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Conformational Analysis of Aliphatic Chains at Interfaces. Influence of the Radius of Curvature

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ABSTRACT: We report a statistical mechanical study of the structure of aliphatic interfaces. A surface molecular model is defined which simulates interfaces of surfactants and microemulsions where molecules are anchored at the surface of spherical micelles. A Monte-Carlo calculation of the conformation properties of the system is carried out, taking into account the rotational isomerism of the chains. In addition, a thermodynamical analysis of the stability of the monolayer is developed through the calculation of the conformational and translational free energies. The influence of the radius of curvature on the structural and thermodynamical behavior of the interface is studied.

Amphiphilic molecules consist of a polar terminal head and at least one aliphatic chain. They are generally found at the interface of two phases of which one is aqueous and in various media such as biological membranes or industrial emulsions. The many interesting properties of these media can be related both at one fundamental or applied levels to, among other things, the conformational properties of the amphiphilic molecules of the interface.[1-5] The configurational behavior of chain molecules at the interface is crucial to the understanding of the macroscopic properties of these amphiphilic systems. Its importance lies in the fact that it provides a link between the molecular and interaction parameters, on one hand, and various features of the interface, on the other. This explains why several groups of workers have tried over the last few years to carry out theoretical studies of the structure of aliphatic chains in these systems.[6-16] Many of these phases consist of relatively short molecular chains of up to 30 C–C bonds for which methods of polymer science are inadequate. On the other hand, any treatment of the macroscopic properties at a molecular level would involve difficulties due to both external and internal degrees of freedom in these multiply interacting chain systems. The chief difficulties encountered are the very large number of conformations of such aliphatic chains and the mathematical description of the energetic interactions between neighboring chains. However, in the past few years a numerical approach in which chains are simulated by a computer has been developed for biological membranes and has given a good understanding of many of their macroscopic properties.[6,9,15,16] In this paper we are concerned with the structure of interfaces encountered in surfactant systems and microemulsions where molecules are anchored at the surface of spherical micelles. We have developed a theoretical model allowing the study of the influence of the radius of curvature on the conformational properties of the aliphatic chains of these molecules according to a Monte-Carlo method.

Theory

1. Chain Model and Intramolecular Interactions. In our model the aliphatic chains include all the carbon and hydrogen atoms with constant C–C and C–H bond lengths for which the currently accepted values of 1.54 and 1.10 Å, respectively, are assumed. Valence angles are constant and assumed to have tetrahedral values. The rotational isomeric state scheme is used.[17,18] Each C–C bond of the chain can rotate about the preceeding one, and its position is defined by its dihedral angle ϕ with respect to the preceeding bond pair. For each bond, three positions are allowed, corresponding to $\phi = 0$ (trans state t) and $\phi = \pm 120°$ (gauche states g^+ and g^-). The trans form of an elementary unit of three bonds is chosen as a reference state and an energy difference $\Delta U_0{}^0$ of 600 cal mol^{-1} is attributed to each gauche form.[19] In addition, interdependence of internal rotations is taken into account[18-20] by associating a supplementary energy of about 1900 cal mol^{-1} to the units of four bonds of the g^+g^- or g^-g^+ type. In our model, two virtual bonds are chosen as a reference plane, and the two first actual bonds can rotate about this plane. So the conformation of a chain will be defined by the set of the rotational state of the various C–C bonds.

Table I
Energetic and Geometric Parameters of Lennard-Jones Potentials

	r^*_{ij}, Å, and ϵ_{ij}, cal mol^{-1}	
	C	H
C	4.12, 38	3.52, 33
H	3.52, 33	2.92, 37

2. Surface Model, Chain Packing, and Intermolecular Interactions. A molecular reference system is attributed to each chain and placed in the plane of the first two virtual bonds. The chain configuration is defined by the set of the three coordinates of the origin of the molecular reference system and by its three Eulerian angles relative to an absolute system. The first actual C–C bond anchored to the surface represents the link between the chain and its polar head. In order to define a model representing a two-dimensional dense fluid on a curved interface, we have considered a central chain surrounded by six neighbors and placed at the sites of a pseudohexagonal lattice. This pseudohexagonal lattice is obtained by projecting a plane hexagonal lattice on a sphere defined by its radius R (see Figure 1) (such hexagonal symmetry is observed in the gel phases of phospholipid bilayers). The distance between the first atoms of two neighboring chains on the surface is noted d. The total energy of the molecular system of the seven chains is calculated for each configuration by adding to the intramolecular part the bond pair interatomic energy contributions between carbon and hydrogen atoms. Carbon–carbon, carbon–hydrogen, and hydrogen–hydrogen interactions are evaluated through semiempirical Lennard-Jones potentials according to the formula:

$$U_{ij} = \epsilon_{ij}\left[\left(\frac{r_{ij}^*}{r_{ij}}\right)^{12} - 2\left(\frac{r_{ij}^*}{r_{ij}}\right)^{6}\right]$$

where r_{ij}^* is a distance parameter and ϵ_{ij} is an energy parameter which depends on the chemical nature of the atoms under consideration. The last term r_{ij} is the distance

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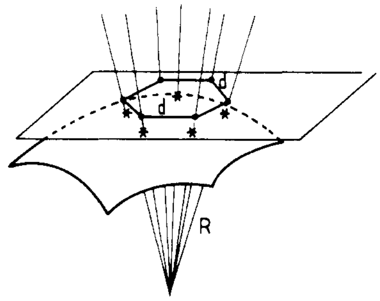

Figure 1. Surface model and chain packing.

between atoms i and j. The values of the above parameters[21] which have been used in this work are summarized in Table I.

