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ORIGINAL CONTRIBUTION

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Dynamic surface elasticity of polymer solutions

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Abstract The surfaces of surfactant solutions exhibit viscoelastic dilational behavior which may be investigated by modern optical and mechanical methods. The present study focuses on the dynamic dilational properties of the polymer solution – gas interface. Linear flexible polymer chains at the surface are considered as consisting of "trains," lying on the surface, and "loops" and "tails" that protrude into the liquid. The Rouse model is used to describe the inner dynamics of the trains, whereas their motion relative to their neighbors on the surface can be described with the help of the reptation conception. An expression for the complex dynamic dilational surface elasticity has been derived. Although, in general, the relaxation of the surface tension is characterized by an infinite series of relaxation times, it is shown that for many systems the dynamics of the surface layer can be described approximately by only two main relaxation times. The dispersion equation, which was obtained earlier for solutions of conventional surfactants, is shown to be fulfilled for polymer solutions also.

Key words Surface elasticity – air-water interface – adsorption flexible polymer chains – dynamic surface behavior

Introduction

During recent years the dynamic properties of insoluble and soluble adsorption films of polymers at the liquid-gas interface, especially the dynamic surface tension (surface pressure) and the shear surface viscosity, have been subjected to intensive research [1]. However, in some cases an interpretation of the results is not simple and progress in this field is restrained by the lack of an elaborate theory . Until now, the dynamics of polymer chains at the free liquid surface has been described with the help of the dumbbell model which can lead to reasonable results only for dilute solutions [2, 3]. It is obvious that in the case of the surface layer of a solution of a surface-active polymer this restriction is too severe and for real systems the surface layer can be considered as a concentrated or semidilute solution.

On the other hand, optical [4] and mechanical [5, 6] methods of measurement have been developed recently that allow reliable determination of the dilational dynamic properties over a broad frequency region. These experimental techniques have some advantages in comparison with the more traditional measurements of the shear surface viscosity. In fact, the classic studies of bulk liquid phases have shown that the dynamic properties connected with the overall expansion (compression) can be presented as a superposition of a finite number of different contributions [7]. Each of them corresponds to a single chemical or physical process in the system and, consequently, the measurements of the dynamic elasticity can be used to study the mechanisms of these processes. On the contrary, shear deformations are connected mainly with the processes of the structural reorganization characterized by a broad and almost continuous spectrum of relaxation times. In addition, the thermodynamic theory of the dilational properties [7] has essentially more general character than the conventional theories of the shear viscosity of complex fluids, which are usually based on particular models.

The general thermodynamic theory of the surface dynamic dilational properties has been constructed also [8–11] and was applied to solutions of conventional surfactants [6]. In this case, it is necessary to take into account the diffusion of the surfactant from and to the surface. However, for macromolecular surfactants the characteristic diffusional time is too large and one can consider only rapid surface strains corresponding to the homogeneous polymer concentration outside the surface layer. Then for the dilational dynamic surface elasticity the following representation can be used [8]:

$$\varepsilon \equiv \frac{\delta\sigma}{\delta \ln S} = \left(\frac{\partial\sigma}{\partial \ln S}\right)_{\xi} - \sum_{i=1}^{N}\left(\frac{\partial\sigma}{\partial \ln S}\right)_{\xi} - \frac{\left(\frac{\partial\sigma}{\partial \ln S}\right)_{\xi} - \left(\frac{\partial\sigma}{\partial \ln S}\right)_{A_i\xi_j}}{1 + i\omega\tau_i}, \qquad (1)$$

where N is the number of normal relaxation processes in the surface layer, σ is the surface tension, S is the area of a surface element, ω is the angular frequency, τ_i is the isothermal relaxation time of a normal reaction (process) i, ξ_i is the chemical variable, A_i is the corresponding reaction affinity. As usual, the lower index ξ_i means that the derivative corresponds to a non-equilibrium process but is taken at the equilibrium values of the thermodynamic variables, in particular, at $\xi_i = 0$; the lower index A_i indicates equilibrium conditions for a normal process i.

Relation (1) describes the frequency dependence of the dynamic surface elasticity. However, a concrete kinetic model of the surface layer is necessary to calculate the relaxation times and the corresponding relaxation strengths. It is noteworthy that in the last two years there has been a considerable progress in the understanding of polymer chain dynamics in solutions [12, 13]. Using these results and the data obtained in the course of the recent studies of the equilibrium surface layer [14] it is possible to determine all parameters of the relation (10) and therefore to calculate the dynamic surface elasticity. The solution of this problem for linear flexible polymers is the main content of the present work.

