A Simple Model for the Dynamic Surface Tension of Polymer Solutions

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Surfactant and polymer solutions are usually used under conditions involving transient dynamic surfaces, and therefore the dynamic surface tension (DST) is important in many industrial and biological fields. In a previous paper, we proposed a new mechanical model for surfactant solutions based on the concept that surfactant molecules rotate during the process of approaching the equilibrium surface state, which is different from the conventional adsorption theory, and a simple expression of DST was obtained as a function of the surface age. In the present paper, we discussed another model for polymer solutions, which is based on the similar concept that polymers rotate during the process of approaching the equilibrium surface state. As a result, a simple expression of DST for polymer solutions was derived as a function of the surface age. The expression was compared with our experimental data, as well as with results reported by other authors, and it was found that they are in good agreement. Furthermore, the characteristic time, which is the only unknown parameter in the model, was shown to be correlated with the weight concentration of the solution regardless of the type of solution examined.

Key Words: Adsorption / Fluid mechanics / Interface / Polymers / Dynamic surface tension / Mechanical simple model

1. INTRODUCTION

The addition of soluble materials in solvents induces considerable changes in the surface tension. In particular, the non-equilibrium surface tension of the solution/air interface of a freshly created solution (namely, the dynamic surface tension (DST)) is divergently changed by the addition from that in the case of pure solvent, which can not be explained by the equilibrium surface tension (namely, the static surface tension).

The first physical model of DST for interfaces with time-invariant areas was derived by Ward and Tordai. This model was based on the assumption that the dependence of the interfacial tension on time is caused by the transportation of molecules in the bulk solution to the interface, i.e., by adsorption. Many theoretical analyses of DST in surfactant solutions have since been undertaken exclusively on the basis of the concept of adsorption, some of them with considerable success. However, the adsorption theory is not self-sufficient and requires two relations; the relation between the interfacial concentration \( \Gamma \) of the adsorbing molecules and the bulk concentration of molecules near and at the surface, and the relation between \( \Gamma \) and DST. There are several expressions proposed for the two relations. In addition, the DST as obtained on the basis of the adsorption theory contains several parameters which must be determined beforehand, which makes it difficult to use the adsorption theory for engineering purposes. There have been a number of reviews on this topic. In a previous paper, the authors presented a model of the dynamic behavior of surfactant molecules at the surface, derived an expression of DST without relying on the adsorption theory, and showed that there is a good agreement between the DST predicted by the model and the one experimentally obtained for various kinds of surfactants. The previous model was based on the idea that molecules rotate about the center of the hydrophilic group due to the upward force exerted on the lyophilic group by the layer of solvent on which the surfactant molecule stands. However, the molecular weight of polymers is higher than that of surfactant molecules, and also their structures are different. Therefore, a different model is needed for the DST of polymer solutions.

In the present paper, we present another model for polymer solutions, by utilizing a similar concept where polymers rotate during the process of approaching the equilibrium surface state, derive a simple relationship for polymer solutions between DST and surface age, and confirm its agreement with
experimental results. It is shown that the resulting expression of DST is simple and convenient to use for engineering purposes.

2. NOMENCLATURE

\[ \begin{align*}
\Gamma & \quad \text{interfacial concentration of the adsorbing molecules} \\
t & \quad \text{arbitrary time or surface age} \\
\theta & \quad \text{rotation angle} \\
\sigma & \quad \text{dynamic surface tension} \\
\sigma_w & \quad \text{surface tension of water} \\
\sigma_s & \quad \text{equilibrium surface tension of samples} \\
\sigma_q & \quad \text{dimensionless dynamic surface tension} \\
f & \quad \text{driving force for rotation} \\
r & \quad \text{representative radius} \\
l & \quad \text{length of molecule} \\
T & \quad \text{rotary torque} \\
A & \quad \text{constant independent of } t \\
\mu & \quad \text{viscosity} \\
Z & \quad \text{coefficient with the dimension of time} \\
C & \quad \text{concentration}
\end{align*} \]