3. Thermodynamical and Structural Properties. We start from the general expression of the total partition function of an aliphatic system which can be written as:

$$Z^\Gamma = K \int_\Gamma \sum_t e^{-U(\mu_t,\gamma)/RT}\, \mathrm{d}\gamma \qquad (1)$$

The integral is taken over the configuration space Γ, and μ_t is any conformation of the chains. The summation on t is taken over the set of the conformations of the chains. The contributions of internal and external vibrations of the molecules are included in the factor K. R is the perfect gas constant and T the absolute temperature. By generalizing the well-known concept of free volume[22,23] (or free surface in two dimensions) to external rotations and translational degrees of freedom (Γ_{free}), we can write the above formula as:

$$Z^\Gamma = K\Gamma_{\mathrm{free}} \frac{1}{\Gamma_{\mathrm{free}}} \int_\Gamma \sum_t e^{-U(\mu_t,\gamma)/RT}\, \mathrm{d}\gamma \qquad (2)$$

or

$$Z^\Gamma = K' Z^\Gamma{}_{\mathrm{transl}}\, Z^\Gamma{}_{\mathrm{conf}} \qquad (3)$$

We now consider the part which is the most sensitive to structural changes of the aliphatic system and which can be written in terms of free energy as:

$$F^\Gamma{}_{\mathrm{total}} = F^\Gamma{}_{\mathrm{transl}} + F^\Gamma{}_{\mathrm{conf}} \qquad (4)$$

with

$$F^\Gamma{}_{\mathrm{transl}} = -RT \ln Z^\Gamma{}_{\mathrm{transl}} \text{ and } F^\Gamma{}_{\mathrm{conf}} = -RT \ln Z^\Gamma{}_{\mathrm{conf}}$$

We can also define the conformational internal energy as:

$$U^\Gamma{}_{\mathrm{conf}} = \frac{\int_{\Gamma_{\mathrm{free}}} \sum_t U(\mu_t,\gamma) e^{-U(\mu_t,\gamma)/RT}\, \mathrm{d}\gamma}{\int_{\Gamma_{\mathrm{free}}} \sum_t e^{-U(\mu_t,\gamma)/RT}\, \mathrm{d}\gamma} \qquad (5)$$

and consequently the conformational entropy as:

$$S^\Gamma{}_{\mathrm{conf}} = \frac{U^\Gamma{}_{\mathrm{conf}} - F^\Gamma{}_{\mathrm{conf}}}{T} \qquad (6)$$

In the same way any average molecular quantity or structural property $\langle G \rangle$ is defined by:

$$\langle G \rangle = \frac{\int_{\Gamma_{\mathrm{free}}} \sum_t G(\mu_t,\gamma) e^{-U(\mu_t,\gamma)/RT}\, \mathrm{d}\gamma}{\int_{\Gamma_{\mathrm{free}}} \sum_t e^{-U(\mu_t,\gamma)/RT}\, \mathrm{d}\gamma} \qquad (7)$$

4. Basic Hypothesis. Considering the great complexity of the total partition function of the system it is not possible to obtain a complete evaluation of this quantity through a simulation of all the degrees of freedom. We, therefore, chose an approximate approach in which the two right terms of eq 3 are evaluated separately and independently.

First we have calculated the conformational contribution of one chain to the thermodynamic properties of the aliphatic systems. In this way we have carried out a Monte-Carlo calculation based on an importance sampling method. This procedure is the first which allows the direct estimation on one hand of any average molecular quantity and on the other hand of the molecular conformational partition function of one chain (see above $Z^\Gamma{}_{\mathrm{conf}}$). These quantities involve both the external degrees of freedom and the internal ones due to internal rotations. In this study, only small independent rotations (±30°) of the reference planes of the seven chains around the axis of the all-extended conformation have been allowed. Since we calculate the single-chain properties, the internal degrees of freedom of the six surrounding neighbors of the central chain are not taken into account in the evaluation of the single chain partition function. In our model they are considered only to simulate the lateral constraints in the layer which occur through the intermolecular interactions of the central chain with its neighbors. An evaluation of the corresponding energy is necessary for each configuration of the system. So for simplicity, and in order to define a model leading to reasonable computing time, the conformations of the neighboring chains will be considered as identical and the same as the conformation of the central chain. This condition defines a moving adapting neighborhood around the central chain. These types of periodic boundary conditions have already been used with success in previous studies. It has been applied to membrane models[16,24] with a single independent chain, to homogeneous alkane liquid with four,[25] one,[26] and seven independent chains,[27] and very recently with a single chain to the problem of surface coverage.[28] It has been pointed out in previous publications[6,8-10,14-16,24] that an important physical property of aliphatic systems in the liquid state is the segment–segment chain correlations arising from van der Waals short-range interatomic interactions. A precise description of the conformational properties of aliphatic layers in agreement with experimental measurements needs a realistic molecular model which takes into account such correlations. The validity of the simplification introduced in this many-body problem using a single chain periodic condition has already been established. This can be seen from the good agreement between experimental quantities and theoretical values calculated according to our model for plane layers. For example, the results concerning as different properties as melting entropy of chains, thickness of the layer, its variation during melting, the variation of the order parameter for each bond along the chain, and the X-ray diffraction spectra have been reported elsewhere.[9,16,24] Furthermore, the thermodynamic and structural behaviors of plane layers have been studied as a function of temperature, and our model leads to the well-known typical phase transition between the crystal and liquid states.[16,24] So it is reasonable to think that the intermolecular correlations between neighboring chains are taken into account in a satisfying way in this simple model and do not introduce any biasing phenomena. Finally these periodic conditions have been used by others as reported by Lal[28] and good agreement is observed with structural properties obtained by simulation of a multiple interacting chain system.

