

# Quantum-Chemical Calculations of the Charge Distribution in Ionic Surfactants

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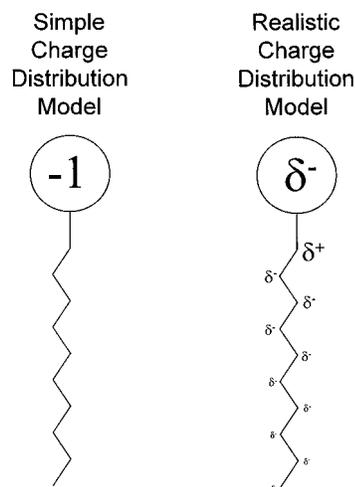
The charge distribution in common ionic surfactant molecules is estimated using quantum chemical methods. Calculations are compared for four widely accepted semiempirical methods (MINDO/3, AM1, PM3, and MNDO/d). The atomic partial charges are calculated for surfactants with linear alkyl tails and common headgroups, including anionic (sulfate, sulfonate, carboxylate), cationic (trimethylammonium, pyridinium), and amphoteric (betaine, dimethylamine oxide) classes. The headgroup charges are shown to distribute to the rest of the molecule, with significant partial charge on the  $\alpha$ -methylene group (3–40%) and a partial charge on the remaining alkyl tail (4–11%). The partial charge distribution influences surfactant self-assembly and physical properties.

## Introduction

The common feature to all surfactants is a dual chemical nature; distinct hydrophilic and hydrophobic domains exist in a single molecule, resulting in unique and useful solution properties. Many common ionic surfactants have a linear hydrocarbon chain as the hydrophobic (tail) domain and an ionic group as the hydrophilic (head) domain. It is this charged ionic headgroup that gives the surfactant molecule a certain amount of water solubility. For ionic surfactants, the entire charge is often considered to be a point charge at the headgroup, but in reality this charge is distributed over several headgroup atoms and even into the surfactant tail (Figure 1). Surfactant tails are often considered to be nonpolar and equal, not influenced at all by the headgroup, but the predicted variation in tail partial charges between surfactant classes suggests that this is not true. Modern semiempirical quantum chemical methods allow the calculation of the charge distribution within a molecule. The ability to model this charge is essential for the estimation of the electrostatic interactions between molecules. Such interactions are an important part of molecular dynamics simulations and can be shown to influence surfactant self-assembly and physical properties.

Semiempirical quantum chemical methods were developed to address problems with *ab initio* (first principle) approaches, namely, speed and accuracy. Semiempirical calculations replace the most computationally demanding terms in the quantum mechanical energy expression with empirical parameters. The time needed for calculation scales as a power of the number of atoms in the molecule, generally to the fourth power for *ab initio* methods and to the third power for semiempirical methods.<sup>1</sup> As larger molecules are considered, the time required for the calculation can quickly become prohibitive, especially for the *ab initio* methods.

The history of the development of semiempirical methods since the 1960s is a story of steady progress in method improvement, aided by a dramatic increase in computer power. For the present work the most popular and accurate approaches are used and compared. The development time line of these methods is briefly outlined here. MINDO/3



**Figure 1.** Ionic surfactants, commonly thought of as having a point unit charge at the headgroup. Quantum chemical calculations suggest that the charge is distributed throughout the molecule.

was developed in 1975 by the Dewar group and was one of the most widely used semiempirical methods.<sup>2</sup> The model had known limitations in its ability to accurately predict physical properties for molecules other than hydrocarbons. This was due to simplifying assumptions made to improve computational speed for calculations of the differential overlap of electron orbitals. To address these problems, MNDO was developed by the Dewar group in 1977,<sup>3</sup> followed by AM1 in 1985.<sup>4,5</sup> The AM1 method improved the empirical functional forms for certain repulsion terms, which led to a model that more accurately reproduced empirical data on heats of formation of a variety of molecules, especially improving on the ability of MNDO to model molecules that form hydrogen bonds. The PM3 model was developed by Stewart in 1989 to

