Registry No. DPC, 102-09-0; DPP, 778-22-3; $HCO_2C_6H_5$, 1864-94-4; $HO_2COC_6H_5$, 13932-55-3; bisphenol A polycarbonate (SRU), 24936-68-3; bisphenol A polycarbonate (copolymer), 25037-45-0.

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Head–Head Interactions in Zwitterionic Associating Polymers

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ABSTRACT: Theoretical calculations are presented, both at the molecular mechanics empirical level and at the Hartree–Fock semiempirical level (MNDO), on molecules containing (ammonioalkyl)sulfonate zwitterions as models for semitelechelic associating polymers. In particular the interactions between the zwitterionic head groups and the evolution of the energetics and structures of the molecules are examined as a function of their aggregation. The clustered zwitterions adopt an extended (all-trans) conformation with their dipoles aligning in an antiparallel fashion in order to favor interchain electrostatic interactions. For large aggregation numbers in apolar solvents, associating polymers with zwitterionic head groups are predicted to form reverse micelles that possess either a tubelike or a disklike structure. Spherical structures are not energetically favorable. The excluded-volume interaction of the long hydrocarbon tails in the semitelechic polymers is expected to favor the tubelike structure.

I. Introduction

Associating polymers[1-7] have attracted considerable interest because they exhibit a number of unique rheological properties in dilute and semidilute solutions, an example being shear thickening.[8-11] Associating polymers consist of long-chain polymers containing a small fraction of strongly associating side groups. Ionomers are one well-studied example.[1-5] Since structure–property relationships for associating polymers are not fully established, it is important to study structurally simplified materials in order to clarify some of the fundamental issues. Recently, Fetters et al.[12,13] have followed that approach and have reported the synthesis and rheological properties of "semitelechelic" polyisoprenes, where long, flexible polyisoprene chains are capped at one end by an (ammoniopropyl)sulfonate zwitterion (see Figure 1). In aliphatic hydrocarbon solvents such as cyclohexane, light-scattering, osmometry, and viscometry experiments give clear evidence of association of the zwitterion groups, i.e., for (reverse) micellization.[12] The characteristic aggregation number is typically on the order of 5–30 and depends strongly on the molecular weight of the long polyisoprene tails. The aggregation number is smaller in aromatic and moderately polar solvents and decreases rapidly with small additions of alcohol.[12]

The conformational properties of these associating polymers in nonpolar solvents are influenced by the competing tendencies coming on the one hand from the lipophobic associating groups which want to aggregate and on the other hand from the long hydrocarbon regions which want to avoid one another. Standard methods of polymer theory have been employed to treat the excluded-volume interaction between tails for the case of spherical clusters.[14-16] However, since there is no precise information concerning the stereochemistry of the zwitterionic head groups, it is not straightforward to formulate a good description of their aggregation. Such a description has up to now been based on rather simple models, for instance the liquid drop model,[17] which assume spherical symmetry and do not take into account the detailed nature of the head–head interactions.

Our purpose in this work is to provide some theoretical insight into the interactions between the zwitterionic head groups (energetics and structure) in order to help refine the aggregation models for this type of associating polymer. We note that the systems considered here are quite dif-

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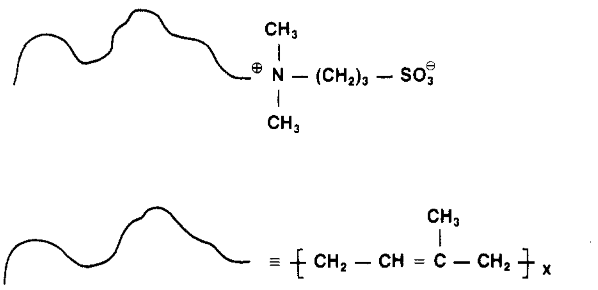


$$\equiv \left[CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH_2 \right]_x$$

Figure 1. Sketch of a semitelechelic associating polymer capped by a zwitterionic end group: polyisoprene capped by an (ammoniopropyl)sulfonate group.

ferent from those comprised of surfactants in aqueous solution, because the solvent has a dramatically lower dielectric constant and in general exerts much less influence on the effective interactions between head groups (the electrostatic forces between zwitterion dipoles can therefore be estimated without taking into account any details of the solvent structure). Furthermore, we also note that the clustering in associating polymers containing long hydrocarbon chains headed by zwitterionic groups is expected to be significantly different from that occurring in ionomers.[1-5] Indeed, in the latter case, only one ionic species is covalently bound to the polymer chain (usually at multiple sites) and the counterion is rather free to move in order to adopt the lowest energy configuration.[18]

In section II we briefly present the methodology used to optimize the conformation of interacting zwitterions in associating polymers of the kind reported by Fetters et al.[12,13] We discuss in section III the results of theoretical studies on the conformation of monomers, dimers, and tetramers of (ammoniopropyl)sulfonate zwitterions with hexyl chains taken as models for the hydrocarbon tails. In order to investigate the influence of the separation between the positive (ammonio) part and the negative (sulfonate) part of the zwitterion, we have also studied the conformations of compounds containing (ammoniomethyl)sulfonate and (ammoniobutyl)sulfonate zwitterions. Results on the latter two systems are discussed in section IV. The implications of these results for larger aggregates are presented and discussed in section V.