5. Monte-Carlo Method. The method consists of a random generation of a sampling of conformations and configurations from which any molecular property can be estimated.[29]

The plane of the two virtual bonds of the central chain is chosen as a reference. Then the relative position, denoted by γ, of the corresponding planes of the six surrounding chains is randomly chosen between −30 and +30°. Now the conformation of the central molecule is built up by generating random steps. Assuming that the conformation of the chain is determined up to n bonds, the procedure is completely defined by describing the sequential process used to add a new bond. So in order to select one of the three states allowed for this new C–C bond and the corresponding positions of the resulting supplementary carbon and hydrogen atoms, we calculate for each of the three possible internal states the contribution of these atoms to the total energy. This contribution for any internal state l is equal to $U_1^{(\gamma)} = V_l + W_l$, $l = 1, 2, 3$, where V_l is the intramolecular energy equal to 600 cal mol^{-1} for gauche isomers with a supplementary energy of 1900 cal mol^{-1} for g^+g^- and g^-g^+ sequences. Furthermore, W_l is the interatomic interaction of these three atoms with all the atoms of the part already built of the six surrounding chains in the same conformation as the preceeding bonds of the central chain. The internal rotational state of the adding segment is randomly chosen with the respective probabilities

$$P_i^{(\gamma)} = e^{-U_i^{(\gamma)}/RT} \Big/ \sum_{l=1}^{3} e^{-U_l^{(\gamma)}/RT}; \qquad i = 1, 2, 3 \tag{8}$$

where $e^{-U_i^{(\gamma)}/RT}$ is the appropriate Boltzmann factor. According to such a procedure, for any given configuration γ, the probability of occurrence of any conformation μ defined by N internal rotational states $i_1, i_2, ..., i_N$ is equal to:

$$P(\mu,\gamma) = \prod_{k=1}^{N} P_{i_k}^{(\gamma)} \tag{9}$$

Finally, it can be shown that the molecular conformational partition function of a single chain can be estimated from any sufficiently large sample of M configurations (γ) and M' conformations μ according to the formula:

$$Z_{\mathrm{conf}} = \frac{1}{MM'} \sum_{u=1}^{M} \sum_{t=1}^{M'} e^{-U(\mu_t,\gamma_{\mathrm{u}})RT} P^{-1}(\mu_t,\gamma_{\mathrm{u}}) \tag{10}$$

where $U(\mu_t,\gamma_{\mathrm{u}})$ is the total energy of conformation μ_t and configuration γ_u. In a similar way the average of any molecular quantity G is estimated by the formula:[16,26]

$$\langle G \rangle = \frac{\sum_{u=1}^{M} \sum_{t=1}^{M'} \mathrm{G}(\mu_t,\gamma_{\mathrm{u}}) e^{-U(\mu_t,\gamma_{\mathrm{u}})/RT} P^{-1}(\mu_t,\gamma_{\mathrm{u}})}{\sum_{u=1}^{M} \sum_{t=1}^{M'} e^{-U(\mu_t,\gamma_{\mathrm{u}})/RT} P^{-1}(\mu_t,\gamma_{\mathrm{u}})} \tag{11}$$

6. Thickness of a Layer. The contribution E of any conformation of the reference chain will be taken as the maximum coordinate over the set of atoms of the chain along the axis of the reference system of the molecule which is perpendicular to the surface.

7. Translational Free Energy. We consider now the contribution to the free energy of the translational degrees of freedom. As an approximation for the crystal state we assume that lateral vibrations of the aliphatic chains on the surface are the same as those in the three-dimensional normal alkane crystals. Their contribution can be simply treated according to the usual harmonic oscillator theory as:

$$F_{\mathrm{vib}} = -kT \ln Z_{\mathrm{vib}}; \; Z_{\mathrm{vib}} = (1 - e^{-\theta/T})^{-1}; \text{ and } \theta = h\nu c/k$$

where h and k are respectively the Planck and Boltzmann constants, c is the light velocity, and ν is the spectroscopic frequency attributed to these movements. For normal alkanes ν is slightly sensitive to the chain length and close to 30 cm^{-1}.[30] The corresponding value of the free energy is about −1400 cal mol^{-1}.

For the free energy of the two-dimensional liquid state we can distinguish two parts. The first one is due to the kinetic contribution which does not depend on the density of the system but which is a function of the temperature and of the mass of the molecule. The second one would need an exact evaluation of the translational partition function depending on the total potential energy of the system. Such an evaluation leads to tremendous difficulties because of the conformational properties of the molecules studied. The free surface available to a chain, involved in the simplest well-known theory of cell model,[16,22,23] depends on the conformation of the molecule considered and on the conformation of its neighbors. So our ambition is only to determine an order of magnitude of the variation of this quantity at a density corresponding to the liquid state. In the way of a critical approach we examine two situations leading to the evaluation of this last contribution.

The first is a very crude model which associates to any conformation a hard cylinder which has the same diameter d_0 as that of the extended chain, chosen to be about 5 Å, and is close to the interchain distance in aliphatic crystals. In this case the free surface available per molecule is:

$$A_{\mathrm{free}} = \Pi(d - d_0)^2 \tag{12}$$

However, we must remark that the gauche conformation fills more space than the trans one. So for gauche conformations d_0 would be greater than 5 Å. In order to improve the model in a way consistent with the idea of mean lattice position and mean conformation we have defined, for plane systems, a hard cylinder of variable diameter. For each density characterized by the interchain distance d we associate with each molecule a hard cylinder whose volume is conserved[11,31] when varying d. This volume is defined as:

$$V = (\Pi/4)\delta^2(d)\langle E \rangle = \text{constant} \tag{13}$$

where $\delta(d)$ is the diameter of the cylinder, $\langle E \rangle$ is the mean thickness of the layer, and the constant is chosen as the molecular volume in the crystal state. We have applied this last method to the case of a curved surface. In this case we have considered the frustrum of a right circular cone of conserved volume with

$$V = (\Pi/12)\delta^2(d)\langle E \rangle[3 + 3x + x^2] = \text{constant} \tag{14}$$

with $x = \langle E \rangle/R$ where R is the radius of curvature. In these last two cases:

$$A_{\mathrm{free}} = \Pi(d - \delta(d))^2$$

Finally, according to the preceeding analysis, the general formula giving the total translational free energy of each molecule is

$$F_{\mathrm{transl}} = -RT[\ln A_{\mathrm{free}} + \ln M + \ln T - 4.72] \tag{15}$$

where R is the gas constant, T is the absolute temperature, M is the molecular weight, and A_{free} is the free surface per molecule in Å^2. At this point it must be noticed that no equivalent theories can be applied to intermediate situations between crystals and "liquid" that do not correspond to stable states. This situation is indicated by broken lines on the corresponding curves.