Model of the surface layer

In this work the concentration of polymer chains in the solution c is assumed to be small ($c \ll 1$). However, c may exceed the overlap concentration. Thus, the solution can be dilute or semi-dilute. The adsorption process leads to a higher concentration in the surface layer. For macromolecular surfactants the adsorption can be so high that a gel-like macroscopic film forms at the gas-liquid interface [15]. If the characteristic scale of the surface perturbation is far greater than the film width, this case is the most simple from the point of view of the surface rheology. Then, on the one hand, the polymer film influence only the boundary conditions for the three-dimensional dynamic equations of the liquid and, on the other hand, the dynamics of the film itself can be described in the frame of the elaborate rheology of homogeneous polymer solutions [13].

The case when the surface layer cannot be represented as a homogeneous film appears to be the most interesting. In fact, numerous investigations of the equilibrium adsorption of flexible polymers have led to a rather simple picture of the surface layer. It can be represented as consisting of two parts: a relatively concentrated region which has a width of about the monomer size (the monolayer) and "tails" and "loops" of polymer chains protruding into the liquid (Fig. 1a). The concentration of monomers depends on the distance from the surface and reaches the value corresponding to the bulk phase when the distance exceeds the size of the polymer coil.

In Fig. 1a some boundary regions ("points") where polymer chains transit from the monolayer to the subphase are also marked. These points hinder the motion of a train on the surface and a chain wriggles (reptates) between them. The set of restrictions can be presented conditionally as a two-dimensional tube with a chain reptating inside (Figs. 1b, 1c). Thus, the motion of a train on the surface can be described with the help of a two-dimensional analog of the reptation model [12]. This model was constructed to describe the diffusion of polymer chains through the net-work of entanglements. In the two-dimensional case the entanglements can be formed, for example, by the intersection points (Fig. 2) when one of the chains covers the other from the liquid side. However, the real nature of the entanglements is not important [12]. In any case, we can use the reptation model and determine a characteristic scale – the mean distance between two neighboring entanglements a without taking into consideration if there are real entanglements or there are only some restrictions formed by the transitional points (the monolayer – the subphase).

Thus, the possibility for the chains to move from the monolayer to the subphase distinguishes the case under consideration from the conventional two-dimensional reptation model. In the following the term "adsorption" will mean the transition of a monomer from the subphase to the monolayer and the term "desorption" will mean the reverse process. While the adsorption equilibrium is being

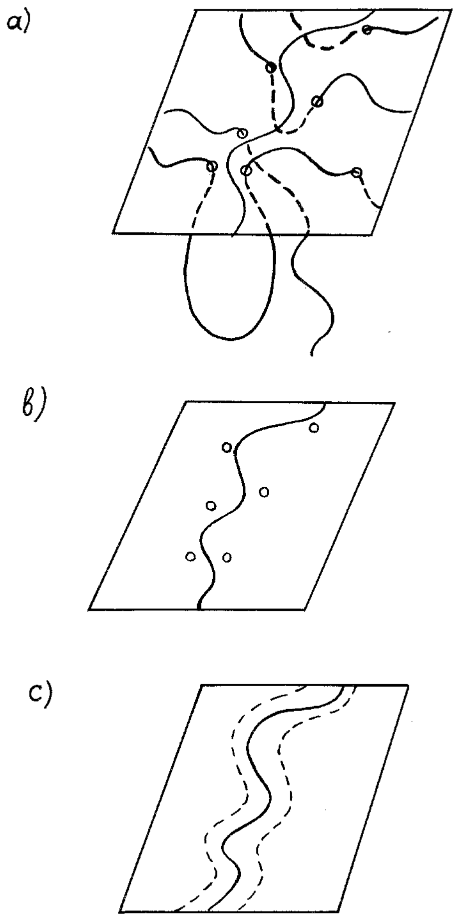

Fig. 1 Model of the surface layer. a) The monolayer, the "tails" and "loops" of polymer chains in the subphase. Transitional regions (the monolayer – the subphase) are marked for adsorbed chains. b) A polymer train in the monolayer. The transitional points (the monolayer – the subphase) are shown for neighboring chains, restricting the motion of the marked chain. c) A polymer train in the monolayer inside a two-dimensional tube, formed by neighboring chains

established the following processes can take place:

1) adsorption of the chain segments at the transitional points (the drawing up of chains on the surface);

2) desorption of the chain segments at the transitional points (squeezing the chains out of the surface);

3) transition of some monomers to the surface when a polymer coil approaches the monolayer (entanglement of the coil);

4) departure of a polymer coil from the surface (disentanglement of the coil);

5) formation or the disappearance of the chain loops as a consequence of a large fluctuation which includes many monomers.