II. Methodology

The molecules under investigation are sketched in Figure 2. They correspond to [(dimethylhexylammonio)*propyl*]sulfonate, [(dimethylhexylammonio)*methyl*]sulfonate, and [(dimethylhexylammonio)*butyl*]sulfonate. The zwitterions are thus located at the end of a hydrocarbon tail represented in our models by a hexyl group. Our initial targets are the relative energies and structures of monomers, dimers, and tetramers of those molecules. We first study the monomer by means of both molecular mechanics (MM)[19] and Hartree–Fock semiempirical modified neglect of diatomic overlap (MNDO)[20] techniques. Due to their sizes, the dimers and tetramers are studied exclusively with the MM method.

The molecular mechanics method is based on the use of empirical energy functions. Its usefulness to investigate the physical properties of a wide variety of large molecules has been demonstrated in recent years.[21-24] We have used the MM technique as developed for the Chem-X set of programs.[25] The total energy of the molecule is expressed in the form

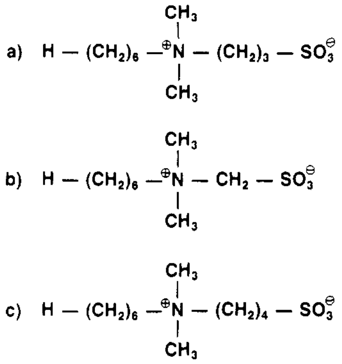
$$E = E(l) + E(a) + E(t) + E(\text{pol}) \qquad (1)$$

where $E(l)$ is the bond stretching term, $E(a)$ is the bond angle bending term, $E(t)$ is the torsion angle term, and

a)

b)

c)



$$\text{a)}\ H-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}-(CH_2)_3-SO_3^{\ominus}$$

$$\text{b)}\ H-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}-CH_2-SO_3^{\ominus}$$

$$\text{c)}\ H-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}-(CH_2)_4-SO_3^{\ominus}$$

Figure 2. Chemical structure of the molecules investigated in this work: (a) [(dimethylhexylammonio)propyl]sulfonate; (b) [(dimethylhexylammonio)methyl]sulfonate; (c) [(dimethylhexylammonio)butyl]sulfonate.

$E(\text{pol})$ is the nonbonded interaction term. The contribution to energy due to bond stretching takes the form

$$E(l) = K(l' - l)^2 \qquad (2)$$

where K is a constant, l' is the standard bond length, and l is the observed bond length. $E(a)$ is calculated in the following way:

$$E(a) = K_a(\theta' - \theta)^2 \qquad (3)$$

where K_a is a constant and θ' and θ are the standard and observed bond angles, respectively. The torsion angle term contribution is

$$E(t) = K(t)(1.0 - \cos [n\omega]) \qquad (4)$$

where $K(t)$ is a constant, n is the number of barriers to rotation, and ω is the torsion angle. The nonbonded interaction term is expressed as

$$E(\text{pol}) = V_1V_2\{[(R_1 + R_2)/r]^{12} - 2[(R_1 + R_2)/r]^6\} + \{KQ_1Q_2/r\} \qquad (5)$$

where V_1, V_2, R_1, and R_2 are constants for each atom type pair, r is the separation between each atom pair, K is a conversion constant, and Q_1 and Q_2 are the partial atomic charges. This nonbonding interaction energy contribution is similar to that used by Allinger in his MM2 program.[26]

All the parameters, which depend on the atom and the type of bonding, are taken as standard parameters from Chem-X.[25] In all instances, we fully optimize the geometry without any constraints. Note that the MM program requires the formal charges to be explicitly indicated. We have therefore located a (+1) charge on the nitrogen and a $(-^1/_3)$ charge on each of the oxygens of the sulfonate group. Note that we are not taking into account any solvent effect in our calculations. We believe, however, that the conformations of aggregated states in nonpolar solvents will be reliably predicted.