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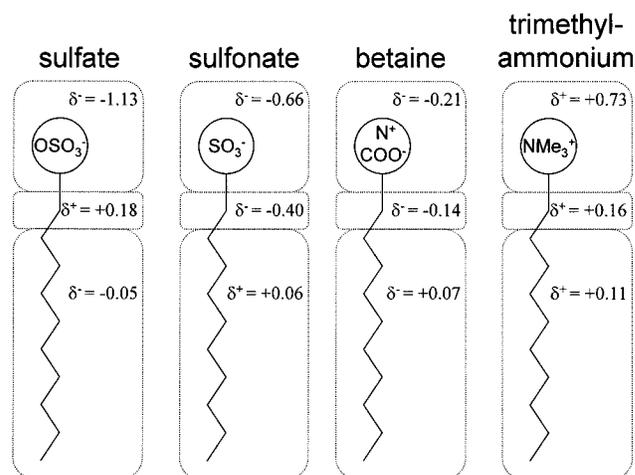
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(1) *HyperChem Computational Chemistry Manual*, Release 5.0 for Windows; Hypercube, Inc.: Gainesville, FL, 1996.

address certain limitations in AM1, changing the optimization technique for parametrization and fitting to a much more extensive database of physical properties.<sup>6-8</sup> The latest extension (1996) to MNDO, termed MNDO/d, allows better handling of d-orbital interactions.<sup>9</sup> This extension improves the calculation for second-row elements, including sulfur and phosphorus, which are present in certain anionic surfactant headgroups. The present work shows good agreement between AM1, PM3, and MNDO/d calculations in most cases.

Relatively few studies involving the application of quantum chemical methods to surfactant properties can be found in the literature. Jacobs and Anacker estimated the headgroup charge distribution in a series of isomeric decylpyridinium salts using a Hückel molecular orbital calculation and were able to correlate the micelle aggregation number to the charge on the pyridinium ring atom of attachment for the alkyl chain.<sup>10</sup> Recently, the atomic partial charge calculations were repeated using AM1, and the influence of the headgroup charge distribution on critical micelle concentration and aggregation number was reinterpreted.<sup>11</sup> Friberg et al. calculated the stability of premicellar association structures in water-in-oil microemulsion systems using the CNDO/2 method (an early method related to MINDO/3).<sup>12</sup> Villamagna et al. studied the design of surfactants for use in water-in-oil emulsions using AM1 calculations.<sup>13</sup> Gadre and Pingale calculated molecular electrostatic potential surfaces for dodecanoate and decyl sulfate, using *ab initio* calculations with a 6-31G basis set, and demonstrated that the surfactant alkyl tails have a negative charge when compared to the equivalent alkane.<sup>14</sup> Huibers et al. used AM1 calculations of the molecular dipole moment as a parameter in the prediction of the influence of molecular structure on anionic surfactant critical micelle concentration (CMC), using a quantitative structure-property relationships (QSPR) approach.<sup>15</sup>

In this study, semiempirical quantum chemical calculations of the atomic partial charges of all atoms are calculated for common surfactant types. The distribution of charge in the surfactant molecule can give insight into the electrostatic repulsion between headgroups. The characterization of this repulsion is important in understanding headgroup interactions, which is itself an important factor in surfactant aggregation structures and one of the most difficult to model.<sup>16,17</sup> The delineation between tail and headgroup can also be determined from consideration of the charge distribution. In most cases the large partial charge on the  $\alpha$ -methylene suggests that it should be considered as part of the headgroup. The presence of a partial charge on the alkyl tails of the surfactants is also predicted in the present work, sug-



**Figure 2.** Distribution of charge in selected surfactants between the headgroup, the  $\alpha$ -methylene, and the remaining alkyl tail. Charges are calculated using the MNDO/d method.

gesting the cause of micelle core polarity. It may also be suggested that all ( $C_{12}$ ) surfactant tails are not equivalent, but vary in charge due to the nature of the headgroup. The influence of the headgroup partial charge on the self-assembly and physical properties of surfactants is discussed, specifically comparing its relationship to the CMC of the surfactant.

