An electrostatic investigation: how polar are ionic surfactant hydrocarbon tails?

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It is shown that a negative molecular electrostatic potential (MESP) surface completely surrounds all the atoms in any surfactant anion; further, negative MESP at the hydrocarbon ends of n-dodecanoate and n-decylsulfate is almost six times that for the n-dodecane and n-decane molecules respectively; this negative MESP build-up from the polar head group through the molecule up to the end of the hydrocarbon tail leads to finite, decreasing hydration probability along the chain.

Conventional surface-active molecules are generally amphiphilic[1] in nature with a polar head group and a hydrophobic hydrocarbon chain. They exhibit self-association in water to yield micellar solutions. A good deal of recent work is in progress for investigating micellar structures by novel experimental methods and computer simulations.[1b,c,2–6] An experimental FTIR spectroscopic study by Holler and Callis[2b] clearly demonstrated that hydrophobic portions of surfactants are not totally shielded from the water molecules as was assumed earlier. Water penetration effects and the nature of molecular interactions essential for the micellar aggregation are issues still[3–7] actively debated. MacKerell[3] has recently shown that the interaction between water and micelles involves the (sulfate) head group and that the interior of the micelle is devoid of water, although sometimes the terminal methyl group may be exposed to solvent due to chain bending. Menger[4a] concluded from his experimental results that water penetration inside the micelle is significant. Casal[4b] confirmed this result but pointed out that the central core of a micelle is devoid of water. Jönsson and coworkers[4c] confirmed by molecular dynamics simulations of sodium octanoate micelle in aqueous solution that the hydration of the carboxylate carbon is the highest, decreasing along the chain, and increasing again at the end of the chain.

Noting that micelle formation has been found[5] in hydrazine, ethylammonium nitrate, formamide and glycols, all of which possess high dielectric constants and hydrogen-bonding ability, Beesley and coworkers[6] concluded, after further experimental studies, that hydrogen bonding is a prerequisite for amphiphilic self-assembly. This seems to be the general consensus, although a noteworthy exception has been expressed by Smit and coworkers[7] who state that *explicit* hydrogen bonding is *not* essential for micelle formation.

It is not clear whether the electronic structure of individual micellar molecules is responsible for this behaviour or whether it is a property of the aggregate. A pertinent question in this connection is: How polar is the hydrocarbon tail in an isolated ionic micellar molecule in comparison to the respective paraffin? However, to the best of our knowledge, such an answer has not been forthcoming in the vast literature on surfactants and micelles.

In this communication, we present the results obtained from the topographical characterization of molecular electrostatic potential[8] (MESP) of anions. The MESP, $V(\vec{r})$, at a point $\vec{r}$ due to a molecular system with nuclear charges $\{Z_A\}$ located at $\{\vec{r}_A\}$ and electron density $\rho(\vec{r})$ is given by eqn. (1).

$$V(\vec{r}) = \sum_A Z_A/|\vec{r} - \vec{r}_A| - \int \rho(\vec{r}')\,d^3r'/|\vec{r} - \vec{r}'| \quad (1)$$

In this equation, the first term on the right hand side represents the nuclear contribution which is always positive and the second term is the electronic contribution which is negative. When the electronic contribution overrides the nuclear one, the net molecular electrostatic potential at that point attains a negative value. A large negative value of the MESP at a given point thus physically implies higher electron localization around it. MESP also represents the electrostatic interaction energy between the static (unperturbed) charge distribution of the system and a unit positive point charge located at the reference point.[8] Pathak and Gadre[9] have earlier proposed a theorem that the MESP of negative ions must exhibit a directional negative valued minimum along any arbitrary outward direction from the nuclei. From the location of these directional minima, the sizes and shapes of anions have been obtained.[9]

In this communication, we present the results of our Hartree–Fock level MESP investigations, using a 6-31G basis-set, of negatively charged gas-phase micellar molecules. For this purpose, we have selected n-dodecanoate and n-decylsulfate as test cases for a comparison with the respective hydrocarbons *i.e.* n-dodecane and n-decane. Fig. 1(a) clearly shows that the entire n-dodecanoate anion is covered by an MESP isovalued surface of value −68.28 kJ mol⁻¹ with only the carboxylate head group covered by the much larger MESP isovalued surface of value −787.64 kJ mol⁻¹ In Fig. 1(b) the isovalued surface of MESP −7.87 kJ mol⁻¹ present around the n-dodecane molecule is displayed and does not even cover the entire molecule. This

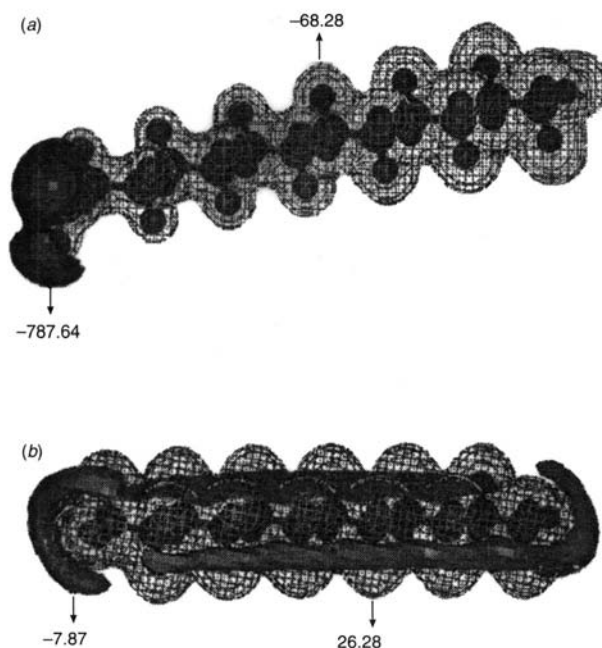**Fig. 1** (*a*) MESP isosurfaces corresponding to −68.28 and −787.64 kJ mol⁻¹ for n-dodecanoate and (*b*) corresponding to −7.87 and 26.28 kJ mol⁻¹ for n-dodecane

