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Molecular Dynamics Study of a Sodium Octanoate Micelle in Aqueous Solution

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The structure of a sodium octanoate micelle, consisting of 15 monomers in aqueous solution, has been studied by molecular dynamics calculations. The micelle was found to be stable over the length of the simulation (0.2 ns). The overall size and net charge of the micelle are both in excellent accord with experimental deductions. Micellization yields an increased proportion of trans conformations in the alkyl chains. The results of our simulation of the micelle and solvent appear to offer support for studies based on more simplified models.

Introduction

The study of micelles has intensified in the past few years. On the experimental side, neutron scattering^{1,2} has proved to be a powerful complement to spectroscopic^{3,4} and magnetic resonance^{5,6} techniques in the study of micellar structure. While theoretical work on models has helped to refine the description of the internal structure,⁷⁻¹¹ a number of controversial issues remain. These include the extent to which water penetrates the core of a micelle¹² and the fraction of the carbon bonds in gauche conformations.^{10,13}

In order to help clarify some of these issues, we have embarked on an extensive series of molecular dynamics calculations. We report here on the simulation of a sodium octanoate micelle consisting of 15 monomers in 0.62 M aqueous solution using realistic interatomic potentials. Our principal finding is that the micelle is stable over the length of simulation (0.2 ns), notwithstanding the fact that there is considerable motion of individual chain molecules and without recourse to any ad hoc scaling of the interionic interactions. The overall size and the net total charge of the micelle are in excellent agreement with deductions based on neutron scattering data. Although the inner core of the micelle is devoid of water molecules, there is nonetheless considerable water penetration into the outer region of the core. The percentage of trans conformations in the alkyl chains is enhanced with respect to that found in liquid hydrocarbons, a finding which is in complete accord with experiment. While we confirm many of the results of other workers, some of our findings differ from a recently

published molecular dynamics study of the same system.¹³ Possible reasons for this are discussed.

Details of the Calculation

The interaction model employed for the simulation is similar in spirit to that employed by other workers. For the alkyl chains we adopted the carbon atom, methyl group, and methylene group Lennard-Jones potential parameters of Jorgensen.¹⁴ The head group oxygen atoms carried a charge of $-0.7 e$ and the head group carbon atom a charge of $+0.4 e$. The Lennard-Jones potential parameters for the head group oxygen were taken from the same source; they were assumed to be the same as those of the oxygen atom in alcohols. For the sodium ions we used the Lennard-Jones potential parameters of Chandrasekhar et al.¹⁵ The C-C bond lengths in the alkyl chains were held rigid by the method of constraints, and the torsional motion was followed by the same procedure as employed in the study of liquid alkanes.¹⁶ For the C-C-C bond angle potential we used the harmonic function of van der Ploeg and Berendsen.¹⁷

For the water potential we used the simple point charge (SPC) effective pair potential which gives a reasonably good account of the properties of liquid water,¹⁸ including the dielectric permittivity.¹⁹

All cross interactions were handled by combining rules. Long-range electrostatic interactions between the charges in the system were calculated by using the Ewald method.²⁰

The system size was essentially the same as in the previous work.¹³ In the present case the use of the Ewald boundary condition yields a periodically replicated system and, hence, effectively a finite monomer concentration. The system for the present calculations consists of 15 monomers and 1068 water molecules in a cubic box with a side length of 34.2 Å which corresponds roughly to a micellar solution of 0.62 M. The effective concentration of micelles is 0.042 M. Experimentally, an aggregation number of 15 ± 1 was determined at 0.60 M surfactant concentration, yielding the micellar concentration of 0.013 M with the free monomer concentration roughly at the critical micelle