## Methods

All calculations were performed using HyperChem 5.1 for Windows (Hypercube, Inc., Gainesville, FL). The MM+ force field was used to optimize the three-dimensional molecular geometry (bond lengths and angles) for all surfactant molecules in a linear configuration. This force field is an extension of the popular MM2 force field.<sup>1</sup> The semiempirical quantum chemical methods MINDO/3, AM1, PM3, and MNDO/d were used to determine atom-centered partial charges. These charges were combined into submolecular groups such as sulfate, sulfonate, methylene, etc. Such grouped partial charges are useful for improved understanding of the interaction between molecules and have direct application to the modeling of the electrostatic interaction energy component in molecular mechanics calculations. Though the partial charge on an atom is not a parameter that can be measured directly, charges can be derived from the electron molecular orbitals that are calculated using quantum chemical methods.

## Results and Discussion

**Partial Charge Distribution Calculations.** Semiempirical calculations of the atom-centered partial charges generate far too many numbers to be easily interpreted, so some systematic means of organization and reduction must be established. This is accomplished by combining the atomic partial charges of several atoms into submolecular groups that are expected to be meaningful to the physical properties of surfactants, as has been previously reported.<sup>11</sup> It is useful to define groups consisting of the ionic headgroup, the  $\alpha$ -methylene group (the first  $CH_2$  group of the alkyl tail, attached to the headgroup), and the remaining alkyl tail (Figure 2).<sup>11</sup> The charges for these groups are tabulated for seven common surfactant molecules in Table 1. It becomes immediately clear from an examination of these charge groupings that not all charge is present in the headgroup, but a significant fraction of the charge is distributed into the  $\alpha$ -methylene and remaining alkyl tail.

Charges are calculated using four different semiempirical methods, as previously described. MINDO/3 calculations have been used for over 2 decades and are

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**Table 1. Grouped Atomic Partial Charges for Selected Surfactants<sup>a</sup>**

surfactant	method	charge on headgroup	charge on $\alpha$ -CH <sub>2</sub>	combined HG + $\alpha$ -CH <sub>2</sub>	charge on alkyl tail
Anionic					
C <sub>12</sub> [SO <sub>4</sub> <sup>-</sup> ], sulfate	MNDO/d	-1.131	+0.185	-0.946	-0.054
	PM3	-1.066	+0.147	-0.919	-0.081
	AM1	-1.071	+0.140	-0.931	-0.069
	MINDO/3	-1.070	+0.218	-0.852	-0.148
C <sub>12</sub> [SO <sub>3</sub> <sup>-</sup> ], sulfonate	MNDO/d	-0.658	-0.397	-1.055	+0.055
	PM3	-0.640	-0.387	-1.027	+0.027
	AM1	-0.465	-0.565	-1.030	+0.030
	MINDO/3	-0.619	-0.376	-0.995	-0.005
C <sub>11</sub> [COO <sup>-</sup> ], carboxylate (soap)	MNDO/d	-0.923	-0.034	-0.957	-0.043
	PM3	-0.897	-0.062	-0.959	-0.041
	AM1	-0.894	-0.060	-0.954	-0.046
	MINDO/3	-0.787	-0.142	-0.929	-0.071
Cationic					
C <sub>12</sub> [N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> ], trimethylammonium	MNDO/d	+0.730	+0.164	+0.894	+0.106
	PM3	+0.928	-0.043	+0.885	+0.115
	AM1	+0.755	+0.132	+0.887	+0.113
	MINDO/3	+0.759	+0.098	+0.857	+0.143
C <sub>12</sub> [(C <sub>5</sub> H <sub>5</sub> N) <sup>+</sup> ], pyridinium	MNDO/d	+0.682	+0.219	+0.901	+0.099
	PM3	+0.884	+0.007	+0.891	+0.109
	AM1	+0.700	+0.187	+0.887	+0.113
	MINDO/3	+0.773	+0.091	+0.864	+0.136
Amphoteric					
C <sub>12</sub> [N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> COO <sup>-</sup> ], betaine	MNDO/d	-0.209	+0.136	-0.073	+0.073
	PM3	-0.010	-0.072	-0.082	+0.082
	AM1	-0.175	+0.099	-0.076	+0.076
	MINDO/3	-0.133	+0.050	-0.083	+0.083
C <sub>12</sub> [N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> O <sup>-</sup> ], dimethylamine oxide	MNDO/d	-0.170	+0.117	-0.053	+0.053
	PM3	+0.051	-0.112	-0.061	+0.061
	AM1	-0.138	+0.083	-0.055	+0.055
	MINDO/3	-0.075	+0.011	-0.064	+0.064