In order to check, at least on the monomers, the validity of the MM geometry optimizations and to obtain the electronic wavefunctions, we have performed quantum-chemical calculations based on the MNDO technique. This method has a well-established record of reliably predicting the geometry of organic molecules.[27,28] One important aspect of the MNDO scheme is that it finds self-consistent-field solutions to a Hartree–Fock hamiltonian containing the kinetic term, the nuclear attraction term, and the nonlocal exchange and Coulomb repulsion terms. All valence electron interactions are included. The computational feasibility of applying the method to relatively large molecular systems comes from neglecting certain selected sets of multicenter integrals and param-

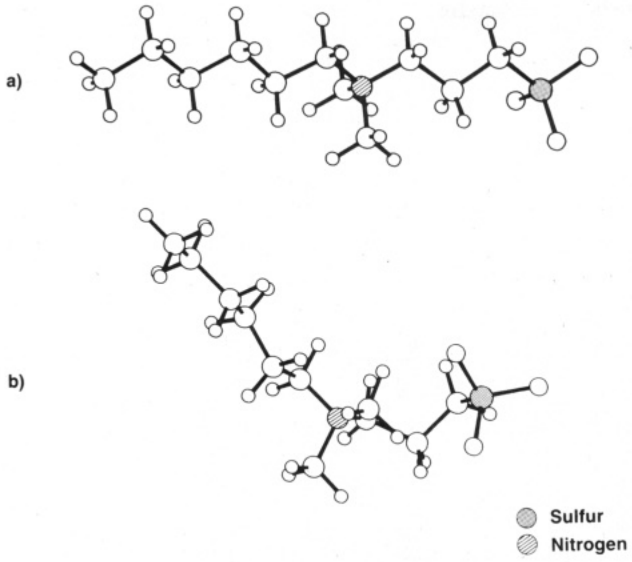


Figure 3. Perspective views of MM-optimized conformations for the [(dimethylhexylammonio)propyl]sulfonate monomer: (a) extended conformation; (b) curled conformation.

eterizing some of the remaining ones. The method is semiempirical in the sense that the parameterization of complex integrals is carried out to optimize the predictive capabilities of the technique for molecular geometries and heat of formation. In effect, the parameterization builds in some allowance for the electron correlation neglected by Hartree–Fock theory.

III. Results and Discussion for (Ammoniopropyl)sulfonate Zwitterion

(a) Monomer. For the monomer of the (ammoniopropyl)sulfonate system, we find two conformations which have high stability. In both situations, the hexyl section assumes an all-trans conformation. The zwitterionic part is found either to be fully extended (all torsion angles along the backbone being about 180°) or to be curled. The two situations, as optimized via MM calculations, are illustrated in Figure 3. At the MM level, the curled conformation is found to be about 6.3 kcal/mol more stable than the extended conformation (−18.7 with respect to −12.4 kcal/mol). The MNDO geometry-optimization results are very similar; they yield a 7.9 kcal/mol stability difference in favor of the curled conformation.

In Table I, we present a comparison of the most significant bond distances, bond angles, and torsion angles as optimized via MM and MNDO techniques for both extended and curled (ammoniopropyl)sulfonate monomers. There are two major discrepancies between the MM and MNDO sets of results relating to the carbon–nitrogen and carbon–sulfur bond lengths. The C–N bonds are calculated on the order of 1.45 and 1.55 Å with MM and MNDO, respectively. The MM C–S bonds are also about 0.1 Å shorter than their MNDO counterparts: 1.74 Å compared to 1.88 Å. There are several ammonio sulfonate salts whose crystal structures are known: (isopropylammonio) sulfonate,[29] (trimethylammonio) sulfonate,[30] and [methyl[2-(3,4-dihydroxyphenyl)ethyl]ammonium 2-sulfonate.[31] (To the best of our knowledge, no crystal structure has been reported to date on ammonio sulfonate salts having more than two methylene units between the nitrogen and the sulfur.) In these compounds the C–N bonds are measured from X-ray diffraction experiments to lie between 1.48 and 1.55 Å and the C–S bonds between 1.77 and 1.84 Å.[29-31] These experimental values are thus intermediate between our calculated values, the MM bond lengths being on the low side and the MNDO bond lengths on the high side.

Table I

Comparison of Selected Atomic Distances, Bond Angles, and Torsion Angles for the Extended and Curled (Ammoniopropyl)sulfonate Monomers, As Optimized at the MM and MNDO Levels[a]

	MM		MNDO	
	extended	curled	extended	curled
C5–C4	1.522	1.525	1.555	1.555
C6–C5	1.516	1.516	1.558	1.558
N7–C6	1.456	1.456	1.558	1.559
C8–N7	1.459	1.455	1.577	1.572
C9–C8	1.513	1.513	1.553	1.556
C10–C9	1.518	1.520	1.527	1.531
S11–C10	1.749	1.735	1.886	1.876
N7–O1	5.21	3.84	5.63	3.97
N7–O2	5.49	3.95	5.67	4.37
N7–O3	6.40	5.46	6.68	5.89
N7–C6–C5	112.1	114.4	117.7	117.5
C8–N7–C6	106.3	107.1	105.7	105.3
C9–C8–N7	111.6	116.3	116.4	117.7
C10–C9–C8	111.9	110.2	111.4	114.6
S11–C10–C9	109.9	114.8	111.6	115.7
N7–C6–C5–C4	179.7	164.5	179.7	183.5
C8–N7–C6–C5	−177.7	−169.5	179.0	−179.3
C9–C8–N7–C6	170.4	159.9	175.4	180.4
C10–C9–C8–N7	166.8	−97.9	172.1	−134.1
S11–C10–C9–C8	−166.3	103.3	188.5	73.8

