0
1
0
1
0
H$_2$O (4Na$^+$,2Cl$^-$)
H$_2$O (2Cs$^+$)
Na$^+$
Cl$^-$
Cs$^+$
0.4
0.6
0.8
1.0
1.2
Distance from C$_{60}$ r / nm

F2


Pair Correlation Functions
4
2
0
2
0
2
0
2
0
2
0
2
0
Cl–H
Cl–O
Na–H
Na–O
Cs–H
Cs–O
0.1
0.3
0.5
0.7
Separation r / nm

F3



0
−0.5
0
−0.5
0.5
0
0
−0.5
0
−0.5
$C_{60}(4Na^+,2Cl^-)$
$C_{60}(Cs^+)$
Na^+
Cl^-
Cs^+
<cosθ>
0.2
0.4
0.6
0.8
1.0
Ion–O distance r / nm