<sup>a</sup> Groups consist of head group atoms (noted by square brackets),  $\alpha$ -methylene, combined headgroup and  $\alpha$ -methylene, and the remaining surfactant alkyl tail. Semiempirical quantum chemical calculations were made using HyperChem 5.1 and MM+ geometrical optimization.

known to work well with hydrocarbons, but have problems with other atom types, and will thus have difficulty with common surfactant headgroup atoms (O, N, S). The calculations are included here for purposes of comparison to the later and more accurate methods. AM1 calculations are demonstrated to have a significant improvement in accuracy over the MINDO/3 and MNDO methods of the 1970s and have been widely used. PM3 calculations are similar in approach to AM1, with improvements in parametrization by the use of an enhanced optimization technique and a larger data set of physical properties. The MNDO/d method is the most recently developed method considered here, modifying the MNDO approach to specifically improve the handling of atoms with d-orbitals, such as sulfur.

A comparison of the results in Table 1 shows that MINDO/3 underestimates the charge on the headgroup and thus overestimates the charge on the alkyl tail in almost every case, when compared to the other methods. The AM1, PM3, and MNDO/d calculations are similar. A comparison of the mean difference in charge distributed into the alkyl tail between MNDO/d and the other three methods indicates an average absolute difference of 0.013 for PM3, 0.010 for AM1, and 0.039 for MINDO/3. The two sulfur containing surfactants (sulfate, sulfonate) have the largest difference, which is expected, as MNDO/d was specifically designed to better handle d-orbital atoms (sulfur). The differences between AM1, PM3, and MNDO/d for the five other surfactant headgroups (dodecanoate, cationic surfactants, amphoteric surfactants) are insignificant.

Several trends are apparent from the partial charge calculations (Table 1). The anionic surfactants have negatively charged headgroups and tails with ~5% negative charge, with the exception of sulfonate (5%

positive charge on the tail). The cationic surfactants have positively charged headgroups and tails with ~10% positive charge. The amphoteric surfactants have ~6% negative headgroup charges and positive tail charges of equal magnitude. In most of the cases a significant amount of the headgroup charge is distributed into the  $\alpha$ -methylene group.

**Extent of the Headgroup.** The headgroup is generally assumed to be solvated, in direct contact with water molecules, while the rest of the surfactant molecule is assumed to be in a water-free hydrophobic micelle core. Several studies modeling surfactant aggregation behavior considered the  $\alpha$ -methylene to be part of the headgroup but provided no quantitative explanation.<sup>18-20</sup> NMR data suggested that the chemical environment of the  $\alpha$ -methylene group was somewhat different from the other methylenes, possibly due to hydration.<sup>21</sup> The influence of the ionic headgroup on these methylenes can now be quantified by a consideration of the partial charge on these groups. The large partial charge that is calculated for the  $\alpha$ -methylene group supports its classification as part of the headgroup. This charge can be as large as -0.40 for sulfonate, due to the highly polar C-S bond. The charge is also significant in pyridinium (+0.22) and sulfate (+0.19) headgroups and smaller (-0.03 to +0.16) for the remaining headgroups considered here (Table 1). It is interesting to note that the charge on the  $\alpha$ -methylene may have either the same or opposite sign of the remaining headgroup.