[a] The backbone atoms are numbered from 1 to 11 starting from the hydrocarbon tail end and ending with the sulfur atom; oxygen atoms are numbered 1 through 3. The atomic distances are given in angstroms and the angles in degrees.

Despite these bond-length differences, both techniques afford a very similar picture for the overall molecular conformation. In the most stable curled conformation, two of the oxygens are significantly closer to the nitrogen than the third one. The shorter N–O distances are about 3.9 Å and the longer one about 5.5 Å. The same situation prevails in the extended conformation but with much longer N–O distances: two at 5.5 Å and one at 6.5 Å. Thus, the larger stability of the curled configuration is mostly due to strong intramolecular electrostatic interactions.

From the wavefunctions provided by the MNDO results, we observe that the highest six occupied molecular orbitals correspond to the oxygen lone pairs. In the curled conformation, those levels lie between −9.47 and −8.71 eV. The electronic level immediately below the lone pair levels lies at −12.96 eV and has contributions coming mostly from the hydrocarbon tail. In the extended conformation, the lone pair electronic levels are located between −9.06 and −8.40 eV and the level below them, at −12.83 eV. In this case, however, the latter level consists mainly of atomic orbitals from the sulfur and the two carbons next to it. In both conformations, the highest occupied molecular orbital also has some important contributions coming from the carbon next to the sulfur. The dipole moments are calculated to be 27.7 and 20.7 D for the extended and curled conformations, respectively.

(b) Dimer. The conformation of the (ammoniopropyl)sulfonate dimer has been optimized by the MM method. The most stable dimer conformation is extended, i.e., the two molecules forming the dimer both adopt an extended conformation. The optimal curled and extended dimer conformations are displayed in Figure 4. The arrangement of the head dipoles is in both instances antiparallel. Further examination of Figure 4 is useful to rationalize the curled-to-extended reversal in stability when going from the isolated monomer to the dimer. In the latter case, an extended conformation leads to large *in-*

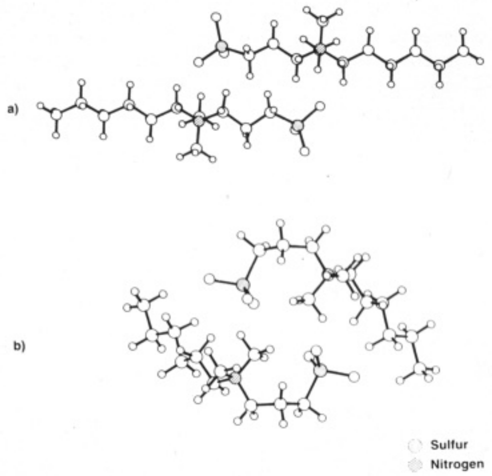


Figure 4. Perspective views of MM-optimized conformations for the [(dimethylhexylammonio)propyl]sulfonate dimer: (a) extended conformation; (b) curled conformation.

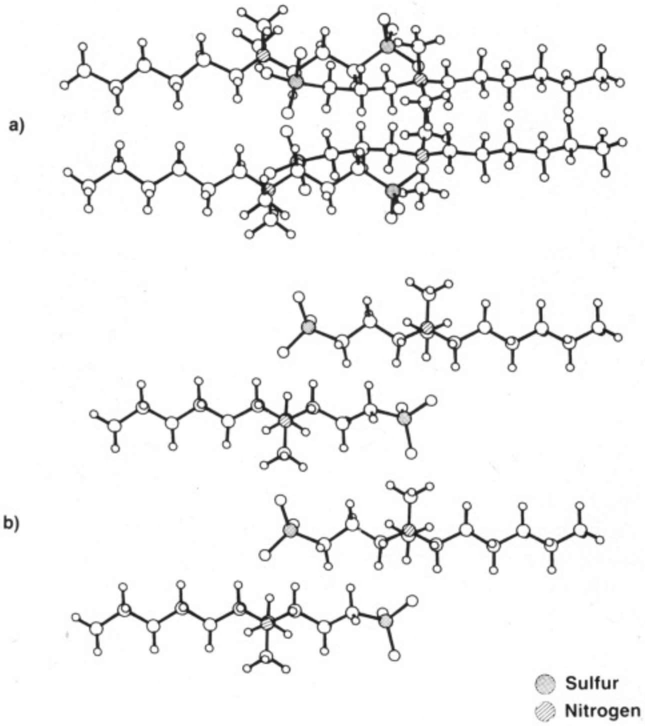


Figure 5. Perspective views of MM-optimized conformations for the [(dimethylhexylammonio)propyl]sulfonate tetramer: (a) square configuration; (b) lateral configuration. In (a) the dimensions of the "square" are approximately 3 Å by 4 Å with roughly the 4-Å dimension projected in the figure.

