Dimeric Surfactants: A Simplified Model for the Spacer Chain

Haim Diamant[†] and David Andelman[*,†,‡]

School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel, and Groupe de Physico-Chimie Théorique, E.S.P.C.I., 10 rue Vauquelin, 75231 Paris Cedex 05, France

Dimeric surfactants are composed of ordinary surfactant monomers for which the polar head groups have been chemically linked in pairs by an alkanediyl chain ("spacer"). This pairwise linking has been shown by experiments to change quite drastically the physical and chemical properties of the surfactant solution, as compared to those of the original monomers.[1-3] In particular, one can mention the influence of the spacer on aggregate morphology,[2] which is directly related to changes in the specific area of the surfactant molecules at interfaces.[3]

In a recent article[4] we presented a theoretical model for the interfacial behavior of dimeric surfactants and its dependence on the spacer carbon number. The model treats a saturated monolayer of soluble dimeric surfactants at an interface and considers the following major factors: (i) hydrophilic–hydrophobic interactions among the surfactant monomers, (ii) translational entropy of the dimers on the interface, (iii) exchange with the bulk solution due to surfactant solubility, and (iv) characteristics of the spacer chain. The latter is the most complicated factor to model, since the spacer chains (containing up to about 20 alkyl groups) are too short to be treated as polymer chains. Hence, we resorted to computer simulations in order to get statistical information on the spacer configurations and then combined the data with the other interactions. The model succeeds in explaining experimental findings regarding the nonmonotonic dependence of the surfactant specific area at the water/air interface on the spacer carbon number. It also shows that the interfacial behavior is dominated by two of the factors mentioned above, namely the interactions between monomers and the characteristics of the spacers linking them.

In this paper we wish to present a further simplification of our model. The main purpose is to significantly facilitate the treatment of the spacer contribution for possible applications in other models involving dimeric surfactants.

Consider an aliphatic spacer chain containing n CH$_2$ groups and connecting two surfactant monomers. Those two end monomers are restricted to lie on the flat water/ air or water/oil interface due to their amphiphilic character. On the other hand, the spacer may take various configurations, each having its own end-to-end distance, r. The configurations differ from those of a free chain, since the hydrophobic spacer groups favor the half-space of the nonaqueous phase, while the spacer ends are kept "pinned" to the interface. If we characterize the probability distribution (g_n) of the end-to-end distance by its mean (R_n) and variance (V_n) and then fit it to a Gaussian distribution (as we did in ref 4 using E_n to denote the mean), the spacer contribution to the free energy per dimer can then be written as

Table 1. "Spring" Parameters for Spacer Chains of n = 1–20 Groups of CH$_2$ at Room Temperature (T = 25 °C), Obtained from Rotational–Isomeric Simulations[a]

n	R_n, Å	K_n, mN/m	n	R_n, Å	K_n, mN/m
1	2.53	∞	11	10.22	93.4
2	3.46	2470	12	10.67	74.8
3	4.61	2690	13	11.16	57.5
4	5.43	1480	14	11.55	48.2
5	6.38	758	15	12.01	39.2
6	7.07	607	16	12.39	34.0
7	7.89	343	17	12.77	28.9
8	8.47	261	18	13.14	25.2
9	9.14	168	19	13.49	22.3
10	9.64	130	20	13.86	20.1

[a] See ref 4 for more information.

$$f_n = -k_B T \log g_n \simeq \frac{k_B T}{2V_n}(r - R_n)^2 \qquad (1)$$

where T is the temperature and k_B the Boltzmann constant. It should be stressed that the Gaussian fit does *not* imply that the chains are Gaussian. This procedure should be regarded merely as a second-moment approximation of the full distribution.

Using eq 1, we may identify the spacer with an analogous "entropic" spring of equilibrium length R_n and spring constant $K_n = k_B T/V_n$. The moments R_n and V_n can be found by simulating hydrocarbon chains under appropriate geometric constraints (the chains are to be restricted to the nonaqueous phase with their ends pinned to the interface). Such simulations, using the rotational–isomeric model, were described in ref 4. They yield, for room temperature, the parameters listed in Table 1. The analogous spring may then be combined with other interactions, in order to examine the influence of the spacer on properties of the dimeric surfactant.

As a demonstration of the usefulness of this simple approach, let us qualitatively examine the dependence of the distance between two monomers of a single dimer on the spacer carbon number. We look at a single dimer participating in a monolayer at a water/oil or water/air interface and consider only the interactions within this dimer. Referring to the notations of our fuller model,[4] this picture corresponds to omitting the contact with the bulk solution ($B = 0$) and the surface translational entropy ($s_{tr} = 0$).