3. MODEL OF THE DYNAMIC BEHAVIOR OF POLYMER SOLUTIONS

Figure 1 shows a schematic representation of adsorption of macromolecules at the liquid interfaces; (a) unfolding molecules, (b) molecules with compact structure.\textsuperscript{6-7} For lower values of \( \Gamma \), molecules make orientation parallel to the interface (a-1 and b-1 in Fig. 1), while for higher \( \Gamma \), molecules are packed in a narrow area and orientated normal to the interface (a-2,3 and b-2 in Fig. 1). Any way, it should be noted that molecules are settled parallel or normal to the interface at the final equilibrium state. This means that molecules which existed at random at the beginning of surface creation have to rotate parallel or normal to the surface during the un-equilibrium process to the equilibrium state. We think it is this rotation that causes DST. Then we assume for convenience of analysis that the shape of the molecules is a rod, as seen in Fig. 2(a) and (b), and that at the time \( t = 0 \) when the surface is freshly created, the axis of the rod is oriented at an angle \( \theta = 0 \) (Fig. 2(a)). The rod rotates as the time \( t \) progresses \( (t = t; \theta = 0) \), approaching the equilibrium state where the rod is perpendicular to the surface \( (t = \infty; \theta = \pi/2) \). As shown in Fig. 1, it depends on the \( \Gamma \)-value whether the orientation of the molecule is perpendicular or parallel to the liquid surface in the equilibrium state. In the present model, the orientation at equilibrium is taken to be perpendicular to the surface (Fig. 2(a)). In the opposite case as well (Fig. 2(b)), if the angle is taken as shown in the figure, the procedure and the result become the same as those obtained in the case of the setup in Fig. 2(a). We assume that the DST is the same as the surface tension \( \sigma_s \) of the solvent (in the present case, water) at the incipiency \( (t = t; \theta = 0) \) and as the static surface tension \( \sigma_s \) of the polymer solution in the final state of equilibrium \( (t = \infty; \theta = \pi/2) \). Then, the dimensionless DST \( \sigma_q \) is defined as

\[ \sigma_q = \frac{\sigma - \sigma_s}{\sigma_w - \sigma_s} \]

where \( \sigma \) represents DST at time \( t \). It is easy to see that in this case \( \sigma_q = 1; t = 0 \) and \( \sigma_q = 0; t = \infty \).

The surface tension can be taken as the surface energy.
per unit area, that is, $\sigma_\alpha$, $\sigma_s$, and $\sigma$ are the surface energy of the solvent, the surface energy of the solution in the static state, and the surface energy of the same solution in the dynamic state, respectively. Furthermore, $f$ is taken to be a representative force per unit area working in the upward direction on the rod representing the polymer (Fig. 3), and we think that the difference between the surface energies in the dynamic and the static state ($\sigma - \sigma_\alpha$) is equivalent to the work performed by rotation from the angle $\theta$ to $\pi/2$ (see Fig. 3). Then, we obtain the following relation:

$$\sigma - \sigma_\alpha = \int_{\theta}^{\pi/2} f \cos \theta \cdot \frac{1}{2} \, d\theta - f \frac{1}{2} (1 - \sin \theta) \tag{2}$$

Similarly,

$$\sigma_s - \sigma_\alpha = f \frac{1}{2} \tag{3}$$

As the result, the following relation is obtained

$$\sigma_\theta = 1 - \sin \theta \tag{4}$$

The same result was derived on the basis of a different idea in the previous paper.\(^5\)

Then, if a polymer rotates about the center of the rod, a rotary torque $dT$ due to solvent viscosity working at the $dr$ section can be expressed as follows:\(^5\):

$$dT = k\mu \frac{d\theta}{dt} r^2 \, dr$$

where $r$ is the radius at an arbitrary position (Fig. 3), $\mu$ is the viscosity and $k$ is a numerical constant smaller than five.\(^5\) Integration with respect to $r$ from 0 to the half of the rod length $l/2$ gives the torque $T$ as

$$T = k\mu \frac{d\theta}{dt} l^3 = A \frac{d\theta}{dt} \tag{5}$$

where $A$ is a constant independent of $t$ but is regarded as a function of $l$ and $\mu$, and $\frac{d\theta}{dt}$ is the angular velocity of the rod, in which the moment of inertia is ignored.