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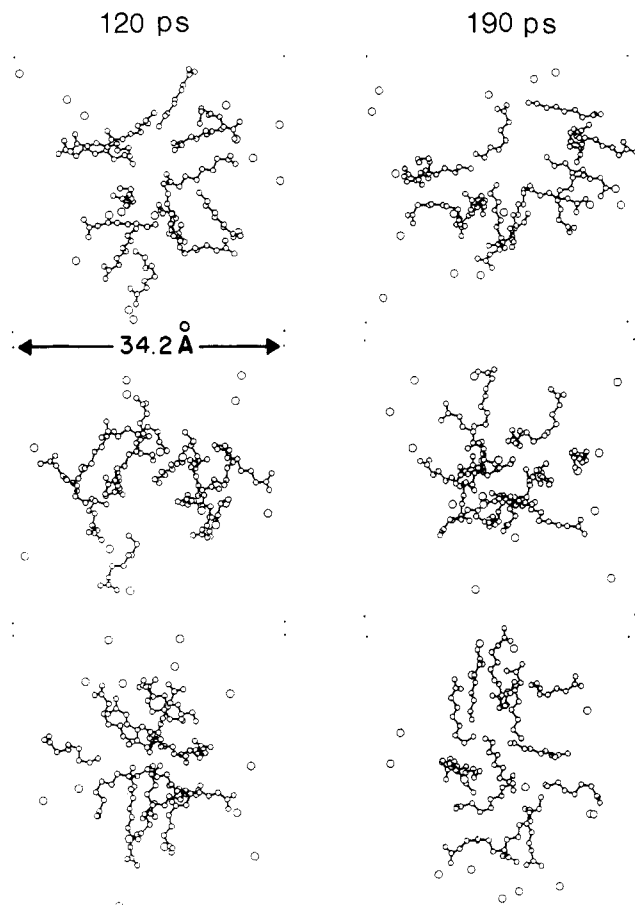


Figure 1. Instantaneous configurations of an octanoate micelle and its counterions at $t = 120$ and 190 ps as viewed from three mutually perpendicular directions. The corners of the cubic simulation box are shown as points. The solvent water molecules have been suppressed for visual clarity.

concentration, 0.4 M .¹ The intermicellar interactions in the present calculations should compare to those found in sodium octanoate solutions at somewhat higher concentration than 0.60 M .

The preparation of the system was done with some care. Initially, the core of the micelle, 15 octanoate ions, was equilibrated in the absence of solvent by constraining the head groups to remain on the surface of a sphere of a given radius. The radius of the sphere was gradually reduced until the core region achieved a density characteristic of a liquid hydrocarbon.⁸ The solvent was prepared by equilibrating a system of 1331 water molecules in a box with side length 34.2 Å . Next, the micelle was inserted at the center of the box, removing all overlapping water molecules. Finally, 15 sodium ions were substituted for an equivalent number of water molecules. The latter were chosen to be approximately on a shell of radius about 6 Å larger than that of the micelle core. The whole system was then equilibrated for 50 ps with the head groups constrained to a spherical shell of 10.8-Å radius after which the full simulation commenced. This time is referred to as $t = 0$ in what follows. The simulation was performed at $T = 300 \text{ K}$, and a time step of 2.5 fs was used. The trajectory to be discussed in this article lasted for a total of 250 ps. Analysis was mostly done on the data obtained during the last 50 ps of the simulation.

Results

The full phase space trajectory of the micelle and solvent generated a vast amount of data. In this article we focus exclusively on the micellar structure and defer until later a discussion of dynamical properties associated with the solvent. Figure 1 shows instantaneous pictures of the micelle and its counterions obtained at $t = 120$ and 190 ps; for clarity the solvent has been suppressed. It is immediately apparent that there is considerable motion of individual monomers and the micellar shape is nonspherical. Indeed, this nonsphericity persisted throughout the simulation,

TABLE I: Selected Quantities Characterizing the Micelle Solution

t , ps	$\langle PE \rangle$, ^a kJ/mol	$\langle P \rangle$, kbar	$\langle \Delta^2 T \rangle$, K ²	\bar{R}_{HG} , ^b Å	\bar{R}_{T} , ^b Å
40	-51.43	-1.16	22	12.0	7.0
60	-51.39	-1.16	29	12.2	7.0
80	-51.33	-1.23	30	11.8	7.5
100	-51.27	-1.40	19	11.9	7.1
120	-51.33	-1.25	26	12.3	6.8
140	-51.46	-1.18	21	11.8	6.1
160	-51.51	-1.07	28	12.1	6.4
180	-51.43	-1.03	24	12.8	7.6
200				13.0	7.3

^a Here, brackets denote averages over 10-ps intervals.

^b Instantaneous position of carboxylate head group oxygen atom (HG) and terminal methyl group (T) measured with respect to micelle center of mass. The bar indicates an average over 15 monomers.