6) reorganization of the polymer chains in the monolayer and two-dimensional crystallization (melting of the chains).

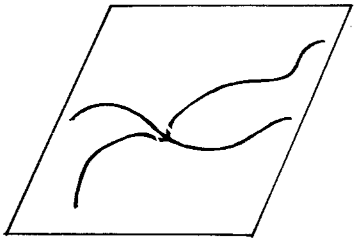

Fig. 2 A region of the intersection of two chains in the surface layer ("two-dimensional entanglement")

The analogy between the adsorption at the liquid-gas interface and two-dimensional crystallization of the polymers was investigated by Ueberreiter et al. [15]. It was shown that solid-like domains can be formed in the surface layer. However, we shall assume that the mobility of the chains in the monolayer is not influenced by the existence of the solid-like regions and so the sixth kind of the process is not taken into account.

It is obvious that the rate of the third kind of process decreases sharply as a function of the surface concentration (surface pressure), and near equilibrium the corresponding contribution is negligible. If the system is not too dilute, the segments of the polymer chain nearly fill the whole monolayer.

The rate of the fourth process is low also. In order to leave the surface the chain has to consist of a long tail in the liquid and a small train in the monolayer. The population of this state is obviously small for long chains.

The formation of a loop needs large scale fluctuations because of the limited flexibility of the chain. Therefore we may consider the fifth kind of process as very slow.

Thus, only the first and the second processes are important. Consequently, the initial undisturbed state of the system can be considered as the dynamic equilibrium when the rate of adsorption 1) approx. equals the rate of desorption 2). This condition does not necessarily correspond to the true thermodynamic equilibrium of the surface layer. Slow processes 3–6 are possible in the system. Our dynamic condition means only that we shall consider only those mechanical perturbations of the surface and relaxation processes which proceed considerably faster then the complete equilibration of the system which has to include the last four processes.

Equations of motion for an adsorbed chain

In the following, the classic Rouse model [12, 13] will be used to describe the dynamics of the parts of polymer chains lying on the surface. The real chain is assumed to consist of N frictional units (Rouse segments). The Rouse segments have the mobility constant B, and are connected by harmonic springs with the mean square separation b^2. Then, the dynamics of the chain are determined by the following equation

$$\frac{\partial r_n}{\partial t} = B\left(f_n + \frac{3k_BT}{b^2}\frac{\partial^2 r_n}{\partial n^2}\right), \tag{2}$$

r_n is the position of the n-th Rouse segment at time t: $N \gg 1$ and n can be considered as a continuous variable; f_n is an external force, k_B is the Bolztmann constant, T is the temperature.

Note that Eq. (2) corresponds to the ideal chain and does not take into account excluded volume effects and hydrodynamic interactions. However, in the region of the monolayer, where the local concentration is high and the chains are unfolded, this assumption can be satisfactory.

The external force can be represented as

$$f_n = f_{n_i} + \tilde{f}_n, \tag{3}$$

where $f_{n_i} = f_{\mathrm{ads}}\delta(n_i - n)$ is the adsorption force acting on the units $n_1, n_2, \ldots, n_i, \ldots$ in the transitional region between the monolayer and the subphase; $\tilde{f}_n$ is a random force ($\langle \tilde{f}_n(t) \rangle = 0$).

Thus, the parts of the chain $[n_1, n_2]$, $[n_3, n_4]$, $[n_{2i-1}, n_{2i}], \ldots$ lie in the monolayer within the two-dimensional tube (Fig.3). It is reasonable to assume that each of these parts contains a great number of monomers ($(n_{2i} - n_{2i-1}) \gg 1$). Then using the analogy with the three-dimensional case, we can utilize the idea of the primitive chain [17]: the shortest curve which has the same topology as the real chain relative to the other polymer molecules (Fig. 4). For long polymer chains in concentrated solutions it is possible to introduce three time scales: τ_A is the characteristic time of a random Brownian motion perpendicular to the primitive chain, τ_B is the characteristic time for intramolecular motion along the primitive chain, and τ_C is the characteristic time for the transfer of the chain as a whole in the tube. Moreover [18],

$$\tau_A \ll \tau_B \ll \tau_C \tag{4}$$

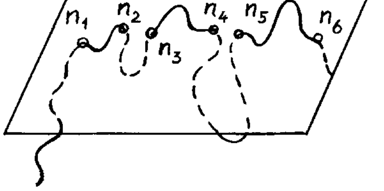

Fig. 3 A polymer chain consisting of several parts $[n_1, n_2]$, $[n_3, n_4], \ldots$, belonging to the monolayer, "tails" and "loops" in the subphase