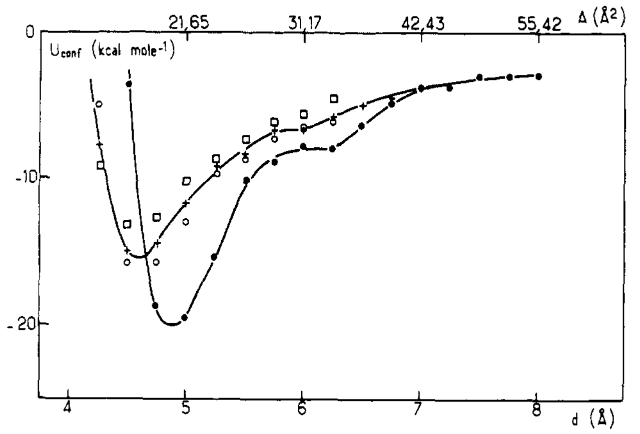

Figure 2. Conformational free energy of a C17 chain for various radii of curvature vs. the distance between chains: (●) $R = \infty$; (○) R = 95 Å; (+) R = 75 Å; and (□) R = 55 Å.

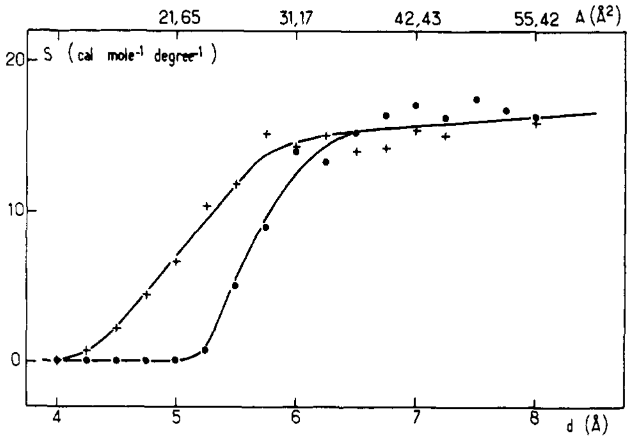

Figure 3. Conformational entropy of a C17 chain for two radii of curvature vs. distance between chains: (●) $R = \infty$ and (+) R = 75 Å.

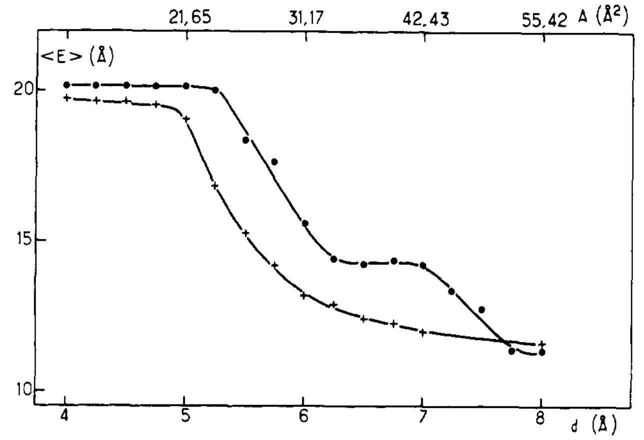

Figure 4. Thickness of a layer of C17 chains for two radii of curvature vs. the distance between chains: (●) $R = \infty$ and (+) R = 75 Å.

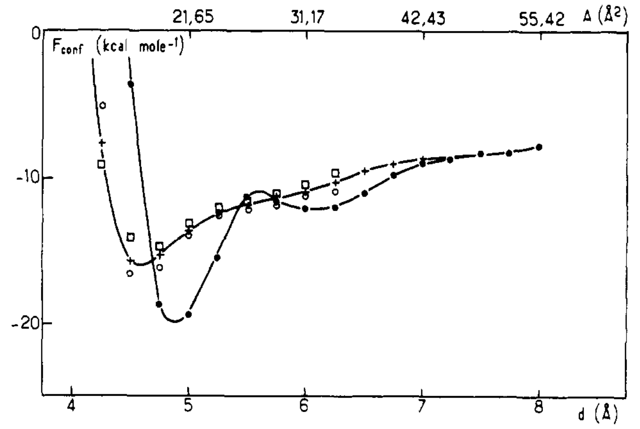

Figure 5. Internal conformational energy of a C17 chain for various radii of curvature vs. the distance between chains: (●) $R = \infty$; (○) R = 95 Å; (+) R = 75 Å; and (□) R = 55 Å.

Results and Discussion

All the calculations have been carried out for a temperature equal to T = 298.5 K. We have studied monodisperse layers of chains with the same length.

In this work we have only considered plane layers and spherical layers as in inverse micelles where the chains are out of the sphere. We have calculated the contribution of a C17 chain to the conformational free energy F_{conf}, to the internal conformational energy U_{conf}, to the conformational entropy S_{conf}, and to the thickness of the layer $\langle E \rangle$. These quantities are plotted vs. the interchain distance d for several radii of curvature (Figures 2–5). We have also indicated the equivalent surface per molecule calculated according to the formula $A = 3^{1/2}d^2/2$. This formula is rigorous for a plane surface but only approximative for curved surfaces.

Two minima can be observed on the curve of conformational free energy of a plane layer (Figure 2). The deepest and narrowest one appears at a value of the interchain distance of about 4.9 Å and, for smaller values of this distance, the curve exhibits a great increase. The second minimum which is larger but less deep appears at a distance of about 6 Å, and the curve increases slightly for larger distances. Curves of entropy (Figure 3) and thickness (Figure 4) vs. d allow us to characterize the corresponding conformational states of the chains situated at these critical distances. The entropy of the chains is zero for interchain distances smaller than 5 Å, indicating that for these distances the system is crystalline and only one chain conformation can be found. By considering, for example, the thickness of the layer, it can be shown that this conformation is completely trans and corresponds to an all-extended conformation as in an alkane crystal. This ordered state is stable at 4.9 Å, but for smaller distances repulsive energy occurring between chains become important and no more minimum exists. This equilibrium distance is very close to that existing between two parallel chains in a three-dimensional alkane crystal and is equal to 4.8 Å. For interchain distances larger than 5.25 Å, gauche isomers appear and a rapid increase of entropy is observed. This entropy reaches an asymptotic value in the dense "liquid state" for a distance of about 6 Å. This great increase of the fluidity of the system corresponds to an important contribution of the chains to the entropy and leads to a second minimum of free energy around d = 6 Å. For larger distances, the increase of entropy is very much less important and cannot equilibrate the decrease of attractive energy (see Figure 5) and a slight increase of the conformational free energy is observed up to the value of the "gas state" ($d = \infty$). This real conformational phase transition between d = 5 and 6 Å is correlated during the fluidification to a rapid decrease of the thickness (Figure 4).