We divide the interactions between the two monomers into two parts: (i) the contribution of the spacer linking the two monomers and (ii) the hydrophilic–hydrophobic interaction due to the attraction between their tails and repulsion between their head groups. For the spacer contribution we use the simplified "spring" term, f_n, described above. In order to estimate the hydrophilic–hydrophobic interaction between the two monomers, let us recall the case of a monolayer composed of *monomeric* surfactants, *i.e.* without any spacer. Using the phenomenological formula introduced by Israelachvili *et al.*,[5] we may roughly estimate the energy of interaction between two monomers in a saturated monolayer by

$$u = \frac{2\gamma}{q\Sigma}(\Sigma - \Sigma_0)^2 = \frac{2\gamma}{q}(r - R_0^2/r)^2 \qquad (2)$$

where Σ is the specific area and r the distance between monomers ($\Sigma = r^2$), Σ_0 and R_0 their optimal values, respectively, γ the water/hydrocarbon surface tension (~50

† Tel Aviv University.
‡ E.S.P.C.I.
(1) Zana, R.; Benrraou, M.; Rueff, R. *Langmuir* **1991**, *7*, 1072–1075.
(2) Zana, R.; Talmon, Y. *Nature* **1993**, *362*, 228–229.
(3) Alami, E.; Beinert, G.; Marie, P.; Zana, R. *Langmuir* **1993**, *9*, 1465–1467.
(4) Diamant, H.; Andelman, D. *Langmuir* **1994**, *10*, 2910–2916.

(5) Israelachvili, J.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc. Farad. Trans. 2* **1976**, *72*, 1525–1568.

mN/m), and $q \sim 6$ the coordination number on the interface (number of nearest neighboring molecules in the saturated monolayer).

We now return to our dimer, combine the spacer and interaction contributions, and minimize the total dimeric free energy, $u + f_n$, with respect to the intermonomeric distance r. The resulting equilibrium distance, r_e, satisfies the equation

$$(K_n + 4\gamma/q)r_e^4 - K_n R_n r_e^3 - 4\gamma R_0^4/q = 0 \qquad (3)$$

If the two competing distances, R_n and R_0, are not too far from one another, and the spacer chain is flexible enough, then r_e is close to R_0. In such a case, eq 2 can also be approximated by a "spring-like" energy, $u \simeq (8\gamma/q)(r - R_0)^2$, and combining the two contributions is analogous to connecting two springs in parallel. The resulting equilibrium distance is just $r_e \simeq (K_n R_n + K_0 R_0)/(K_n + K_0)$, where $K_0 = 16\gamma/q$ is the interaction "spring constant".

Let us consider as an example the special case of $[N^+(CH_3)_2C_{12}H_{25}Br^-]_2(CH_2)_n$ dimers, which are DTAB monomers linked by a $(CH_2)_n$ spacer. The distance between surfactant molecules in a saturated DTAB monomeric monolayer is known to be $R_0 \simeq 7.4$ Å. The dependence of the intermonomeric distance, r_e, on the spacer carbon number, n, can be calculated from eq 3 using Table 1 and is depicted in Figure 1. For $n = 10-13$, the intermonomeric separation stops increasing and starts decreasing with increasing carbon number. This non-monotonic behavior has been obtained here for a single dimer, but should naturally affect the molecular area in the entire dimeric monolayer, as indeed found by experimentation.[3] Looking at Figure 1, we find that r_e remains close to R_0 for $n = 5-20$. Indeed, one may use in this case the simpler concept of "parallel springs" mentioned above and obtain a curve similar to that of Figure 1.

Note, that we have used several simplifying assumptions and assigned estimated values to a few parameters, yet no free parameter has been adjusted to obtain the results of Figure 1. It should be stressed, however, that such results are merely qualitative. In order to get a more accurate, quantitative description of the interfacial behavior, one will have to include additional interactions such as chain—chain interactions between spacers of neighboring dimers.

The following two conclusions can be drawn. First, we infer that, in spite of its extreme simplicity, a naive "spring"
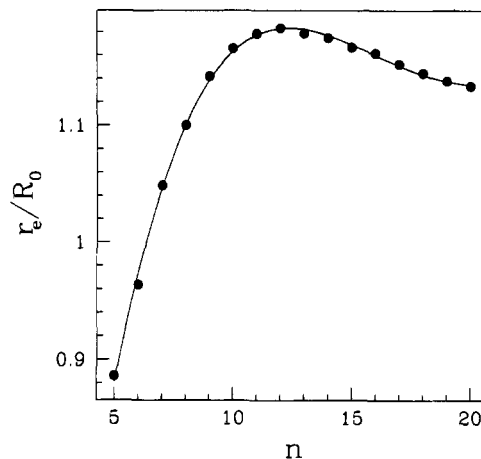

Figure 1. Dependence of the intermonomeric distance in a DTAB dimer at an interface on the spacer carbon number. No free parameters are used.

model of the spacer chain is still able to capture the essential effect of the spacer on features of dimeric surfactants. The second conclusion refers to the non-monotonic dependence of the specific area in a dimeric monolayer on the spacer carbon number. As mentioned above, this effect was observed in experiments and also obtained by our earlier, more elaborated model. It has been further shown in this paper that the nonmonotonic behavior is not only a quality of the entire monolayer but appears already when considering interactions within a single dimer. The phenomenon is a result of a basic competition between the spacer characteristics (length and flexibility) and the other interactions that exist between monomers. We suggest, therefore, that a similar nonmonotonic dependence on the spacer carbon number should also be observed for higher multimers of the same monomer (trimers, quadrimers, etc.). Such molecules have been lately synthesized,[6] and this prediction must be confirmed by future experiments.

(6) Zana, R. Private communication.