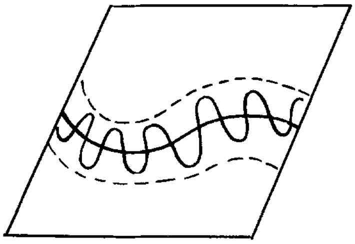

Fig. 4 An illustration of the concept "primitive chain"

Since we are interested in long time intervals approximately equal to τ_B and τ_C, we can average over the shortest time scale in Eq. (2) and consider only a motion of the primitive chain [18]:

$$\frac{\partial S_n}{\partial t} = \frac{3k_BTB}{b^2}\frac{\partial^2 S_n}{\partial n^2}, \tag{5}$$

where S_n is the distance from the first monomer measured along the primitive chain. It is assumed here that the force $\tilde{f}_n$ oscillates with a frequency more than τ_B^{-1}.

If the system is close to equilibrium, the probability for a monomer to move from the subphase to the surface layer approximately equals the probability of the reverse transition (from the monolayer to the subphase). The surface pressure results in a force that squeezes the chain out of the surface layer. This force is balanced by the adsorption force acting in the reverse direction. Therefore, the polymer train in the monolayer proves to be in a more compressed state in comparison with the parts of the chain in the subphase. Moreover, if the solution is dilute, the chain in the bulk phase is not restricted by a tube. Although in the case of semi-dilute solution some restrictions exist, the corresponding parameter a essentially exceeds the value for the monolayer.

Evidently, Eq. (5) does not take into account the action of the tube on the chain. Instead of the strict accounting of the tube potential in Eq. (5), it is possible to introduce a fictitious stretching force acting on the chain [18]:

$$F = \frac{3k_BTL}{N_0 b^2} = \frac{3k_BT}{a}, \tag{6}$$

where $L = N_0 b^2/a$ is the distance between the ends of the chain in he monolayer, N_0 is the number of monomers inside the tube, and b can be considered as the effective bond length of the real chain.

Then for the situation that Eq. (5) describes i.e., the motion of the part of the chain $[n_{2i-1}, n_{2i}]$ in the monolayer, the following boundary conditions can be imposed (at $n = 2i - 1$ and $n = 2i$):

$$\frac{3k_BT}{b^2}\frac{\partial S_n}{\partial n} = \frac{3k_BT}{a},$$

or

$$\frac{\partial S_n}{\partial n} = \frac{b^2}{a} \equiv l_0. \tag{7}$$

For an instantaneous small surface strain the length of a small element of the primitive chain Δl changes by the quantity $\Delta l\theta|\cos\alpha|$, were θ is the relative dilation ($\theta \ll 1$); α is the angle between direction of the compression or of the expansion (we consider here the unidirectional dilation) and the vector $u = \partial R(s,t)/\partial S$. Here, $R(s,t)$ is the curve of the primitive chain. The dilation is followed by a relaxation process including the desorption or the monomer adsorption from the subphase. Because the restrictions on the chain motion in the subphase are less severe than in the monolayer, it is possible to assume that the strain impulse is not transmitted in the bulk phase during the desorption (adsorption) process of several monomers. Only the nearest neighbors in the subphase take part in the motion. Consequently, if $\theta \ll 1$ and $n_{2i} - n_{2i-1} \gg 1$, Eq. (5) has to be fulfilled for a part of the chain in the monolayer, and the influence of the "loops" or "tails" can be taken into account only by the boundary conditions.

Because α is a stochastic function of n, we can consider only the mean deformation of the primitive chain: $2\theta\Delta l/\pi$. Then, the initial condition for Eq. (5) can be presented as

$$\left.\frac{\partial S_n}{\partial n}\right|_{t=0} = l_0 + \frac{2\theta l_0}{\pi}. \tag{8}$$

The solution of (5), (7), and (8) is

$$\frac{\partial S_n}{\partial n} = l_0\left[1 + \frac{2\theta}{\pi}\sum{}' \frac{4}{p_0\pi}\sin\left(\frac{p\pi n}{N_0}\right)\exp\left(-\frac{tp^2}{\tau_B}\right)\right], \tag{9}$$

where

$$\tau_B = \frac{b^2N_0^2}{3\pi^2k_BTB} \tag{10}$$

and the sum includes only the odd terms.

Note that at $p \Rightarrow \infty$ the absolute values of the terms in the series diminish very fast.