On the other hand, $T$ is expressed as shown in Fig. 3,

$$T = f \cos \theta \cdot \frac{l}{2} \tag{6}$$

Therefore, we obtain the following expression from Eqs. (5) and (6),

$$\frac{d\theta}{dt} = \frac{1}{Z} \cos \theta \tag{7}$$

where $Z = \frac{2A}{l^3}$ and this has the dimension of time.

Equation (7) is integrated from the beginning of rotation ($t = 0; \theta = 0$) to an arbitrary state ($t = t; \theta = 0$), and yields

$$t = \frac{Z}{2} \ln \left| \frac{1+\sin \theta}{1-\sin \theta} \right| \tag{8}$$

Introducing Eq. (4), we obtain the following final expression for the relation between $t$ and $\sigma_\theta$:

$$t = \frac{Z}{2} \ln \frac{2 - 1}{\sigma_\theta} \tag{9}$$

4. COMPARISON BETWEEN THE MODEL AND EXPERIMENTAL RESULTS

Figure 4(a) and (b) shows the experimental results for two kinds of polyethylene oxides(PEO) of m.w.$2\times10^6$ and m.w.$12\times10^6$ as obtained by the authors with the pendant drop method.\(^5\) The solid and the dotted lines represent the best fit to the present model, showing a rather close agreement between the model prediction and the experimental results. Since the model does not fit the data with a concentration of 10 ppm by weight as shown in Fig. 4(b), a certain error in the experiment is thought to be included in this case. The values of $Z$ for the best fit are given in this figure. Another example of experimental data is given in Fig. 5 for PEO (m.w.$8\times10^5$) solutions\(^5\) where good agreement between the experimental data and the model prediction is seen in the entire range of values of $\sigma_\theta$. Each value of $Z$ used in the fitting is described in the figure. Figure 6 illustrates the experimental results for 1-decanol (m.w.$158$), which were obtained with the pendant bubble technique.\(^5\) The solid and the dotted lines show the best fit for the model, where the value of $Z$ is shown in the figure. It can be seen that the agreement is good in the middle range of values for $\sigma_\theta$, although the agreement is somewhat worse near the ends, where the predicted values of $\sigma_\theta$ are lower, and this is particularly apparent for higher concentrations. Factors such as intermolecular interaction or adsorption, both of which are ignored in the present model,
might play a role in delaying the rotation of the molecules in these ranges. Also, an example is shown in Fig. 7, where \( \sigma_q \)'s of different human liquids; serum, cerebrospinal fluid, and gastric juice, from patients suffering from various diseases are displayed\(^{11}\), since DST measurements have been utilized recently for the diagnosis of diseases. In this case, the values of \( \sigma_q \) did not appear in the literature, and the minimum value of the measured \( \sigma \) values was adopted as \( \sigma_0 \) for each sample. It is clear that a fairly good agreement exists between the data and the model prediction.

In this way, the present model provides a general description of the experimental results for several polymer solutions and biological liquids.

\( Z \) has the dimension of time, and if \( Z \) is substituted for \( t \) in Eq. (8), we obtain 49.6° as the value for \( \theta \), which corresponds to 0.236 for \( \sigma_0 \). Therefore, \( Z \) can be taken as the time necessary for a molecule to perform a rotation of about 50°. The smaller the value of \( Z \), the faster the molecule rotates. However, in the present model, DST was derived by considering the behavior of only one molecule, regardless of the concentration of the solution. Therefore, it should be noted that \( Z \) does not represent the time required for an actual molecule to rotate.

Fig. 4. (a) Dimensionless dynamic surface tension \( \sigma_q \) plotted against the surface age \( t \) for polyethylene oxide (m.w.2×10\(^4\)). Solid and dotted lines show the model prediction. The tube diameter used in measurement of \( \sigma \) was 0.27 mm.\(^{10}\)

(b) Dimensionless dynamic surface tension \( \sigma_q \) plotted against the surface age \( t \) for polyethylene oxide (m.w.2×10\(^4\)). Solid and dotted lines show the model prediction. The tube diameter used in measurement of \( \sigma \) was 0.27 mm.\(^{10}\)

Fig. 5. Dimensionless dynamic surface tension \( \sigma_q \) plotted against the surface age \( t \) for polyethylene oxide (m.w.8×10\(^3\)). Solid and dotted lines show the model prediction.