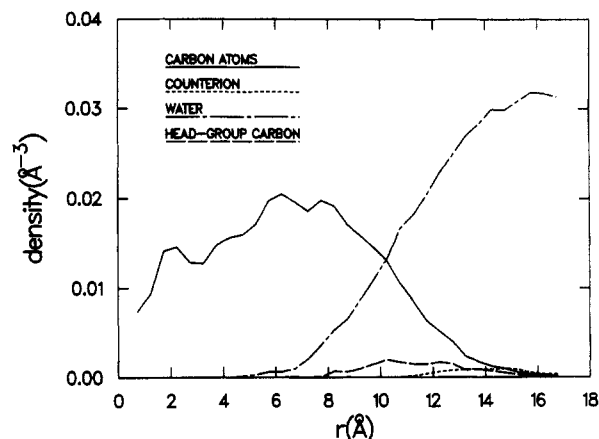


Figure 2. Density profiles with respect to the micelle center of mass, total carbon density, solvent water density, counterion density, and the head group carbon atom density. All quantities are averaged over the last 50 ps of the run.

the average ratios of the principal inertial moments being 1.7:1.5:1 during the last 50 ps of the simulation. The mean radius of the micelle derived from the positions of the head group carboxylate oxygen atoms (\bar{R}_{HG}) is $12.7 \pm 2.0 \text{ Å}$, which is larger than the value at $t = 0$ but in good agreement with the value $11.7 \pm 0.3 \text{ Å}$ derived from neutron scattering data.¹ Some indication of the diffusional stability of the micelle is given by the variation with time of \bar{R}_{HG} and the corresponding quantity for the terminal methyl group, \bar{R}_{T} . Table I shows some instantaneous values of these quantities along with thermodynamic data averaged over 10-ps segments. The entries in Table I confirm the presence of large fluctuations, but the micelle is nonetheless stable. Our choice of system (box) size has led to a small negative pressure. However, since the calculations proceeded at constant volume, this should not cause mechanical instability in the system.

Figure 2 shows the total carbon atom density profile as measured from the center of mass of the micelle. Also shown in this figure is the density profile for solvent water molecules measured with respect to the same origin. There is a considerable penetration of water into the micelle. Figure 3 compares probability distribution profiles of different carbon atoms; carbon atoms are labeled C1 through C8 counting from the head group carbon. The distribution profiles for different carbons become progressively broader from the head group to the terminal methyl group as found by previous workers.^{10,13} The average distances from the center of mass of the micelle to carbon atoms, C1 to C8 are 12.1 ± 2.0 , 11.0 ± 2.0 , 10.2 ± 2.0 , 9.2 ± 2.1 , 8.6 ± 2.1 , 7.9 ± 2.2 , 7.5 ± 2.4 , and $7.1 \pm 2.6 \text{ Å}$. A comparison of the carbon atom distributions with the water density profile (Figure 2) shows the extent of hydrocarbon-water contact for different methylene groups and the terminal methyl group. The number of water molecules within 4.0 Å of carbon atoms, C2 to C8, are 2.14, 1.60, 0.75, 0.65, 0.51, 0.50, and 0.68. The distribution of the C1 atoms is compared with the total carbon atom distribution in Figure 2.

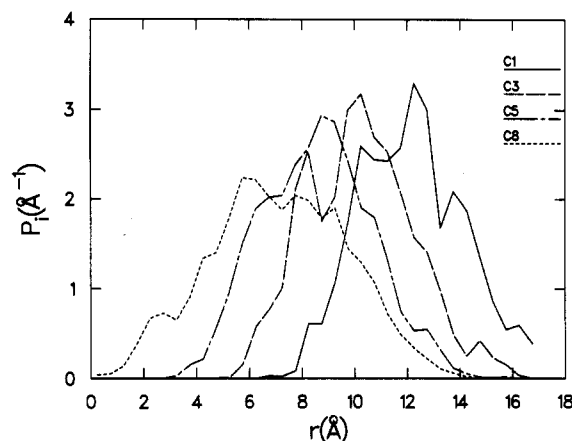


Figure 3. Probability distribution $P_i = 4\pi r^2 \rho_i(r)$ for different carbon atoms with respect to the micelle center of mass.

Our results are in excellent agreement with the work of Owenson and Pratt¹¹ which is based on a Monte Carlo investigation of a simple lattice model.

The alkyl chains comprising the micelle are, of course, continually changing their conformations. However, on average, the percentage of trans bonds was found to be $78 \pm 2\%$, a value which is significantly larger than we found for a single isolated octanoate ion, namely, $66 \pm 2\%$. Haile and co-workers¹⁰ also found an increased trans bond ratio of 72% in their thorough studies of the internal structure of micelles. Owenson and Pratt¹¹ also found that the surfactant molecules in the aggregates are stretched relative to a free-chain molecule while the lengths of hydrocarbon chain are comparatively unaffected by the aggregation into liquid hydrocarbon droplets. The result we found in our molecular dynamics simulation, however, differs from the value of 50% reported by the Lund group for the same system¹³ possibly due to their use of different dihedral potential. Experimental resonance and spectroscopic studies leave little doubt that an increased proportion of trans conformation occurs in the alkyl chains upon micellization,^{3,5,6} a result which is in excellent accord with our simulation.