Calculation of the dynamic surface elasticity

In the general case there are three kinds of polymer chains in the monolayer: the chains completely lying on the surface, the parts of the chains with one transitional point the monolayer-the subphase ("tails" lying on the surface), and the trains with two transitional points. The corresponding mean numbers of monomers are N_1, N_2, *and* N_3. x_1, x_2, x_3 be the corresponding molar fractions ($x_1 + x_2 + x_3 = 1$), and $\tilde{n}$ the number of trains per unit of the area. Then, the number of monomers per unit of area can be represented in the following form:

$$\Gamma = N_1x_1\tilde{n} + N_2x_2\tilde{n} + N_3x_3\tilde{n}. \tag{11}$$

If the number of "loops" and "tails" in the subphase is not too large, we can consider that the surface pressure $\tilde{\pi}$ is determined only by the concentration of monomers in the monolayer, that is, by Γ:

$$\begin{aligned}\Delta\tilde{\pi} &= \frac{\partial\tilde{\pi}}{\partial\Gamma}\Delta\Gamma = \frac{\partial\tilde{\pi}}{\partial\Gamma}\Bigg[\Delta\tilde{n}(x_1N_1 + x_2N_2 + x_3N_3)\\ &\qquad + \tilde{n}x_2\Delta\left(\frac{L_2}{l_2}\right) + \tilde{n}x_3\Delta\left(\frac{L_3}{l_3}\right)\Bigg]\\ &= \frac{\partial\tilde{\pi}}{\delta\Gamma}\left(\Gamma\theta + \tilde{n}x_3\Delta N_3 + \frac{\tilde{n}X_2}{l_2}\Delta L_2 + \tilde{n}x_2\Delta N_2'\right),\end{aligned} \tag{12}$$

where L_1, L_2, and L_3 are the lengths of trains lying on the surface, and l_1, l_2, l_3 are the corresponding lengths per monomer. During derivation of relation (12) it was assumed that $N_1 = \text{const}$, $|\Delta N_2/N_2| \ll 1$, $|\Delta N_3/N_3| \ll 1$ and the term corresponding to the "tails" lying on the surface is divided into two parts: the contribution from the variation of the chain length and the contribution of the inner deformation of the chain. $\Delta N_2'$ is the variation of the number of monomers at the expense of the latter process.

Therefore, the adsorption (desorption) can be represented as a sum of two processes: the relaxation of the deformed chain (deformation of the chain is the consequence of both the external surface strain and the excessive surface pressure in the monolayer), and the squeezing out (drawing in) the whole train under the action of the excessive surface pressure. In the latter case the chain velocity is proportional to the force

$$\Delta\tilde{\pi}a = \frac{N_2}{B}\frac{d\Delta L_2}{dt}. \tag{13}$$

We have taken into account that the tube diameter approximately equals a.

The variation of ΔN_3 in the equation (12) can be determined with the help of the equality (9), where N_0 has to be changed by N_3. In fact,

$$\begin{aligned}\Delta N_3 &= \frac{L - L_0}{l_0} = \frac{1}{l_0}\left[\int_0^{N_3} l_n\,dn - N_3l_0\left(1 + \frac{2\theta}{\pi}\right)\right]\\ &= \frac{16N_3\theta}{\pi^3}\sum{}' \frac{1}{p^2}\exp\left(-\frac{tp^2}{\tau_B}\right) - \frac{2\theta N_3}{\pi}.\end{aligned} \tag{14}$$

The relaxation of ΔN_2 is also described by Eq. (5). However, in this case it is necessary to use the other boundary condition at $n = 0$

$$\frac{3k_B}{b^2}\frac{\partial S_n}{\partial n}\bigg|_{n=0} = \frac{3k_BT}{a} + \Delta\tilde{\pi}a,$$

or

$$\frac{\partial S_n}{\partial n}\bigg|_{n=0} = l_0\left(1 + \frac{a^2}{3k_BT}\frac{\partial\tilde{\pi}}{\partial T}\Delta\Gamma\right) \tag{15}$$

The boundary condition at $n = N_2$ and he initial condition maintain their form (8).