terchain interactions, the interchain N–O distances becoming as short as 3.0 Å. This calculated behavior is fully consistent with what is observed in the crystalline state where interchain interactions are also found to dominate the packing mode and result in extended molecular conformations.[29–31] From these results it would appear that the MM technique is reliably reproducing the conformational trends in these zwitterionic molecules.

The MM energy for the extended dimer conformation is calculated to be −86.5 kcal/mol, 7.7 kcal/mol more stable than the curled conformation. With respect to two isolated monomers, the dimer stabilization energy is about 50 kcal/mol when considering in each situation the lowest energy conformation. We have calculated the dimer stabilization energy with a variety of angular variations. The results are typical of dipolar interactions with the energy rising sharply with deviation from the antiparallel configuration. We conclude that the antiparallel arrangement is strongly favored energetically.

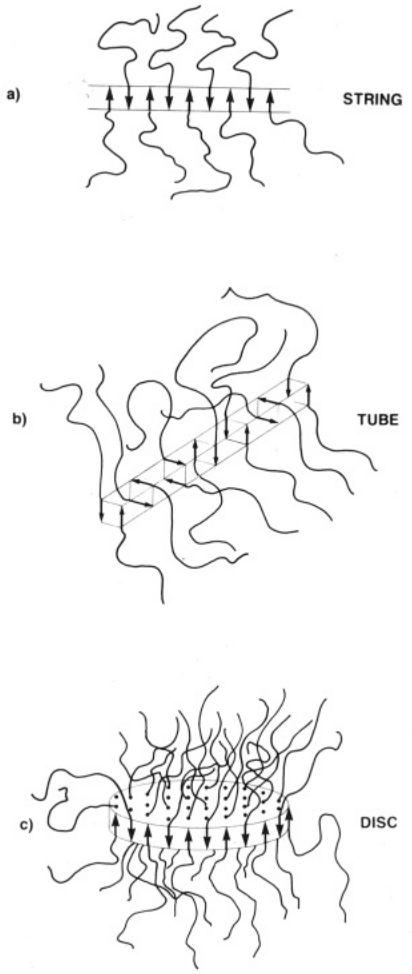


Figure 6. Illustration of the string (a), tube (b), and disk (c) structures that can arise for large aggregation numbers in zwitterion end-capped associating polymer.

(c) Tetramer. In the case of the tetramer, it seems reasonable to consider only an extended conformation for the individual chains. We have considered two overall configurations: (i) a cubic configuration, in which a dimer is located on top of another dimer in an antiparallel fashion (Figure 5a); (ii) a lateral configuration, in which the dimers are side by side (Figure 5b). In case of aggregation numbers larger than four, the latter configuration would give rise to a string type of structure (one-dimensional growth) and the former configuration either to a disklike structure (two-dimensional growth) or a tubelike structure (one-dimensional growth), as is illustrated in Figure 6. In contrast to the situation found in ionomers,[18] spherical structures would be energetically unfavorable because they would require an almost parallel alignment of the dipoles. The large polydispersity observed for the aggregates is consistent with a nonspherical head-group configuration.[12]

The lateral configuration is calculated by MM to be slightly more stable than the square configuration: −269 kcal/mol relative to −262 kcal/mol. At the equilibrium positions found by MM and using the charges on the individual atoms, we find that the electrostatic attraction energy is >80% of the interaction, so that these forces are the dominant influence in small aggregates, as expected.

Close examination of the lateral and square configurations indicates that the tetramers can be adequately described as pairs of interacting dimers. Indeed, the chains mostly retain two by two, the conformation of the dimer, and the chain–chain average distance between the dimers is larger than within the dimers. For instance, the smaller nitrogen–oxygen separation within a dimer is about 3 Å, the same as that in an isolated dimer; between the dimers, it is about 3.4 Å in the lateral configuration and 4.0 Å in the square configuration. The shortest interdimer distance in the lateral configuration can be the reason why this configuration is calculated to be slightly more stable. (In the case of equally spaced dipoles, simple electrostatics would favor the square configuration.[32]) Note that in both configurations, the hydrocarbon chains radiating from the heart of the micelle run roughly parallel to one another, about 6–7 Å apart.