We can analyze the behavior of curved layers according to the same scheme.

We can first remark that curves of conformational free energy corresponding to the three radii of curvature R = 55, 75, and 95 Å are very close (Figure 2). Furthermore they differ markedly from the curve of the plane layer only

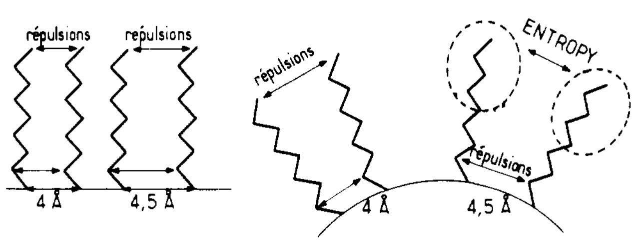

Figure 6. Steric effects induced by the curvature at short distances.

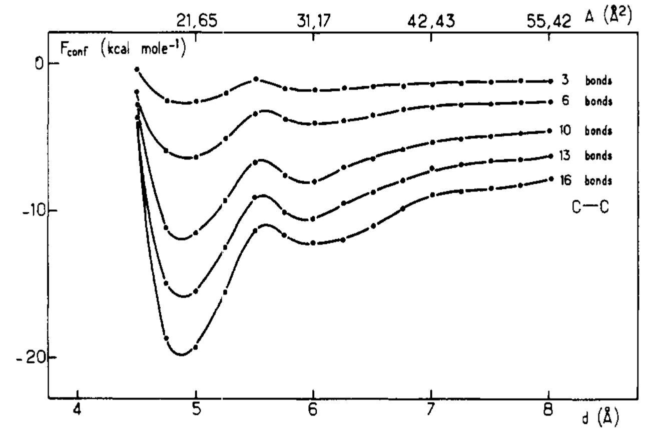

Figure 7. Conformational free energy of a plane layer for various chain lengths vs. the distance between chains.

for interchain distances of about that of the crystal. For these curved layers a minimum of conformational free energy can be found for interchain distances around 4.5 Å, but this minimum is less deep than that for the plane layer. In this situation chains are not crystallized since some entropy already exists (see Figure 3). Crystallization of chains appears for distances smaller than 4 Å, but repulsive forces occurring between the closest atoms near the surface become important. This difference of behavior is due, in the case of curved layers, to the angle which exists between the axes of two chains in their all extended conformations when they are perpendicular to the surface. This angle induces an increase of the distance between the atoms of two neighboring chains when they are placed along the chain at high levels from the surface (Figure 6). This variable interaction along the chain in the curved layer leads to the disappearance of the second minimum for interchain distances of about 6 Å corresponding to the liquid state. The curves of conformational free energy of micellar layers are, in this region, very close to that of the plane layer but slightly less stable. The increase of this curve for distances larger than 4.5 Å is much less important than that in the case of the plane. In fact, in the case of micelles, a real melting of the chain appears from the end at the exterior of the sphere, very rapidly when the distance between chains increases from 4.5 Å. In contrast, in the case of the plane layer, and near the crystallized state, all the atoms have the same atomic surroundings. So when the first gauche states appear for a distance between chains of 5.25 Å, a sharp phase transition is induced for which each bond gives the same contribution. This variation of the fluidity of chains as a function of the distance between chains can be observed from the curves of entropy. The entropy of the micellar layer is always larger than that of the plane layer for an interchain distance smaller than 6 Å. But this difference cannot equilibrate the larger attractive energy which can be observed for the plane system. The curves of thickness exhibit in both cases a sharp variation from about 5 to 6 Å at the same time that the entropy reaches an asymptotic value in the "liquid state". For larger distances the variation of thickness is very much less important.

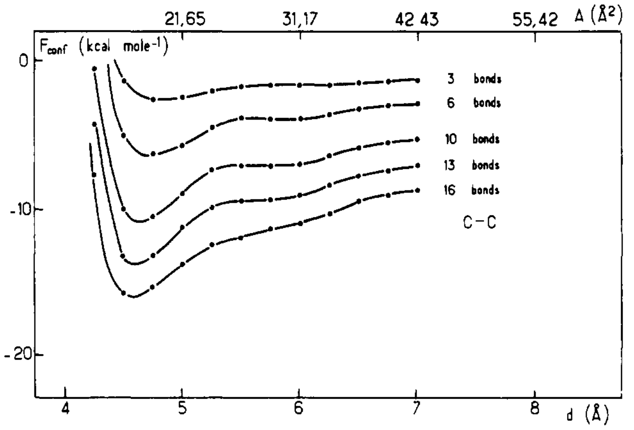

Figure 8. Conformational free energy of a curved layer (R = 75 Å) for various chain lengths vs. the distance between chains.

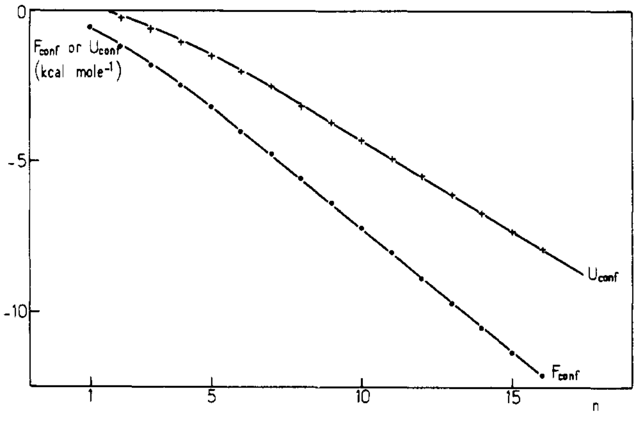

Figure 9. Conformational free energy and internal conformational energy of a plane layer for a distance between chains of d = 6 Å vs. the chain length.