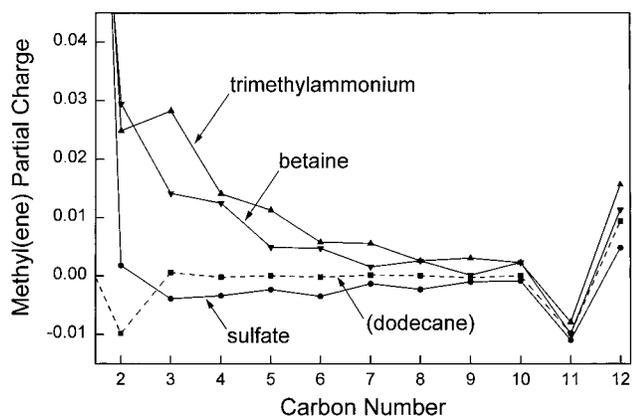
**Partial Charge on Surfactant Tail.** The prediction

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**Figure 3.** Distribution of charge along the alkyl tail for selected surfactants. Charges are calculated using the MNDO/d method. Carbon number 1 is the  $\alpha$ -methylene; carbon 12 is the terminal methyl group.

of the existence of a small charge on the surfactant alkyl tail is an interesting result to come out of this study and has broad implications in the understanding of surfactant behavior. It is commonly assumed that all of the surfactant charge lies in the headgroup and that all alkyl tails are nonpolar and equal. A partially charged tail has implications effecting the modeling of headgroup repulsion, the characterization of the polarity of the micelle core, and the nature of synergism in mixtures of different surfactant types.

Alkyl tail partial charges are estimated to be greatest in the cationic surfactants, where approximately 10% of the positive charge resides on the tail (not including the  $\alpha$ -methylene partial charge), according to MNDO/d calculations. The amphoteric surfactants are estimated to have a smaller (+5 to +7%) but partial positive charge on the tail. In both the cationic and amphoteric cases, the alkyl tail is attached to a nitrogen atom in the headgroup. Analogous to the cationic surfactants, the anionic surfactants have the same sign charge on the tail as in the headgroup, with a 5% negative charge apparent on the tail. Dodecanesulfonate is an interesting exception and is predicted to have a 5% positive tail charge (Table 1).

The partial charge distribution along the length of the tail is presented for representative surfactants from each class in Figure 3. The charge distribution in the alkane dodecane is included for comparison. All molecules show a similar positive charge for the terminal methyl group, which influences the neighboring methylene (carbon number 11) to be negative in charge. Compared to the zero charge along the length of the dodecane molecule, the anionic surfactant tail is more negatively charged, while the cationic and amphoteric surfactant tails are consistently more positively charged. In all cases, the  $\alpha$ -methylene (carbon number 1) is highly charged and off the scale in this figure.

**Polarity of Micelle Core.** The existence of a partial charge on the alkyl tails of surfactants requires a reexamination of the nature of the micelle core. In the treatment of micellar packing and solubilization, the commonly used "oil-drop" model assumes that the surfactant tails form a region that is equivalent to an alkane oil droplet. The surfactant tail packing density may differ significantly from that of an alkane if the tails have a partial charge, due to electrostatic repulsion not present in alkanes. There is experimental evidence that the polarity of the micelle interior is intermediate between alkane and water, through the use of solvatochromic dyes whose absorption spectra change with the polarity of their

environment.<sup>22</sup> Similar results have been obtained with fluorescent probe molecules.<sup>23</sup> Common explanations include such concepts as the presence of water in the core, or the partitioning of the probe molecule to the interfacial region, but it may simply be that the core is a more polar environment than alkane oils, due to the surfactant tail partial charge.

**Influence of Headgroup Charge on CMC.** The small partial charge on the tail apparently has little effect on the solubility of the molecule. It is expected that a charge of a few percent will not be sufficient to enhance the ordering of water around the tail, with the resulting increase in solubility. A greater effect is apparent from the loss of charge on the headgroup. Micelles are formed and stabilized by a balance of forces; the insolubility of the alkyl tail promotes aggregation (hydrophobic force), and the electrostatic repulsion of the ionic headgroups inhibits aggregation. The effect of a small change in the latter can be seen in experimental data for the critical micelle concentration (CMC) as a function of surfactant class and length of the alkyl tail.

