



Theoretical Study on Surfactant Adsorption of Glycine Betaine on Gas-Liquid Interface

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Glycine betaine is known as an excellent surfactant and osmolyte from organisms. To investigate the mechanism of glycine betaine, dodecyl hydroxypropyl sulfo betaine is chosen as an example to simulate its adsorption with water on gas-liquid interface by quantum chemistry. With the methods of B3LYP, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are figured out and we find that LUMO of dodecyl hydroxypropyl sulfo betaine is more likely to gather to the positive charge center. Information of hydrogen bonds, charge change and bonding energy are listed, with the suggestion that number and position of water impacts adsorption obviously.

Keywords: Glycine betaine, Surfactant adsorption, Gas-liquid interface, Theoretical study.

INTRODUCTION

Glycine betaine (GB) is widely detected in various kinds of organisms¹. As N-methyl substituted glycine derivative, they are also neutral amino acids, a zwitter ionic compound, which is reported to be stable when water molecules are added explicitly^{2,3}. Otherwise, earlier reports have focused on the function of glycine betaine as osmolytes. Glycine betaine can help to protect plants against extreme environmental stress and improve botany biomass⁴⁻⁹. Protein stability were found strengthened because of preferential exclusion from the protein surface^{10,11}. And the melting of proteins and nucleic acids also link to glycine betaine¹². The negative charge center of sulfo glycine betaine molecular structure loads with highly acid sulfo group. Strong alkali quaternary ammonium ion can equilibrate with acidic sulfo group, thus glycine betaine can coordinate with all other surfactant and have high melting point with better calcium soap dispersion^{13,14}. Some simulation studies have been arranged to investigate mechanism of glycine betaine as osmolytes and acquired some energy and dynamics data^{15,16}. But more details should be further studied.

Dodecyl hydroxypropyl sulfo sugar beets, for example, has quaternary ammonium cation and sulfonic anion which contribute to excellent surface properties, nice water resistance, good calcium soap dispersion, low irritation and obvious synergistic effect with other surfactants distribution¹⁷. For hard surface and textiles, it has high cleaning performance.

While in strong acid and strong alkali solution, glycine betaine has good chemical stability. In a wide range of pH distribution, sulfo betaine amphoteric surfactant also show outstanding foam properties and thickening effect when coordinate with other surfactant. The structure of dodecyl hydroxy-propyl sulfo betaine (DHSB) has been shown in Fig. 1.

COMPUTATIONAL METHOD

Density functional theory (DPF) has been proved accurate and efficient to study hydrogen-bonding systems. As one of the best DPF method, B3LYP had been employed in this paper. Geometry optimization of dodecyl hydroxypropyl sulfo betaine was calculated at 6-31+G(d) level. And frequency analysis was carried out to confirmed its configuration minimum point. Computation expression of binding energy D_0 is $D_0 = -\Delta E = E_{SDS} + nE_{H_2O} - E_{SDS(H_2O)_n}$. To elaborate effect of every single H_2O to hydration layer stability, we depicted linear relation diagram of D_0/n and n . Atomic charge was acquired by Mulliken by charge analysis method. All the calculation were implemented using Gaussian 03¹⁸.

RESULTS AND DISCUSSION

Molecular structure and the atomic number of dodecyl hydroxypropyl sulfo betaine has been illustrated in Fig. 1. Fig. 2 shows highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of dodecyl hydroxy-propyl sulfo betaine. In Fig. 3, the structure of hydrophilic

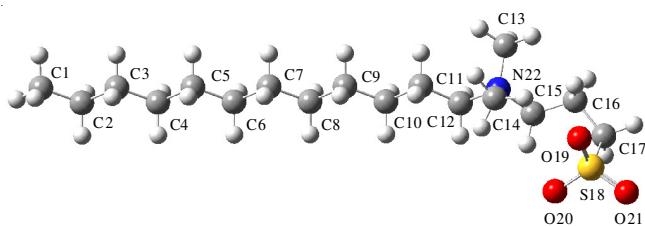


Fig. 1. Molecular structure of the dodecyl hydroxypropyl sulfo betaine and atomic number

groups surrounded with 10 water molecules and the water molecules number are given. Corresponding hydrogen bonding structure are listed in Table-1. Table-2 shows the change of total charge and atomic charge of hydrophilic groups with growth of H₂O molecules. While Table-3 shows the variation of bond length and bond angle.

Single molecular structure of dodecyl hydroxypropyl sulfo betaine: In order to explore the dodecyl hydroxypropyl sulfo betaine active site, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of surfactant were calculated (Fig. 2). HOMO of dodecyl hydroxypropyl sulfo betaine molecules are all in the sulfonic acid functional groups. Thus we suggested that the activity of the surfactant are more likely to concentrate in the sulfonic acid functional groups. Meanwhile, the LUMO of dodecyl hydroxypropyl sulfo betaine tends to gather to the positive charge center, which shows the electron affinity ability to focus more on this area.