We have calculated the conformational free energy as a function of the distance between chains for various lengths of chains equal to 3, 6, 10, 13, and 16 bonds for the plane layer and for different radii of curvature equal to 55, 75, and 95 Å. We have plotted some of these results in Figures 7 and 8.

The most important modification of the results due to the variation of the chain length appears for the free energy of the plane surface (see Figure 7). In this case, and for the shortest chains, the two minima of free energy, in the "crystal state" and in the "liquid state", are almost identical. When the chains are longer, the two corresponding minima become deeper and narrower, particularly for the first one. It must be noticed that positions of these minima are independent of the chain length. In the case of curved layers, the modification of the curves of conformational free energy due to the variation of chain length is essentially the same for all the radii of curvature. This modification consists essentially of the disappearance of the minimum situated at an interchain distance of 4.5 Å for the shortest chains (Figure 8) and more rapid disappearance for smaller radii of curvature.

We have studied the variation of F_{conf}, U_{conf}, S_{conf}, and $\langle E \rangle$ as a function of the length n of the chain for a plane layer and for a curved layer (R = 75 Å) and for two states of the system corresponding to d = 5.25 and 6 Å. For the plane surface with d = 5.25 Å, all the above quantities are found to be linear with chain length. The entropy is zero for all lengths, and the chains are all extended. For d =

Table II
Translational Free Energy of C17 Chains for Various Models of Free Surface as a Function of the Interchain Distance *d*

	d in Å									
	5.25	5.50	5.75	6.00	6.25	6.50	6.75	7.00	7.25	7.50
$F_{tr}{}^a$		-3679	-4160	-4500	-4765	-4980	-5163	-5321	-5461	-5585
$F_{tr}{}^b$		-3612	-3946	-3758	-3835	-4349	-4580	-4793	-4856	-4948
$F_{tr}{}^c$		-3334	-3396	-3396	-3865	-4088	-4424	-4612	-4787	-4940

[a] $A_{free} = \Pi\,(d - 5)^2$. [b] $A_{free} = \Pi\,(d - \delta(d))^2$ for a plane monolayer and eq 13. [c] $A_{free} = \Pi\,(d - \delta(d))^2$ for a curved monolayer and eq 14.

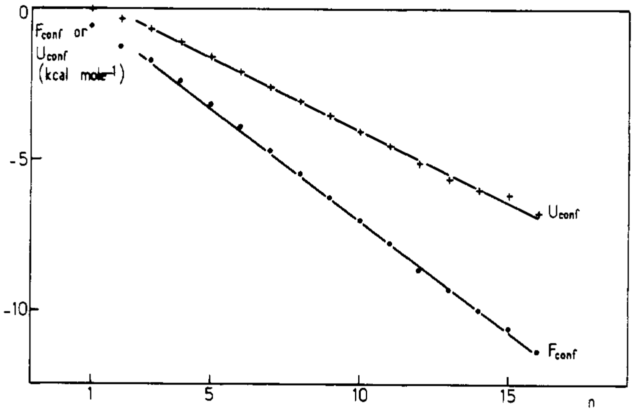

Figure 10. Conformational free energy and internal conformational energy of a curved layer (R = 75 Å) for a distance between chains of d = 5.75 Å vs. the chain length.

6 Å (see Figure 9), the chains are flexible and can be found in numerous gauche conformations; nevertheless we always observe perfect linearity of all the calculated quantities for lengths longer than four bonds. In the case of the micellar layer (R = 75 Å) with d = 5.25 Å, only the conformational free energy is linear for all n. The entropy is not yet zero, and the curves of internal conformational energy, entropy, and thickness show a break at around eight or nine bonds. These two straight lines arise probably from a variation of the flexibility along the backbone of the chain. This effect can be explained by the modification of the repulsive interactions existing between atoms engaged in gauche conformations according to their position along the chain. For d = 5.75 Å (see Figure 10), and in spite of the curvature, all the calculated quantities exhibit a perfect linearity as a function of n for more than four bonds. At this distance the fluidity of the chain is the same along the backbone, and each atom is surrounded by the same almost homogeneous surrounding.

We have reported in Table II the translational free energy of a C17 chain calculated according to formula 15. We have considered the various models of free surface, already defined, which correspond to hard volumes of constant or variable diameters. The main difference can be observed between the first model, eq 12, and the last two, eq 13 and 14. The first model involving a hard cylinder of constant diameter leads to a constant increase of the translational free energy upon the interchain distance for all d values. It can be thought as already pointed out that the order of magnitude of this variation is overestimated because of the existence of gauche conformations. The last two models lead to similar results but differ from the preceding one. In particular, it can be noticed that for these models the translational free energy is sensibly constant for interchain distance corresponding to stable conformational liquid states (around 5.75 to 6 Å). Only for larger distances can a significant variation be observed.

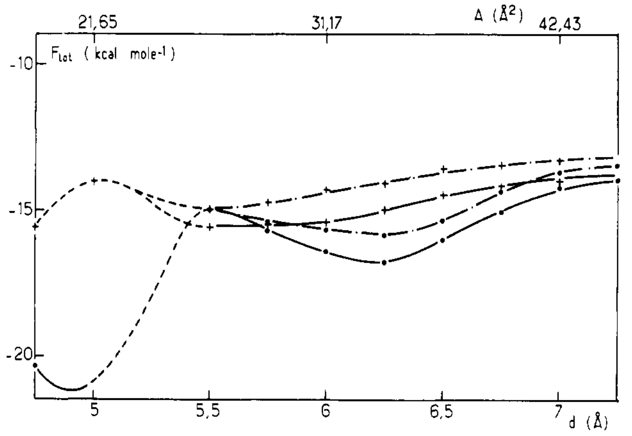

Figure 11. Total conformational and translational free energy of a C17 chain vs. the distance between chains for various models of free surface and for two radii of curvature: (●) $R = \infty$ and (+) R = 75 Å; (—) model a of Table II and (---) models b and c of Table II.