It is well-known that the CMC has a strong dependence on the alkyl chain length ( $N_c$ ) of a surfactant and has been described by eq 1.<sup>24</sup> In this equation,  $A$  varies widely

$$\log \text{CMC} = A - B(N_c) \quad (1)$$

and depends on the headgroup, temperature, and type of counterion.  $B$  is approximately 0.3 for anionic and cationic surfactants and  $\sim 0.5$  for nonionic surfactants, as summarized by Rosen.<sup>25</sup> The coefficient  $B$  represents the contribution of each methylene group in the lowering of CMC by the tail. It is well-known that nonionic surfactants have a much lower CMC than ionic surfactants of equivalent alkyl chain length. This clearly indicates that the electrostatic repulsion between ionic surfactant headgroups plays an important role in micelle formation and monomer solubility. For this study, the Klevens rule (eq 1) was reexamined for surfactants of  $N_c = 10-18$ , taken from the best available CMC data,<sup>15,25</sup> to allow more precise calculation of the  $B$  term, including the error (at 95% confidence interval,  $2\sigma$ ). The  $B$  values were calculated to be as follows: betaine,  $0.510 \pm 0.020$ ; amine oxide,  $0.486 \pm 0.054$ ; trimethylammonium,  $0.313 \pm 0.008$ ; pyridinium,  $0.309 \pm 0.016$ ; sulfate,  $0.289 \pm 0.004$ . Surfactants with alkyl tails shorter than 10 carbons were not included, as a deviation from the Klevens rule is apparent in some cases. This may be due to the inherently high CMC values for these shorter surfactants, with correspondingly high solution ionic strengths at CMC, resulting in a partial shielding of headgroup repulsion that is not present for the other surfactants in the family (that have longer alkyl tails and thus lower CMC's). Inclusion of such high CMC values does not provide an accurate representation of the incremental contribution of the methylene group to CMC.

Taking advantage of the difference in the magnitude of the tail charges between the anionic and cationic surfactants and the accuracy of the revised Klevens rule estimates, a correlation is apparent between the  $B$  term and  $q^2$ , the square of the headgroup charge (including the  $\alpha$ -methylene). A best linear fit results in the following relation.

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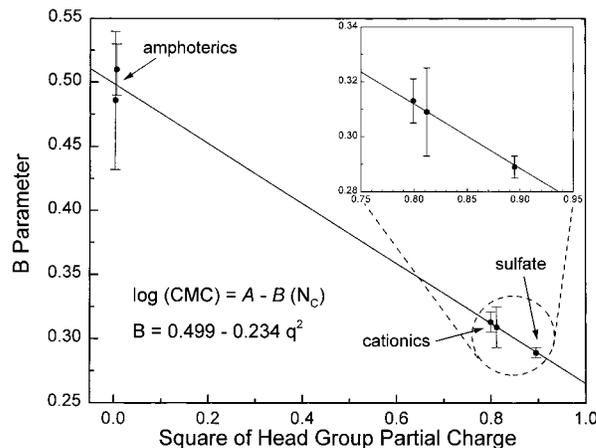
$$B = (0.499 \pm 0.007) - (0.234 \pm 0.011)q^2 \quad (2)$$

The term  $q^2$  represents the electrostatic repulsion between headgroups, the force counteracting micelle formation. Figure 4 shows that  $B$  is influenced by the charge on the headgroup, as  $B$  increases with decreasing headgroup charge. For the cationic surfactants, the value of  $q^2$  is slightly lower and  $B$  is slightly higher than for the anionic surfactants, and the inset (Figure 4) suggests that this increase in  $B$  is statistically significant. In the balance of forces present during micelle formation, it is clear that the ability of alkyl tails to lower CMC is not constant but depends on the magnitude of the charge on the attached headgroup. A larger value of  $B$  indicates that each additional methylene group has a greater effect in lowering the CMC, implying that the headgroup is not playing as strong a role in countering the tail insolubility. For the case of nonionic surfactants, where there is essentially no headgroup charge,  $B$  is large, falling in the range of 0.48–0.51,<sup>25</sup> similar to the value seen for the amphoteric surfactants, which have a low headgroup charge of  $-5$  to  $-7\%$ . This dependence is clear experimental evidence of the influence of surfactant charge distribution on molecular self-assembly.