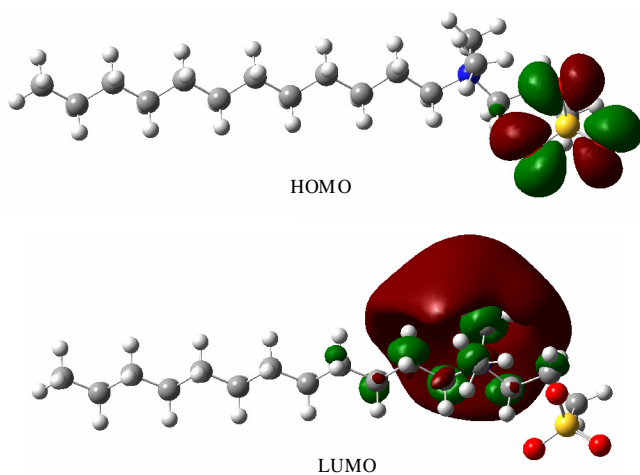


Fig. 2. Highest occupied orbital (HOMO) and did not occupy the lowest orbit (LUMO) of dodecyl hydroxypropyl sulfo betaine

Hydrogen bond formation of dodecyl hydroxypropyl sulfo betaine and H₂O molecule: Hydrophilic groups surrounded with ten water molecules is taken as an example to introduce bond formation. As is shown in Table-1, hydrogen bond length is in a range from 1.739 to 2.167 Å. Twelve H₂O which form hydrogen bond structure can be divided into two types. Oxygen atoms in hydrophilic group can be attacked by water molecules directly to form hydrogen bonds, such as W1, W2, W3, W4, W5, W6 and W7. The other kind of connection refers to the water molecules which link to the oxygen atom of other H₂O (W8, W9 and W10) (Fig. 3).

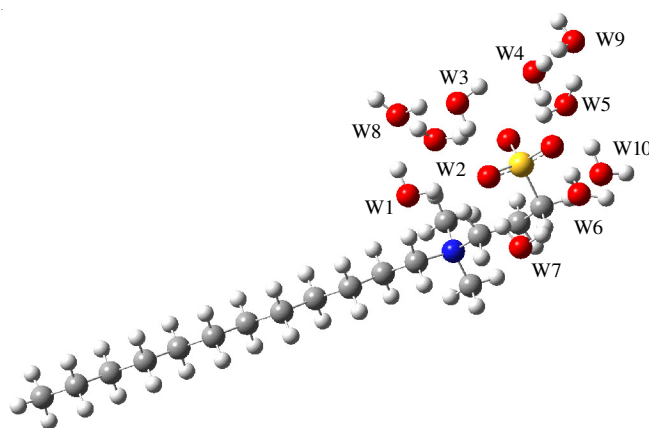


Fig. 3. Dodecyl hydroxypropyl sulfo betaine (H₂O) number 10 hydration layer molecular structure and water molecules

Comparison between two types of hydrogen bonds is clearly listed in the Table-1. We discover that hydrogen bonds length between water molecules cover a range from 1.739 to 1.858 Å, with average of 1.791 Å. While the length of hydrogen bonds which connect with hydrophilic groups are 1.773-2.167 Å, longer than bonds between water molecules with weaker force.

TABLE-1
HYDROGEN BONDING LAYER STRUCTURE

Y-H...X	Y-X	H...X
O(W1)-H...O20	2.966	2.015
O(W2)-H...O19	2.885	1.917
O(W3)-H...O20	2.943	2.003
O(W4)-H...O21	2.757	1.773
O(W5)-H...O19	2.859	1.893
O(W6)-H...O21	2.849	1.878
O(W7)-H...O20	3.024	2.167
Formation of hydrogen bonds between water molecule		
O(W8)-H...O(W3)	2.720	1.739
O(W9)-H...O(W4)	2.835	1.858
O(W10)-H...O(W5)	2.754	1.778

Charge change of hydrophilic groups and the change of the bond length of the hydrophobic groups: Table-2 clearly lists atomic charge and the total charge of hydrophilic group. The total negative charge decreased from -0.568 to -1.117. This result demonstrates that hydrophilic group is hydrogen bonding electron donor and water is the electron acceptor hydrogen bonds. Thus we get the evidence that hydrophilic group provides the interaction force between surfactant molecules and solvent molecules, when the surfactant adsorbs at the interface.

