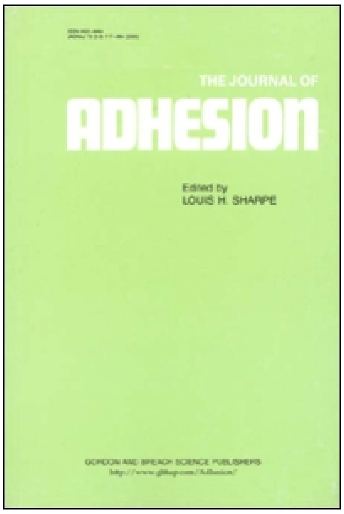

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The Concentration Dependence of Surface Tension of Polymer Solutions

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This paper is a critical review of present methods of estimating polymer surface tension. The authors propose the thermodynamic consideration of concentration dependence of the surface tension of polymer solutions leading to the equation which includes the surface tension of the solid polymer. The latter can be calculated in this way without any arbitrary assumptions.

INTRODUCTION

The surface tension of solid polymers represents the free energy of new surface formation and is one of the most essential characteristics of polymers, especially when the processes of adhesion, wetting and others are considered. The surface tension determines also the cohesive strength of the solid in thermal and mechanical equilibrium, as it is known that

$$W_c = 2\gamma_s \tag{1}$$

where W_c is the cohesion energy and γ_s the surface tension at the solid–vapor interface.

Polymers are solids which have low surface energy. There are many data in the literature concerning the values of the surface tension of polymers. Nevertheless, these values lead to the conclusion that the cohesive strength of organic liquids and solid polymers are equal, independent of phase or aggregate state. From this viewpoint there is a great interest in finding out the true values of surface tension of polymers.

In this article the authors have as an aim the critical review of present methods of estimating polymer surface tension and propose the thermodynamic consideration of concentration dependence of the surface tension of polymer solutions leading to the equation which includes the surface tension of the solid polymer. The latter can be calculated in this way without any arbitrary assumptions.

1 THE DEMERITS OF PRESENT THEORIES

The main method of estimating the surface tension of solid polymers is one proposed by Zisman[1,2] and based on the measurement of contact angles of different liquids on solid polymers. For the equilibrium at the interface liquid–solid–vapor the Dupre–Young equation can be applied:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \tag{2}$$

where θ is the contact angle, γ the surface tension at the interface, solid–liquid (SL) and liquid–vapor (LV). Zisman has found the existence of the linear relationship between $\cos \theta$ and γ_{LV} for homologous series of liquids on solid surfaces. The value of γ_{LV} at $\cos \theta = 1$ which can be found by extrapolation is known as critical surface tension of wetting, γ_c. Some authors believe[3,4] that γ_c is identical with γ_{SL}. Really at $\theta = 0$, Eq. (2) may be written as

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}$$

At this point

$$\gamma_{LV} = \gamma_c$$

and then

$$\gamma_c = \gamma_{SV} - \gamma_{SL} \tag{4}$$

To obtain the equality ($\gamma_c = \gamma_{SV}$) is is necessary to suppose that $\gamma_{SL} = 0$. It can be shown from the linear relationship between $\cos \theta$ and γ_{LV} that there really is an associated decrease in γ_{SV} when γ_{LV} decreases. This fact, however, does not mean that $\gamma_{SL} \to 0$ when $\theta \to 0$. To prove the above-mentioned identity some trials were made to use the Antonov rule in following form for the interface SL:

$$\gamma_{SL} = \gamma_{LV} - \gamma_{SV} \tag{5}$$

The combination of Eqs. (5) and (3) leads to the identity $\gamma_{SV} = \gamma_{LV} = \gamma_c$. However, some experimental data[5,6] show that the values of solid surface tension calculated with the aid of the Antonov rule are too low and therefore the correctness of this rule seems to be questionable and hence the identity $\gamma_{SV} = \gamma_c$ is again not proven.

Sell and Newman[7,8] proposed another method of analysis of experimental data. Instead of $\cos\theta$ the values of $\gamma_{LV}\cos\theta = \beta_{sf}$ may be used. In this case all experimental results independent of the liquid nature may be represented by a single curve and the critical surface tension will be defined as

$$\lim_{\theta\to 0} \gamma_{LV}\cos\theta = \beta_{sf}^{crit} \tag{6}$$

The author has made an attempt to prove that

$$\gamma_{SV} = \beta_{sf}^{crit} = \gamma_{LV} \tag{7}$$

based on the fact that experimentally

$$\lim \frac{d\gamma_{LV}\cos\theta}{d\gamma_{LV}} = 0 \text{ (at } \theta \to 0) \tag{8}$$

Then using Eq. (2) it may be shown that

$$\lim_{\theta\to 0} \frac{d(\gamma_{SV} - \gamma_{SL})}{d\gamma_{LV}} = -\lim_{\theta\to 0} \frac{d\gamma_{SL}}{d\gamma_{LV}} = 0 \tag{9}$$

It was said above that for solids of low surface energy the value γ_{SL} decreases when γ_{LV} diminishes. Taking this into account and using the Eq. (9) the author has made the conclusion that

$$\lim \gamma_{SL} = 0\,(\theta \to 0) \tag{10}$$

But the equality of the first derivative to zero even when the function is diminishing shows only that at $\theta \to 0$ the function[9] has some definite value which only in a special case may be equal to zero. The trial to use the relationship of Girifalco and Good[9] to prove the identity $\gamma_{SV} = \gamma_c$,

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\Phi(\gamma_{SV}\,\gamma_{LV})^{1/2} \tag{11}$$

where Φ is the relation of the reversible adhesion work and the geometric mean of the cohesion work of two phases does not improve the situation since from this equation it follows that at $\theta \to 0$,

$$\gamma_{SL} = \gamma_c/\Phi^2$$

This shows the lack of the identity of γ_{SV} and γ_c and the dependence of γ_{SL} on the correlation of molar volumes of liquid and polymer. In such a way the proposed treatment cannot demonstrate the validity of the equation

$\gamma_{SV} = \gamma_c$. All of the above allows one to conclude that neither γ_c nor β_{sf}^{crit} are identical to γ_{SV}.