Tetramer formation is thus favored over the formation of two dimers by about 100 kcal/mol and over the absence of aggregation by about 200 kcal/mol, i.e., 50 kcal/mol per chain. This rather large value is similar to that calculated for alkyllithium clusters (30–40 kcal/mol),[33] where the charges are smaller than in the present case. These large energies suggest large aggregation numbers. The same conclusion would be reached on the basis of electrostatics since, in that framework, a cluster with $2N$ dipoles is always found more stable than two N-dipole clusters. As will be discussed below, the limits on the aggregation number that are observed experimentally can be related to excluded-volume interactions occurring in the hydrocarbon tails, interactions which are not included in our calculations. This explanation is in agreement with the experimental data of Fetters et al.,[12] which demonstrate decreasing association with increasing hydrocarbon (polyisoprene) chain length. Their data suggest that the aggregation number as a function of molecular weight (N) has approximately a N^{-1} dependence.

IV. Results and Discussion for (Ammoniomethyl)sulfonate and (Ammoniobutyl)sulfonate Zwitterions

We have investigated the conformations of monomers and small clusters of (ammoniomethyl)sulfonate and (ammoniobutyl)sulfonate zwitterions in order to analyze the influence of the length of the alkyl moiety between the charge-carrying atoms.

The conformation of the (ammoniomethyl)sulfonate compound has been studied by both MM and MNDO techniques. Contrary to the (ammoniopropyl)sulfonate system, the monomer is found to be more stable in the extended all-trans conformation. The stability difference between the extended and curled conformations is 7.7 kcal/mol at the MM level. At the MNDO level, the full geometry optimization always results in the extended conformation, meaning that there is no deep local minimum associated with the curled conformation. These results can be explained by the observation that the N–O distance (charge separation) is only about 3 Å in (ammoniomethyl)sulfonate, to be compared with 5.5 Å in the (ammoniopropyl)sulfonate extended conformation. Therefore, curling of the chain does not lead to a significant decrease in charge separation in (ammoniomethyl)sulfonate.

The dimer and tetramer MM optimum conformations are also extended. The stabilization energy gained by the formation of a dimer with respect to two isolated monomers and the stabilization energy of a tetramer relative to two dimers is on the order of 50 kcal/mol in both cases. The dimerization energy is thus comparable to that in (ammoniopropyl)sulfonate, but the tetramerization energy (and thus the driving force toward large aggregation) is only about half as large.

For the (ammoniobutyl)sulfonate system, we have worked only at the MM level and have considered only the monomer and dimer conformations. In the monomer case, the optimal structure has the curled conformation. The total energy is about 7 kcal/mol lower than that of the extended all-trans conformation (−10 kcal/mol relative to −3 kcal/mol), a value similar to that obtained in the (ammoniopropyl)sulfonate case. The optimal curled conformation has three gauche units in the butyl section of the molecule. In the case of the dimer, the extended conformation becomes favored, much more so than for (ammoniopropyl)sulfonate. The extended dimer conformation has an MM total energy of −91.4 kcal/mol compared to −42.4 kcal/mol for the curled dimer conformation. The dimerization energy is about 70 kcal/mol, a value significantly larger than in (ammoniomethyl)sulfonate or (ammoniopropyl)sulfonate.

V. Larger Aggregates

Since electrostatic forces fall off more slowly than other forces (both repulsive and attractive), electrostatics should dominate the energies of the larger aggregates. Based only on enthalpic considerations of the type presented above, we would predict the formation of large aggregates.

As stated above, the aggregates can be expected to form as disks, tubes, or strings, but *not* spheres. The attractive electrostatic forces favor the most compact structure, i.e., disks, followed by tubes and then strings. Simple electrostatic calculations predict that the energy of interaction for these structures is given by (n is the number of monomers)

$$E_{\text{disk}} = -A_{\text{d}}n + B_{\text{d}}n^{1/2} \tag{6}$$

$$E_{\text{tube}} = -A_{\text{t}}n + C_{\text{t}} \tag{7}$$

$$E_{\text{string}} = -A_{\text{s}}n + C_{\text{s}} \tag{8}$$

In these expressions, the leading term is the bulk contribution, and the next term represents end or edge effects. The n-scalings for the various terms are specific examples of the general $n^{-1/d}$ behavior for E/n in d-dimensional growth of clusters.[34] We have found that these formulas fit the electrostatic energies of arrays of n dipoles even to quite small values of n. Our simple electrostatic model for the extended zwitterionic head is two charges separated by approximately 5.5 Å. Such a model is used to simulate aggregates by putting two monomers approximately 3 Å apart and then aggregating the dimers into tubes and disks with dimers approximately 4 Å apart or into strings with dimers approximately 3.4 Å apart, as found in the above molecular mechanics calculations (see Figure 6). For this model, with no other repulsive forces included, we find A_{d} approximately 160 kT, B_{d} approximately 110 kT, A_{t} approximately 130 kT, C_{t} approximately 70 kT, A_{s} approximately 140 kT, and C_{s} approximately 100 kT.