value is almost one tenth that for the *n*-dodecanoate molecule. The rigorously characterized MESP values at (methyl) minima and saddles for *n*-dodecanoate are -103.79 and -98.98 kJ mol^{-1} respectively. The minimum and saddle values of MESP for *n*-dodecane are only -16.54 and -12.86 kJ mol^{-1} respectively. Similarly, Fig. 2(*a*) shows that the whole *n*-decylsulfate anion is covered by a sheath of MESP isovalued surface (value -70.88 kJ mol^{-1}) and with the sulfate group engulfed by the much larger MESP isovalued surface of value -656.39 kJ mol^{-1}. From Fig. 2(*b*), it is clear that the much lower MESP isovalued surface of -7.87 kJ mol^{-1} does not even cover the entire *n*-decane molecule, but is present in patches around the molecule. This value is also approximately one tenth of that for the *n*-decylsulfate molecule. The results do depend on the basis-set to some extent but the essential topographical features are independent of the basis used.[10] Further, SCRF-model studies[11] have revealed that the anionic MESP topography is perturbed only to a small extent by water as compared to the gas-phase ones.

Thus, we have obtained an apparently surprising result that the hydrocarbon end in an anionic molecule is *much* more negative than the corresponding neutral hydrocarbon molecule.

Table 1 Typical *ab initio* water interaction energies in kJ mol^{-1} with *n*-dodecanoate and *n*-dodecane molecules, at the STO-3G basis set level. See text for details

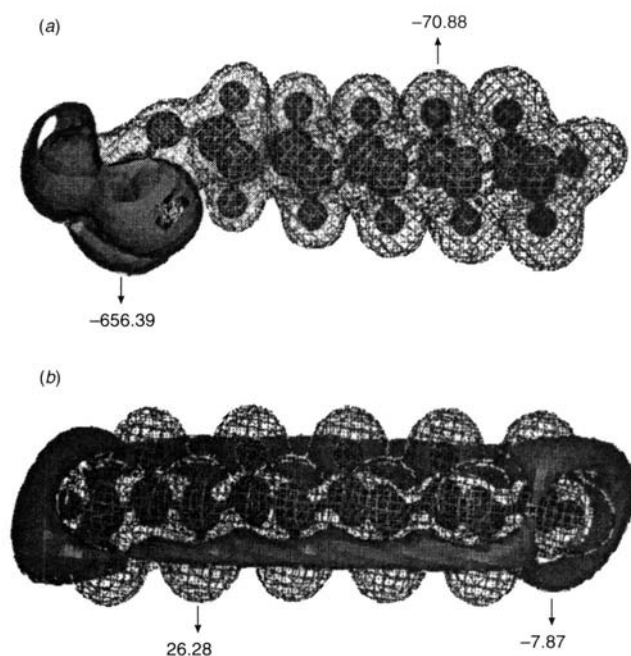| Site of water interaction	*n*-Dodecanoate	*n*-Dodecane
head-group region	-117.56	—
middle region:		
third carbon from head group	-13.59	$\left.\right\}-0.70$
fifth carbon from head group	-7.02	
tail group region	-1.99	-0.56

Fig. 2 (*a*) MESP isosurfaces corresponding to -70.88 and -656.39 kJ mol^{-1} for *n*-decylsulfate and (*b*) corresponding to -7.87 and 26.28 kJ mol^{-1} for *n*-decane

This shows a negative MESP build-up through the molecule from the highly negatively charged head group to the 'hydrophobic' hydrocarbon tail group in anionic micelles. This effect would be even more enhanced for conformations in which the tail turns around as compared to the straight models studied here, as noted by Jönsson *et al.*[4c] We have also calculated *typical* interaction energies of water with *n*-dodecanoate and *n*-dodecane employing undistorted individual molecular geometries in order to qualitatively study the repercussion of the above observations on hydration energies. For this purpose, a water molecule is rotated and translated w.r.t. the anion/hydrocarbon in a given restricted region. The results reported in Table 1, although at minimal (STO-3G) level, clearly establish the energetic significance of our MESP topographical studies. The interaction energy values results suggest maximal hydration at the polar head group with progressively lower values as one proceeds to the tail, as seen above.[3,4] Also note that the hydration energy of *n*-dodecanoate in the proximity of a tail methyl group is typically 3.5 times that for *n*-dodecane. This MESP build-up characteristic of the anionic molecule holds good for cationic surfactants as well, since any cationic molecule is always surrounded by a positive-valued MESP surface.

In summary, the 'tail' groups of isolated charged micellar molecules are fundamentally different than those in hydrocarbons. Such effects could be significant for simulating the process of micelle formation as well as hydration studies of long-chain ionic surfactants.

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