With growth of water molecules, length of C1-C12 remains about 14.085 Å (Table-3). No obvious length change has been observed in C12-N22, C15-N22, C15-C16 and C19-C17. Specific variation happens in the bond between C17 and S18. The bond length of this bond cut down from 1.843 to 1.818 Å by adding molecules. This fully shows that C17-S18 bond become stronger because of the interaction of hydrophilic group and the water on the gas-liquid interface. Otherwise, S18-O20 tends to be shorter and length of S18-O21 increase because of H₂O adding.

TABLE-2
HYDROPHILIC GROUPS OF TOTAL CHARGE AND ATOMIC CHARGE OF SODIUM DODECYL SULFATE (H₂O)_n (n = 1-10)

n	0	1	2	3	4	5	6	7	8	9	10
q(SO3)	-0.568	-0.580	-0.685	-0.702	-0.704	-0.788	-0.757	-0.950	-1.042	-1.075	-1.117
q(S)	1.468	1.541	1.551	1.580	1.578	1.556	1.570	1.414	1.309	1.362	1.150
q(O19)	-0.686	-0.688	-0.677	-0.654	-0.626	-0.600	-0.674	-0.635	-0.608	-0.691	-0.719
q(O20)	-0.710	-0.797	-0.933	-0.966	-0.932	-0.905	-0.869	-0.982	-0.903	-0.902	-0.813
q(O21)	-0.640	-0.636	-0.626	-0.662	-0.724	-0.839	-0.784	-0.747	-0.840	-0.844	-0.735

TABLE-3
CHANGE OF BOND LENGTH AND BOND ANGLE WITH THE CHANGE OF WATER MOLECULE NUMBER N

n	0	1	2	3	4	5	6	7	8	9	10
R(C1-C12)	14.085	14.089	14.085	14.088	14.084	14.083	14.084	14.085	14.085	14.085	14.085
R(C12-N22)	1.533	1.531	1.533	1.534	1.535	1.535	1.535	1.536	1.536	1.536	1.538
R(C15-N22)	1.536	1.535	1.536	1.535	1.534	1.534	1.534	1.534	1.533	1.533	1.533
R(C15-C16)	1.538	1.539	1.538	1.539	1.540	1.540	1.539	1.536	1.535	1.539	1.538
R(C16-C17)	1.535	1.536	1.535	1.536	1.538	1.537	1.536	1.537	1.536	1.535	1.536
R(C17-S18)	1.843	1.844	1.843	1.840	1.836	1.833	1.830	1.829	1.825	1.823	1.818
R(S18-O19)	1.492	1.495	1.492	1.489	1.485	1.483	1.498	1.494	1.490	1.490	1.497
R(S18-O20)	1.521	1.515	1.521	1.524	1.515	1.510	1.506	1.520	1.510	1.511	1.508
R(S18-O21)	1.474	1.475	1.474	1.475	1.488	1.501	1.493	1.492	1.509	1.505	1.507
∠(C17-S18-O19)	104.242	103.954	104.212	104.415	104.763	105.498	105.191	105.979	106.689	106.779	106.931
∠(C17-S18-O20)	103.786	103.317	103.786	103.333	103.577	104.469	105.158	105.833	106.520	106.895	107.989
∠(C17-S18-O21)	105.809	105.691	105.809	106.346	105.961	105.765	106.432	106.591	105.617	105.521	105.879

Change of the binding energy: From Fig. 4, we can find that number of molecules has strong relationship with binding energy (D_0). With the increase of the number of water molecules, the binding energy D_0 increases. With increase of the number of water molecules, the stability of the hydrate is in enhancement. However, when probing into D_0/n with change of n , we acquire falling D_0/n values, suggesting that every water molecule addition to dodecyl hydroxy-propyl sulfo betaine make the influence for binding energy increase decline. This is similar with the result of sodium dodecyl sulfate.

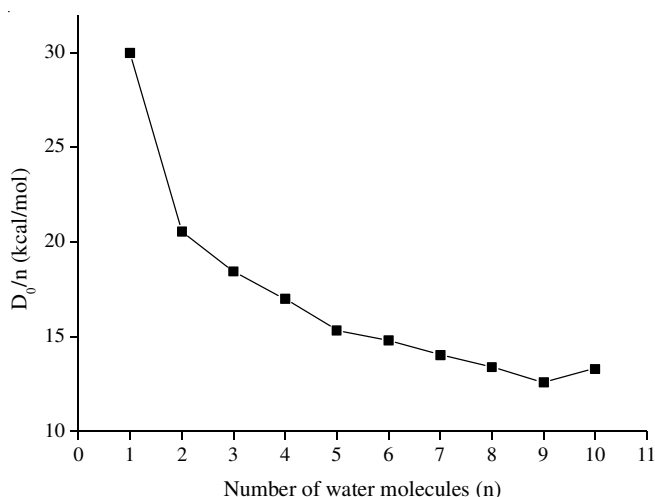


Fig. 4. Binding energy change with the increase in the number of water molecules

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