Fig. 6. Dimensionless dynamic surface tension \( \sigma_q \) plotted against the surface age \( t \) for 1-decanol (m.w.158). Solid and dotted lines show the model prediction.

Fig. 7. Dimensionless dynamic surface tension \( \sigma_q \) plotted against the surface age \( t \) for \( \times \) serum, \( \square \) liquor, and \( \triangle \) gastric juice. Solid and dotted lines show the model prediction.
by, but rather a measure of the time necessary for a solution to reach the equilibrium surface state. Figures 8 and 9 show \( Z \) for polymer solutions for which a fitting was performed in the present paper with respect to molar concentration and weight concentration, respectively. Although no correlation was obtained for the molar concentration (Fig. 8), a fairly good relation was obtained between \( Z \) and the weight concentration, regardless of the kind of polymers examined (Fig. 9). However, the data for the 10 ppm PEO solutions clearly deviate from the correlation, which might be caused by an as yet undetermined experimental error. In any case, the relationship is given by the expression \( Z = 2370C^{-1.9} \), where \( C \) is presented by [ppm].

5. DISCUSSION

The above mentioned correlation of DST with the weight concentration and not with the molar concentration means that the molecular weight, or the molecular size is not a main factor for determining DST, but the main factor is suggested to be the number of the molecular “units” (here the term units is used to mean elementary molecules of low molecular weight composing a polymer). That is, a polymer consists of many units, say \( n \) numbers of units, and the number of units in a long polymer is thought to be the same as the total number of units in short polymers if the weight concentration is the same between solutions of long and short polymers. The idea stated below on the kinematic behavior of polymers comes from referring to Fig. 1: An example is shown in Fig. 10 where \( n \) is taken to be six: (a) shows a group of short polymers each of which consists of two units, and (b) exhibits a long polymer consisting of six units. At the moment when a new surface is created, a group of six units in short polymers are freely dispersed near the surface (Fig. 10(a-1)), while another group of six units exists as a long polymer under the surface (Fig. 10(a-2)). As time has elapsed and adsorption has been completed, each short polymer is set parallel to the surface if \( \Gamma \) is low (Fig. 10(a-3)), and partly parallel and partly perpendicular to the surface if \( \Gamma \) is high (Fig. 10(a-3)). On the other hand a long polymer which existed freely under the surface becomes parallel to the surface if \( \Gamma \) is low (Fig. 10(b-2)), but it makes conformation where some units are perpendicular to the surface and the other units are attached and parallel to the surface (Fig. 10(b-3)). Like this, both groups of \( n \) units in short polymers (Fig. 10(a)) and a long one (Fig. 10(b)) rotate in the same manner, that is, there is no difference between short and long polymers concerning their rotations if the weight concentration is the same. This is thought to be the reason why \( Z \) is correlated with the weight concentration.

Fig. 8. Model constant \( Z \) plotted against the molar concentration \( C \).

Fig. 9. Model constant \( Z \) plotted against the weight concentration \( C \).

Fig. 10. Model of the dynamic behavior of polymers at the surface (see Fig. 1 as a reference). (a) A group of three short polymers each of which consists of two units. (b) A long polymer composed of six units.
6. CONCLUSION

In our previous paper, we proposed a new mechanical model for the dynamic surface tension (DST) of surfactant solutions based on the concept that surfactant molecules rotate during the process of approaching the equilibrium surface state, which is different from the conventional adsorption theory, and obtained a simple expression of DST as a function of the surface age. In the present paper, we presented another model for polymer solutions based on the similar concept that polymers rotate during the process of approaching the equilibrium surface state. Consequently, we obtained a simple expression for DST for polymer solutions as a function of the surface age. Good agreement was obtained upon comparing the expression with our experimental data as well as with experimental results reported by other authors. Furthermore, the characteristic time, which is the only unknown parameter in the model, was shown to be correlated with the weight concentration of the solution, regardless of the type of solution examined. Discussion was made on the correlation of DST with the weight concentration.

REFERENCES