In Eq. (15) the quantity $\Delta\Gamma$ can be considered as a determined function of the time. The problem proves to be more complex in comparison with (5), (7), or (8). However, as before, standard methods [19] allow the solution to be obtained as,

$$\begin{aligned}\frac{\partial S_n}{\partial n} = l_0\Bigg\{&1 + \frac{a^2}{3k_BT}\frac{\partial\tilde{\pi}}{\partial\Gamma}\Delta\Gamma\left(1 - \frac{n}{N_2}\right)\\ &+ \theta\Bigg[\left(\frac{2}{\pi} - \frac{a^2}{3k_BT}\frac{\partial\tilde{\pi}}{\partial\Gamma}\right)\sum{}' \frac{4}{\pi p}\sin\frac{\pi pn}{N_2}\exp\left(-\frac{p^2t}{\tau_B}\right)\\ &+ \frac{2a^2}{3k_BT}\frac{\partial\tilde{\pi}}{\partial\Gamma}\Gamma\sum_{p=1}^{\infty}{}' \frac{(-1)^{p+1}}{\pi p}\sin\frac{\pi pn}{N_2}\exp\left(-\frac{p^2t}{\tau_B}\right)\Bigg]\Bigg\}.\end{aligned} \tag{16}$$

Using Eq. (16) and the following relation:

$$\Delta N_2 = \frac{1}{l_0}\left[\int_0^{N_2} l n \mathrm{d}n - N_2 l_0(1 + 2\theta/\pi)\right],$$

we find the necessary quantity

$$\begin{aligned}\Delta N_2' = N_2\Bigg\{&\frac{a^2}{6k_BT}\frac{\partial\tilde{\pi}}{\partial\Gamma}\Delta\Gamma - \frac{2\theta}{\pi}\\ &+ \theta\left(\frac{4}{\pi} - \frac{a^2}{3k_BT}\frac{\partial\tilde{\pi}}{\partial\Gamma}\Gamma\right)\sum{}' \frac{4}{\pi^2p^2}\exp\left(-\frac{p^2t}{\tau_B}\right)\Bigg\},\end{aligned} \tag{17}$$

where $\Delta\Gamma$ is determined by relation (12).

Substituting (12), (14), and (17) into relation (13), one obtains an ordinary differential equation of the first order which describes the relaxation in the surface layer. It follows then that the system is characterized by an infinite series of relaxation times $\tau_p = \tau_B/p^2$, where p is the multitude of odd numbers. To this series one has to add an extra relaxation time: $\tau_2 = N_2l_2/B\tilde{n}x_2a(\partial\pi/\partial\Gamma)$. This corresponds to the process of squeezing out (drawing in) the chains of the monolayer by the excessive surface pressure. However, the general solution is rather cumbersome and therefore it is necessary to consider only an important particular case: the surface layer containing long chains with many transitional points (monolayer – subphase). Then, $x_2 \ll 1$ and, consequently, $\tau_2 > \tau_B$. In this case, one can neglect the last term in relation (12). However, the previous term has to be retained. At $t > \tau_B$ the first two terms do not compensate each other and the slow relaxation characterized by the time τ_2 continues. The quantity ΔL_2 continues to change. However, we will consider $|\Delta N_2/N_2| \ll 1$, so the following unequalities fulfill $|\Delta N_3/N_3| < |\Delta N_2/N_2| \ll 1$. In this case, the relation (13) takes the simple form

$$a\frac{\partial\tilde{\pi}}{\partial\Gamma}\left(\Gamma\theta + \tilde{n}x_3\Delta N_3 + \frac{\tilde{n}x_2}{l_2}\Delta L_2\right) = \frac{N_2}{B}\frac{d\Delta L_2}{dt}, \tag{18}$$

where ΔN_3 is determined by Eq. (14).

At $t > \tau_B$, one can use the relation $|\Delta N_3| \cong \Delta N_{3\infty} \equiv 2\theta N_3/\pi$. Taking into account the initial condition $\Delta L_2|_{t=0} = 0$, we obtain the solution in the form

$$\Delta L_2 = -\frac{l_2}{\tilde{n}x_2}(\Gamma\theta - \tilde{n}x_3\Delta N_{3\infty})(1 - e^{t/\tau_2}). \tag{19}$$

Hence, an expression for the adsorption follows,

$$\begin{aligned}\Delta\Gamma &= \Gamma\theta + \tilde{n}x_3\Delta N_3 + \tilde{n}x_2\Delta N_2 \cong\\ &\cong \theta\Bigg[\frac{2\tilde{n}x_3N_3}{\pi}\sum{}' \frac{8}{p^2\pi^2}\exp\left(-\frac{tp^2}{\tau_B}\right)\\ &\quad + \left(\Gamma - \frac{2\tilde{n}x_3N_3}{\pi}\right)\exp\left(-\frac{t}{\tau_2}\right)\Bigg].\end{aligned} \tag{20}$$