Finally, we note that some of the counterions condensed to form contact ion pairs with the carboxylate head groups. Our micelle consisted of 15 monomers, and during the last 50 ps of the molecular dynamics trajectory, on average, there were 6.3 sodium ions in contact with at least one head group. Thus, the net charge of the micelle was effectively $-8.7 e$, which can be compared with a value derived from neutron scattering data of $-(10 \pm 2) e$.¹ Figure 4 shows the radial distribution function for the head group carbon and the sodium ion. There is a strong peak at 2.85 Å corresponding to the counterions in contact with the head group oxygens. A weaker peak arising presumably from the solvent-separated pairs is observed at 5.0 Å. The distribution of the counterions is also shown in Figure 2 with respect to the center of mass of the micelle. The counterions do not penetrate into the core region of the micelle along with the solvent but remain in the outer region of the micelle, strongly correlating with the distribution of the carboxylate head groups. On the average, 3.9, 6.4, and 8.4 counterions are found within 14, 15, and 16 Å, respectively, from the center of the mass of the micelle.

Discussion

We have reported on the essential structural information contained in our molecular dynamics simulation of a sodium octanoate micelle in 0.62 M aqueous solution. We find that at least on the time scale of our simulation (0.2 ns) the micelle is stable. The information on internal structure of the micelle,

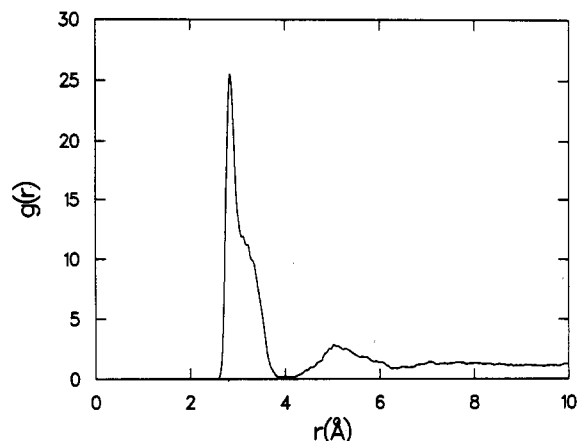


Figure 4. Sodium-carbon (head group) radial distribution function.

particularly the alkyl chain conformation, accords well with the molecular dynamics studies of Haile and co-workers,¹⁰ who did not explicitly include the solvent. The head group and the total carbon density profiles are also in remarkable agreement with the Monte Carlo results of Pratt and co-workers based on a simple lattice model.¹¹ Comparison with our results suggests that these more simplified calculations^{10,11} do indeed yield valuable and reliable information on complex systems.

In a recent study Jönsson et al. reported two simulations on essentially the same system.¹³ In one, unscaled charges were used, and in the other an ad hoc scaling of the long-range Coulombic interactions was invoked. The former calculation gave an aggregate with a very loose structure, while the latter calculation, carried out with ionic charges scaled by a factor of 2, was found to give a more compact micelle. Scaled charges were used because it was speculated that SPC water yields inadequate screening of the ionic interactions due to a low dielectric permittivity. In view of this possible difficulty with SPC water, we carried out a calculation of this quantity; we find a reasonable value, namely, 65 ± 9 .¹⁹ Such a value certainly does not justify scaling the electrostatic interactions by a factor of 4.

Although the mean radius of our micelle, measured by the averaged radial distance of head groups from the center of mass, is similar to that found by the Lund group using unscaled Coulombic interactions, their distribution functions for different carbon atoms have much broader profiles than those shown in Figure 3. Our distribution functions show distinct peaks and closely resemble in shape the Lund group's results with scaled charges. One possibility for the differences between the two calculations may be related to the difference in the treatment of the long-range Coulombic forces. The Lund group uses a simple truncation of the electrostatic interactions for distances greater than 10 Å, a procedure which means that head groups on one side of the micelle do not interact directly with those on the opposite side. In our work, the use of an Ewald boundary condition circumvents this difficulty.

In summary, we have carried out a molecular dynamics calculation on a sodium octanoate micelle and found excellent accord with available experimental structural information. The molecular dynamics trajectory also contains valuable dynamical information on this system, the analysis of which will form the basis of a forthcoming article.

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