Insufficient CMC data are available in the literature to derive accurate Klevens rule parameters for the carboxylate surfactant class. This may be due to the pH dependence of the equilibrium between ionized and nonionized carboxylate (fatty acid) components, as mixtures complicate the CMC measurement process and interpretation. The CMC data for the sulfonate class are not of the same quality as those for the other classes, resulting in a large error in  $B$ . The sulfonate case is apparently an outlier in the relationship (Figure 4) between  $B$  and  $q^2$ , possibly due to the unusual nature of the charge distribution within this molecule. This is not surprising, as this surfactant is the one exception among anionic and cationic surfactants, having a tail with charge opposite that of the head. It is also the surfactant with the largest partial charge on the  $\alpha$ -methylene group, due to the polarity of the C–S bond. The value of  $q^2$  calculated for sulfonate by simply summing headgroup and  $\alpha$ -methylene group charges is greater than 1. To fall on the line, it must be lower, suggesting a more complicated headgroup interaction for sulfonates than can be modeled by this simple  $q^2$  calculation. If the charge repulsion contribution from the headgroup and  $\alpha$ -methylene were handled differently, for example as a sum of squares rather than a linear sum of charge contributions, the value of  $q^2$  would be much smaller, and the sulfonate point would fall closer to the linear relationship seen for the other surfactants.

**Future Work.** It is of interest to extend this study to examine quantum chemical calculations with the solvation models presently under development. The “gas phase” calculations presented here reveal the native electronic distribution within the surfactant molecules, unperturbed by external interactions. These calculations allow for a comparison between different surfactant types.

Modeling the solvent environment is an extremely complex task, and solvation models have been developed that represent the solvent as a continuous medium of certain dielectric strength. These calculations are much faster than models of discrete solvent molecules and have been shown to be accurate for many cases. Such models may easily handle the characterization of the solvent environment for a surfactant monomer in aqueous solution. No model is currently available that will handle the solvation environment for a surfactant molecule incorporated into a micelle. Such a model would be of value as



**Figure 4.** Headgroup total charge, an influence on the CMC dependence on the alkyl tail. The  $B$  parameter from the relationship  $\log \text{CMC} = A + BN$  is plotted vs the square of the total headgroup charge (including the  $\alpha$ -methylene). Charges are calculated using the AM1 method.

it is clear that the surfactant molecule in a micelle does not experience a uniform solvent environment. It is well-known that the headgroup is in contact with water and surrounded by some fraction of the counterions, and the alkyl tails should be in the dehydrated micellar core. Modeling this extreme “solvation” gradient along the length of the surfactant molecule is beyond the ability of available computational tools. The state of development for solvation models is still in flux, and future improvements in both model ability and computational speed should allow one to address systems as complex as surfactant micelles.

It is expected that the influence of solvation on the molecular charge distribution may perturb charge distributions locally in the molecule but will not change the overall distribution between the headgroup and the tail, from which these conclusions are derived. It will be worthwhile to revisit these calculations in the future with solvation models, to determine the perturbation to the molecular charge distribution of the surfactant molecule caused by extremes in possible solvation environments.

## Conclusion

The charge distribution in common surfactant molecules has been estimated using semiempirical quantum chemical methods. Calculations are compared for four widely accepted methods (MINDO/3, AM1, PM3, and MNDO/d). The atomic partial charges are calculated for surfactants with linear alkyl tails and common headgroups, including anionic (sulfate, sulfonate, carboxylate), cationic (trimethylammonium, pyridinium), and amphoteric (betaine, dimethylamine oxide) classes. The headgroup charges are shown to partially distribute to the rest of the molecule, with significant charge on the  $\alpha$ -methylene group and a partial charge on the remaining alkyl tail. The variation in tail partial charge with headgroup suggests that all surfactant alkyl tails are not equal, and potentially explains the polarity of micelle cores. Headgroup charge repulsion influences self-assembly processes, which is apparent from a correlation of the headgroup charge to the methylene group contribution to CMC for different surfactant classes.