Because the first term in the sum gives the main contribution, it is possible to approximately write

$$\begin{aligned}\Delta\Gamma \cong \theta\Bigg[&\frac{16\tilde{n}x_3N_3}{\pi^3}\exp\left(-\frac{t}{\tau_B}\right)\\ &+ \left(\Gamma - \frac{2\tilde{n}x_3N_3}{\pi}\right)\exp\left(-\frac{t}{\tau_2}\right)\Bigg].\end{aligned} \tag{21}$$

Then, the relation (12) allows us to obtain the dynamic surface tension $\Delta\sigma = -\Delta\pi$. Hence, using the Fourier transformation [11]

$$\varepsilon = -\int_0^{\infty}\Delta\sigma\, e^{-i\omega t}dt\Big/\int_0^{\infty}\theta e^{-i\omega t}dt, \tag{22}$$

we find the complex dynamic surface elasticity in the general case

$$\begin{aligned}\varepsilon = -\frac{\partial\sigma}{\partial ln\Gamma}\Bigg\{&\frac{2\Gamma_3}{\pi\cdot\Gamma}\sum{}' \frac{8i\tau_B\omega}{p^2\pi^2(1 + i\omega\tau_B/p^2)}\\ &+ \left(1 - \frac{2\Gamma_3}{\pi\Gamma}\right)\frac{i\omega\tau_2}{1 + i\omega\tau_2}\Bigg\},\end{aligned} \tag{23}$$

where $\Gamma_3 = \tilde{n}x_3N_3$.

The separation of the two main relaxation processes allows us to obtain the following approximate relation,

$$\varepsilon = -\frac{\partial\sigma}{\partial ln\Gamma}\left\{\frac{16\Gamma_3}{\pi^3\Gamma}\frac{i\omega\tau_B}{1+i\omega\tau_B/p^2} + \left(1-\frac{2\Gamma_3}{\pi\Gamma}\right)\frac{i\omega\tau_2}{1+i\omega\tau_2}\right\}, \tag{24}$$

Discussion of the results

In many cases the dynamic surface elasticity of solutions of surfactants can be investigated analytically . However, even a slight increase in the complexity of the system usually leads to extremely cumbersome expressions hindering their application [9–11]. Therefore, it seems quite surprising that the results for such complex systems as polymer solutions Eqs. (23), (24) prove to be relatively simple. We note, however, the great number of different assumptions made in the course of the derivation. Most of them are not purely intuitional but are based on the results of the numerous previous studies devoted to the physical chemistry of polymer solutions [12, 13]. Some of these assumptions considerably restrict the number of systems described by Eqs. (23) and (24), first of all, the limitations concerning the chemical nature of the polymer chains and the concentration range, such as the supposition about the structure of the surface layer for example. Probably, the most severe restriction is connected with the assumption of the monodispersity. However, if the chains are so long that the condition $x_2 \ll x_3$ is fulfilled, the polydispersity of the molecules does not influence the results. Only the influence of the polydispersity of the parts of the chains lying on the surface can be important. Although the length of these trains is limited from both sides (by the finite flexibility of the chains and by the low probability of the complete unfolding of the long chain on the surface), a noticeable polydispersity can exist for real systems. In this case, instead of the discrete spectrum of relaxation times at $\tau_2 \gg \tau_B$, it is possible to discriminate only between two different bands. Moreover, the distribution of polymer trains in the monolayer can depend on the conditions of the formation of the systems, not only on the thermodynamic parameters and the chemical nature of the molecules. In other words: after the formation of an occasional distribution within the characteristic time of molecular diffusion, the further transition to the thermodynamic equilibrium proceeds so slowly that it cannot be noticeable during the time accessible to the experiment. Then, the dynamic surface elasticity can depend on the experimental conditions. But even in this case the measurements of the imaginary and the real. parts of ε allow us to obtain significant information about the structure of the surface layer and the kinetics of the processes in it.

To compare the relations (23), (24) with the expression (1), it is necessary to use "quasichemical" approach and consider the following reactions in the surface layer (in the case of compression)

$$X_1^M + X_2^M \longrightarrow X_1^{M1} + X_2^S \tag{25}$$

$$X_3^M \longrightarrow X_3^S. \tag{26}$$

The reaction (26) is the desorption of monomers belonging to the trains on the surface with two transitional points, the monolayer – the subphase. The reaction (25) corresponds to the desorption of monomers belonging to the parts of chains with one transitional point (X_2^M). This process proceeds under the action of the chains lying completely on the surface (X_1^M). Therefore, one can imagine that the monomers on the surface move to an inactive state marked by an additional upper index 1. The reactions (25) and (26) are linearly independent and, consequently, correspond to normal processes. If we introduce the following quantities $\Gamma \equiv \tilde{n}x_1N_1$ and $\Gamma_2 \equiv \tilde{n}x_2N_2$, the thermodynamic derivatives in the relation (1) can be rewritten in the form