The MM and MNDO calculations described in section III have been carried out for molecules in the gas phase. Since the dominant interactions are electrostatic (particularly for larger aggregates), a good estimate of the energies of interaction *in solution* can be found by dividing the MM results ($\sim$50 kcal/mol per monomer) by the dielectric constant of the solvent. In the case of the zwitterionic capped polymers in cyclohexane, we have $\epsilon = 2.0$. This leads to a *qualitative* estimate of A_i in eq 6–8 of $\sim$25 kcal/mol per monomer ($\sim$40 kT/monomer at room temperature). This value is in the same range as that found experimentally in Li–alkyl clusters.[33] We should note, however, that the effect of ϵ could be underestimated. The effective ϵ for the aggregates might be better approximated by ϵ for the tail ($\epsilon \sim 2.0$) with only minor perturbation due to the solvent. When ϵ for the solvent is greater than 2, this effect would also tend to decrease the energy of the free molecule in solution relative to that of the aggregate.

Addition of small amounts of heptanol to the cyclohexane solutions reduces the aggregation number (n).[12] At 1% heptanol n is reduced moderately; 5% heptanol essentially eliminates aggregation. These results are understandable in our model as a reduction in head-group interaction energy due to the high dielectric constant of heptanol ($\epsilon \sim 12$). Less easy to understand are the results for toluene solvent[12] where little or no aggregation is found. Though toluene is more polar than cyclohexane, ϵ is only about 20% larger ($\epsilon = 2.4$ for toluene). We doubt that this difference in ϵ is sufficient to explain the experimental results. It is more likely that these results point to one missing energetic element in our analysis—namely, solvation energy for the solvent–head group interaction. Toluene should be a better solvent for zwitterions than cyclohexane. In fact, this is well-known to be the case for Li–alkyl compounds.[33] These solvation energies would lower the energy of the free molecule in solution with respect to the aggregate, thereby causing lower aggregation numbers. Solvation effects could also play a role in explaining the heptanol results.

Large aggregates are clearly suggested if enthalpic considerations alone are included. However, entropic considerations are extremely important and will dominate for *long-chain* compounds. As pointed out by Pincus and Witten[17a] and Bug et al.,[17b] the excluded-volume repulsive interactions between the chains attached to the zwitterionic head groups are large and can be expected to limit the size of the aggregate. This effect can be divided into two terms: that from the region very near to the head groups and that from the region farther away. The inner region interactions will reduce the free energy of interaction of heads and will be largely independent of N; the outer region interactions will be dependent on N.

Inner region effects are seen in the dilute solution behavior of star polymers with a large number of arms.[35] Here the high segment density near the core exerts a strong influence on the dimensions of the star when the chain is small.

In the present case inner region effects are dependent on the shape of the aggregate since the repulsive forces are greater for more compact structures. Thus, the effective free energy of the core (head groups plus inner region) will be reduced by these repulsive forces, and the less compact structures (tubes and strings) will be favored over more compact structures (disks) with the same electrostatic attractive energies. We believe these effects may well be significant so as to partially compensate the large attractive electrostatic energies in the core region.

The effect on the free energy of the repulsive forces between chains in the *outer* region in *spherical* aggregates has been found[17] to have a rather weak dependence on N, either $N^{1/5}$ (mean field) or log N (scaling), both of which are too soft to explain the strong dependence of aggregation number on tail molecular weight (N). (Henceforth, we refer only to the $N^{1/5}$ spherical result.) However, this effect is strongly dependent on the shape of the aggregates,[36] because in disks and tubes the chains are forced to pack more closely together than they do in a sphere. For a *long* tube or stringlike structure, the chains in the middle of the structure will feel more repulsion; the excess free energy is expected to scale as $N^{1/2}$.[36] The chains on the end of the string will behave more like those in spherical structures, leading to a free energy scaling as $N^{1/5}$ (see above). The manner in which the free energy per chain changes as one goes from the interior of the string to the end of the string is not known. For a *short* tube or string, the free energy per chain should scale like the spherical result. Thus, the free energy due to interchain interactions for tubes and strings can be expected to take the form

$$F_{\text{tube}} = \alpha_t(n,N)n + \beta_t(N) \tag{9}$$

with

$$\alpha_t(n,N) \sim N^{1/2} \qquad n \text{ large}$$
$$\alpha_t(n,N) \sim N^{1/5} \qquad n \text{ small}$$
$$\beta_t(N) \sim N^{1/5} \qquad \text{all } n$$

where the α coefficient governs the behavior in the interior of the structure and the β coefficient describes the ends.