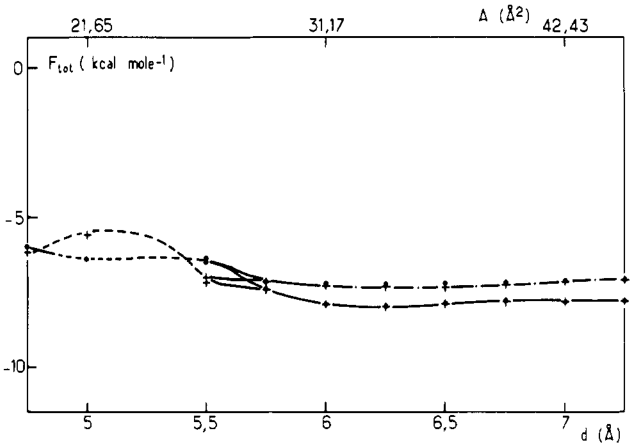

Figure 12. Total conformational and translational free energy of a C7 chain vs. the distance between chains for various models of free surface and for two radii of curvature: (●) $R = \infty$ and (+) R = 75 Å; (—) model a of Table II and (---) models b and c of Table II.

We have plotted, Figures 11 and 12, the contribution of a single chain to the total conformational and translational free energy of plane and curved layer (R = 75 Å) vs. the interchain distance d. We have studied two chain lengths of 16 and 6 bonds for various models of free surface as indicated in Table II. In a general way, the contribution of the translational free energy leads to a deeper minimum of the liquid state of the plane layer and in all cases to an enlargement of the corresponding dip. This effect is very slight for models b and c but much more marked for model a. However, the position of this minimum is unchanged and is always situated about 6 Å as for the conformational one. Concerning the shortest C7 chains (see Figure 12), for both plane or curved layers, the "liquid state" minimum is changed on the same level.

We have analyzed the variations of F_{conf}, F_{total}, S_{conf}, and $\langle E \rangle$ obtained at two distances corresponding to the liquid

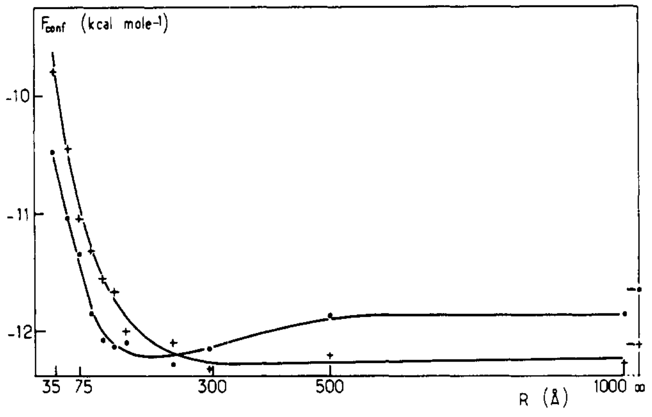

Figure 13. Conformational free energy of a C17 chain for two distances between chains vs. the radius of curvature: (●) d = 5.75 Å and (+) d = 6 Å.

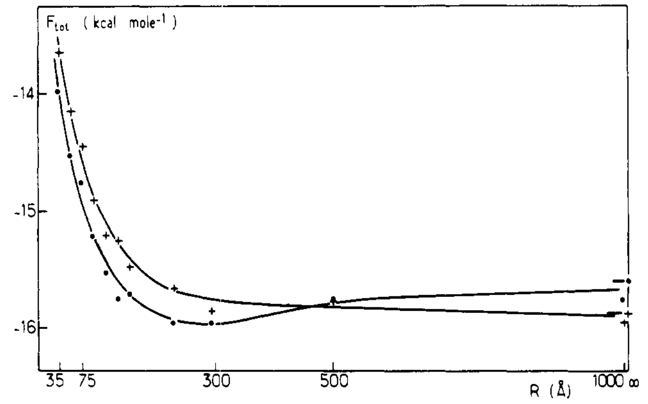

Figure 14. Total conformational and translational free energy of a C17 chain vs. the radius of curvature calculated according to model c of free surface and for two distances between chains: (●) d = 5.75 Å and (+) d = 6 Å.

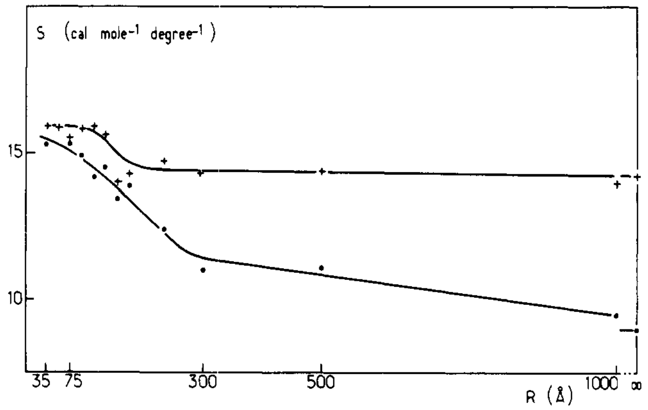

Figure 15. Conformational entropy of a C17 chain for two distances between chains vs. the radius of curvature: (●) d = 5.75 Å and (+) d = 6 Å.