$$\left(\frac{\partial\sigma}{\partial\ln S}\right)_\xi = -\frac{\partial\sigma}{\partial\ln\Gamma}$$

$$\left(\frac{\partial\sigma}{\partial\ln S}\right)_{A_2,\xi_1} = -\frac{\partial\sigma}{\partial\ln(\Gamma_1+\Gamma_2)} = -\left(1-\frac{\Gamma_3}{\Gamma}\right)\frac{\partial\sigma}{\partial\ln\Gamma}$$

$$\left(\frac{\partial\sigma}{\partial\ln S}\right)_{A_1,\xi_2} = -\frac{\Gamma_3}{\Gamma}\frac{\partial\sigma}{\partial\ln\Gamma}, \tag{27}$$

where we take into account that $\partial\sigma/\partial\Gamma_1 = \partial\sigma/\partial\Gamma_2 = \partial\sigma/\partial\Gamma_3 = \partial\sigma/\partial\Gamma$, because the contributions of different monomers to the surface pressure are the same. The relaxation times were calculated earlier. Note that chains in the monolayer are not identically deformed and we have to use the factor $2/\pi$ before Γ_3. Then, Eq. (1) takes the form

$$\varepsilon = -\frac{\partial\sigma}{\partial ln\Gamma}\left[1 - \frac{\frac{2}{\pi}\left(1-\frac{\Gamma_1}{\Gamma_2}-\frac{\Gamma_2}{\Gamma}\right)}{1+\mathrm{i}\omega\tau_B} - \frac{1-\frac{2\Gamma_B}{\pi\Gamma}}{1+\mathrm{i}\omega\tau_2}\right]$$

$$= -\frac{\partial\sigma}{\partial ln\Gamma}\left[\frac{2\Gamma_3 i\omega\tau_B}{\pi\Gamma(1+i\omega\tau_B)} + \left(1-\frac{2\Gamma_3}{\pi\Gamma}\right)\frac{i\omega\tau_2}{1+i\omega\tau_2}\right]. \tag{28}$$

If we neglect a slight difference in numerical coefficients before the first terms, the last relation coincides with Eq. (24). This difference, apparently, is connected with the approximate nature of both relations (24) and (28).

The remarkable simplicity of the "quasichemical" approach becomes obvious if one takes into account that τ_B is the fundamental relaxation time of a polymer chain consisting of N_3 monomers, and the time τ_2 can be determined from the simple considerations as well. An advantage of a more strict approach consist only in clearing up the physical nature of numerous assumptions.

The main application of the obtained results is connected with the investigation of mechanical waves on the surface of polymer solutions. Recently, Harden, Pleiner, and Pincus have studied carefully different wave modes on the surface of semi-dilute solutions [20]. Their results, however, correspond only to polymers without surface activity. The analysis presented in this work shows that if the wavelength exceeds the thickness of the surface layer (for dilute solutions even the thickness of the monolayer), then some theoretical results obtained earlier for conventional surfactants can be transferred to the case of polymers. For example, the dispersion equation for surface waves [10] can also be used for polymer surfactants

$$(\rho\omega^2 - \sigma k^3 - \rho g k)(\rho\omega^2 - mk^2\tilde{\varepsilon}) - \tilde{\varepsilon}k^3(\sigma k^3 + \rho g k) - 4i\rho\mu\omega^3k^2 + 4\mu^2\omega^2k^3(m - k) = 0, \qquad (29)$$

where ρ is the density of the liquid, μ is the shear viscosity of the liquid, g is the gravitational acceleration, ω is the angular frequency, k is the complex wave number, $m^2 = k^2 - i\omega\rho/\mu$, $\mathrm{Re}(m) > 0$, and the dynamic surface elasticity ε for polymer solutions is determined by Eqs. (23) and (24) if it is possible to neglect the surface shear viscosity.

For semidilute solutions it is necessary to take into account that μ is a complex quantity and depends on the frequency. Then, for $\varepsilon = 0$, (29) reduces to the dispersion relation derived in [20].

However, the number of solutions of (29) is considerably greater. It is well-known that the account of surface elasticity leads to new solutions corresponding to longitudinal waves [10]. It is noteworthy that for polymer surfactants analysis of the dispersion relation has not been made until now.

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