For a *large* disk-shaped aggregate, the chains in the center will be very extended in order to reduce interchain interactions, leading to a free energy scaling as N.[36] The chains on the edge will behave roughly as they do in tubes or strings, i.e., a free energy scaling roughly as $N^{1/2}$ in large disks. For *small* disks, the chains are able to take on a largely spherical shape in the outer region; therefore, the free energy should scale as $N^{1/5}$. Thus, the free energy due to interchain interactions for disks is expected to be

$$F_{\text{disk}} = \alpha_d(n,N)n + \beta_d(n,N)n^{1/2} \tag{10}$$

with

$$\alpha_d(n,N) \sim N \qquad n \text{ large}$$
$$\alpha_d(n,N) \sim N^{1/5} \qquad n \text{ small}$$
$$\beta_d(n,N) \sim N^{1/2} \qquad n \text{ large}$$
$$\beta_d(n,N) \sim N^{1/5} \qquad n \text{ small}$$

where α and β define the bulk and edge, respectively. Though it is clear that the repulsive interactions are very important in determining the size and shape of the aggregates, eq 9 and 10 must be taken as speculations awaiting more detailed calculations of tail–tail interactions in these configurations.

In order to compute the equilibrium aggregation numbers as a function of chain length, more precise forms for α_d, α_t, etc. must be found. However, the value of n at which α_t and α_d crossover from $N^{1/5}$ to a more strongly varying function ($N^{1/2}$ or N) is not known at present and could itself be N dependent. Note, however, that the head-group region of aggregates with n between 4 and ~30 has linear dimensions of order 15–150 Å (tubes) or 5–25 Å (disks), while the radii of gyration of the *free* chains is in the range 50–300 Å.[37] This suggests that the tail repulsions we have discussed play an important role in determining both the size and shape of the aggregates.

Our electrostatic calculations for aggregates of up to 50 monomers show that the interaction energy in a disk is more negative than that in tubes. However, the difference in this energy is less than 10% of the total for aggregates of this size. For small N, the distinction between disks and tubes is of no real significance. For large N, the tail repulsive interactions can be expected to determine the equilibrium shape of the aggregates. This leads to the prediction that tubelike *structures* are the best compromise between the electrostatic forces and the interchain repulsive forces for large aggregates. These structures would account for the unusual rheological properties of the melts of zwitterion-capped polymers as suggested by Fetters et al.[13] However, there is not yet any direct structural evidence in support of these conclusions. In any case, since tail–tail interactions are very different for melts versus dilute solutions, the melt results can only be taken as supporting our position relating to the important role of the head group in determining aggregate structure.

VI. Conclusions

We have performed molecular mechanics (MM) and semiempirical quantum chemical calculations on monomers and small clusters of (ammonioalkyl)sulfonate compounds with alkyl = methyl, propyl, and butyl. These molecules are taken as models for semitelechelic, zwitterionic, associating polymers. We find that except for the methyl compound, the monomers adopt a curled conformation in order to increase the *intramolecular* electrostatic interactions. In all instances, in aggregates of two or more molecules, the molecular conformation becomes fully extended (all-trans) in order to increase the *interchain* interactions. This trend is confirmed by available crystal structures for (ammonioalkyl)sulfonate molecules.

The antiparallel alignment of zwitterionic head groups strongly suggests the formation of disklike, tubelike, or stringlike structures for the aggregates. A spherical structure for the head-group region is not expected, since this would require the approximately parallel alignment of the zwitterionic dipoles leading to large repulsive energies of interaction.[38] Thus, the liquid-drop model for the head-group geometry appears to be inadequate.

Based on enthalpic considerations alone, the aggregation numbers would be expected to be very large. However, excluded-volume interactions (*interchain* repulsions) limit the size of the aggregate. These repulsions are smallest in a spherical aggregate, intermediate in a tube (or string) shape, and largest in a disk shape. On the other hand, the attractive interactions are largest in a disk, only slightly smaller in a tube, and smallest in a sphere. As a result, the best compromise among these shapes is a *tubular* aggregate which maximizes attractive energy without sacrificing too much in repulsive energies.

Note Added in Proof. Similar conclusions regarding the relative stability of different head-group configurations have been reached recently be Balazes et al. using simulation techniques.[39]

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Registry No. [(Dimethylhexylammonio)propyl]sulfonate, 92096-52-1; [(dimethylhexylammonio)methyl]sulfonate, 113976-19-5; [(dimethylhexylammonio)butyl]sulfonate, 113976-20-8; [(dimethylhexylammonio)propyl]sulfonate dimer, 113976-21-9; [(dimethylhexylammonio)propyl]sulfonate tetramer, 113976-22-0.

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