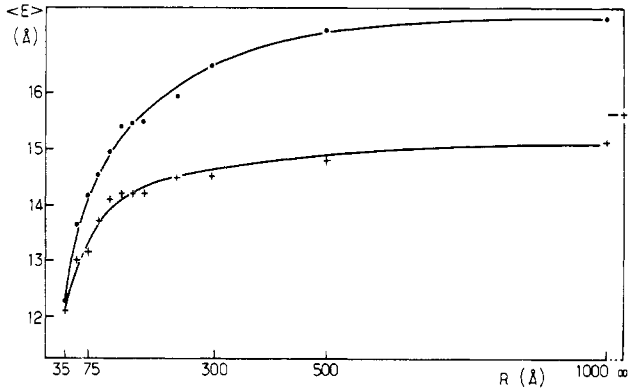

Figure 16. Thickness of a layer of C17 chains for two distances between chains vs. the radius of curvature: (●) d = 5.75 Å and (+) d = 6 Å.

state (always situated between 5.75 and 6 Å) as a function of the radius of curvature for two chain lengths. In the case of C17 chains (Figure 13) a rapid decrease of the conformational free energy is observed for an increase of the radius of curvature up to 150 Å. For larger values of R the free energy exhibits only a slight variation about its asymptotic value. The behavior of the total free energy (Figure 14) is the same. The more stable state appears at d = 6 Å although this "liquid state" minimum is larger especially for small radii of curvature. For d = 6 Å and for R larger than 150 Å a real decrease of the entropy takes place down to an asymptotic value (Figure 15). The behavior of the thickness is exactly the opposite since up to R = 150 Å we can see a sharp increase of this quantity, the variation being much less important for larger values of R (Figure 16). In the case of C7 chains the behavior is approximatively the same but with greatly reduced variations. The minimum corresponding to the liquid state is obtained at an interchain distance of about 6 Å and is very broad. For radii larger than 150 Å the total free energy does not vary.

The variation of the thickness of a C17 chain as a function of the radius of curvature is about 17% between R = 35 and 150 Å and 6% for larger radii. These variations are respectively equal to 10 and 2.5% for C7 chains.

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Sodium Ion Diffusion Coefficients in Aqueous Salt-Free Polyelectrolyte Solutions

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ABSTRACT: Counterion tracer diffusion coefficients of the sodium ion in aqueous salt-free solutions of sodium alginate, sodium ι-carrageenan, and sodium dextran sulfate are found to be dependent on polyion concentration over the range (3×10^{-5})–(8×10^{-2}) equiv/L. The diffusion coefficients obtained are fairly constant over a limited range varying in polyion concentration from (1×10^{-2})–(1×10^{-3}) equiv/L. In this flat region a minimum value for the diffusion coefficient is observed, which is used to correlate with the Manning and Yoshida theoretical predictions.

Studies pertaining to the diffusion of counterions in aqueous salt-free polyelectrolyte solutions are important in the understanding of small ion–polyion and polyion–polyion interactions in aqueous solutions. However, few such studies have been done with polyelectrolytes other than poly(styrene sulfonate) (PSS) and polyacrylate (PA).[1-4] The purpose of this counterion tracer diffusion study was to investigate how well modern polyelectrolyte theories predict the behavior of other polyelectrolytes, namely the sodium salts of dextran sulfate, ι-carrageenan, and alginate in aqueous salt-free solutions, and to determine the dependence of the sodium ion diffusion coefficient on the polyion concentration of these ionic polysaccharides.

The Manning theory[5-7] has proven most useful in describing the transport and equilibrium properties of polyelectrolyte solutions. Comparison of the theoretical diffusion coefficients of counterions in polyelectrolyte solutions containing simple salt, for example, has shown good agreement with experiment at low concentrations.[8-12] This is expected since the Manning theory is a limiting law and strictly can only be applied at the limit of infinite dilution.

In the salt-free limit for monovalent counterions, the Manning theory states that the ratio of the diffusion coefficient of the counterion i in the presence of the polyion D_i to the diffusion coefficient of the counterion in water D_i^0 is a constant and is given by

$$D_i/D_i^0 = 0.866/\xi \qquad \text{for } \xi > 1 \tag{1}$$

$$D_i/D_i^0 = 1 - (0.55\xi^2)/(\xi + \pi) \qquad \text{for } \xi < 1 \tag{2}$$

where ξ is a linear charge density parameter

$$\xi = e^2/\epsilon kTb \tag{3}$$

where e is the protonic charge, ϵ is the dielectric constant of the solvent, T is the temperature, b is the average distance between charge groups on the polyelectrolyte, and k is the Boltzman constant. The theory predicts that condensation occurs in solution if ξ_c is less then ξ, where ξ_c is the critical charge density parameter

$$\xi_c = |z_i z_p|^{-1} \tag{4}$$

where z_i is the valence of the counterion and z_p is the valence of the polyion. Condensation continues until the effective value of ξ is reduced to an effective ξ_c; at this point the uncondensed mobile ions in solution interact with polyion via Debye–Hückel forces. The theory thus predicts that when $\xi > 1$ for a system containing only monovalent counterions the fraction of undissociated ions is $(1 - \xi^{-1})$ and the fraction ξ^{-1} makes up the diffuse ion atmosphere. The fraction of condensed ions in the theory is assumed to have negligible mobility along the polyion chain. The site bound ions are those which lose their hydration shells and bind close to the polyion bringing about a strong decrease in the electrostatic field in the space surrounding the charged site and the ion. These ions have negligible mobility for the most part because of the strong electrostatic interactions. Ionic atmosphere bound ions, on the other hand, retain most of their hydration shell and bind at larger distances from the polyion. These ions are less tightly held than the site binding ions and are free to move parallel to the axis of the polyion.

A phenomenological approach to diffusion in salt-free polyelectrolyte solutions has been developed,[13] and Yoshida has developed a molecular theory.[14] Yoshida uses many of the assumptions of the Manning model.[14] Like the Manning theory, Yoshida predicts that the diffusion coefficients of the counterion in the presence of a polyion in salt-free aqueous solutions should be constant and a function of the linear charge density parameter only. The Yoshida equation is

$$D_i/D_i^0 = (1 + 1.300/\xi)/3 \qquad \text{for } \xi > 1 \tag{5}$$

However, Yoshida's theory differs from Manning's theory in that he assumes the condensed ions are able to move parallel to the axis of the polyion, taking into account the mobility of these condensed ions by assuming that it is equal to one-third that of the free ions in solution. Such an assumption seems more reasonable than Manning's assumption of negligible condensed ion mobility especially in light of recent evidence from NMR studies performed by Leyte et al.[15,16] Since both of these theories predict that there is no concentration dependence on the polyion in the salt-free case, it is difficult to compare literature values,[1,2]

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