There are some more methods of estimation of surface tension[10-12] based on a temperature extrapolation and the concept of the parachor. It follows from many experiments that the melt-solid transition in the course of crystallization or glass formation is accompanied by a sharp change in entropy. Therefore, the validity of the extrapolation to the temperatures where definite changes in structure take place is doubtful and the coincidence of values found by this method with γ_c cannot be considered as evidence that these values are correct.

As for the parachor, it is well known that even for liquids the parachor is not always additive and the precision of its estimation does not exceed 10%. Taking the parachor as a parameter for surface tension evaluation we assume that parachors calculated for the liquid state are valid for the solid. This cannot be proved without special determinations. We must say that even for liquid polyisobutylene[11] the accordance of calculated values of the surface tension, based on parachor, and experimental values has not been found. The coincidence of values found by the method of temperature extrapolation and by using the parachor may be explained by the general assumption for both cases, that the transition into the solid state does not lead to the changing of the surface entropy, i.e., the polymers are supposed to have the structure of supercooled liquids.

We can therefore conclude that from the physical point of view the validity of current theories of surface tension of solid polymers is questionable. Meanwhile, the values which have been found are connected with the real surface energy of solid polymers. This was shown recently by Zisman[13] who found that γ_c and γ_{LV} coincide only when dispersion and orientation forces are operating at the interface. So γ_c and β_{sf}^{crit} represent only that part of the real surface energy which is determined by molecular forces common to the solid polymer and the spreading liquid. On the other hand, these values may be applied only to those polymers which have the structure of supercooled liquids.

All of the above has prompted us to search for some new principles to describe the surface tension of solid polymers.

II THE CONCENTRATION DEPENDENCE OF SURFACE TENSION IN POLYMER SOLUTIONS

The main principle we have used is that of the identity of molecular packing in the surface of a solid polymer and in a saturated adsorption layer of polymer at the liquid (polymer solution) interface vapor.

Let us consider such a polymer solution where the dissolved polymer shows surface activity. It is known for this case that as a result of adsorption of the dissolved substance at the interface there takes place the substitution of solute molecules for solvent molecules in the surface layer. The surface concentration of solute c_s in solution is related to its volume concentration c by the equation[14]

$$c_s = c + \Gamma/\delta \tag{12}$$

where Γ is the surface excess according to Gibbs and δ the thickness of the adsorption layer, which is an arbitrary value. From this equation for the regular solution we have

$$\frac{c_s}{c} = 1 - \frac{1}{RT\delta} \cdot \frac{d\gamma}{dc} \tag{13}$$

The value c_s/c we define as the relative surface concentration. This value has the following property. In the range of small volume concentration it is equal to

$$\frac{c_s}{c} = 1 - \frac{K}{RT\delta} \tag{13}$$

where K is the surface activity. When the volume concentration increases c_s/c diminishes and at the limit, when $d\gamma/dc \to 0$, approximates one.

Such a concentration dependence is typical[15,16] for the surface tension of surfactant solutions where the surface tension monotonically changes from the value of the pure liquid, γ_0, to a limit value γ_{lim} at large concentrations of the surfactant. On this basis we suppose the existence of a linear relationship between the relative surface concentration in the surface layer and the surface tension of the solute.

Really, $\gamma = \gamma_0$ when

$$\frac{c_s}{c} = 1 - \frac{K}{RT\delta}$$

and $\gamma = \gamma_{\text{lim}}$ at $c_s/c = 1$. The correlation between the relative surface concentration and the surface tension may be presented then as

$$\frac{\gamma - \gamma_{\text{lim}}}{\gamma_0 - \gamma_{\text{lim}}} = \left(\frac{c_s}{c} - 1\right)\frac{RT\delta}{K} \tag{15}$$

δ taken in such a way that it will not depend on solution concentration. If so, we can combine the Eqs. (13) and (15) and after solving at the boundary conditions $\gamma = \gamma_0$ at $c = 0$, we have

$$\gamma = (\gamma_0 - \gamma_{\text{lim}}) \exp\left\{-\frac{Kc}{\gamma_0 - \gamma_{\text{lim}}}\right\} + \gamma_{\text{lim}} \tag{16}$$

It was said above that γ is equal to γ_{lim} for the saturated surface layer, i.e. at $c_s/c = 1$. At the same time c_s is equal to c only for the pure substance. Therefore γ_{lim} ought to represent the surface tension of the dissolved surfactant.

We must note that the method proposed above does not include any arbitrary suppositions as to the validity of an extrapolation such as that for the method mentioned earlier. Eq. (16) is based only on a usual thermodynamic statement. The values which can be calculated refer to one temperature whereas the other methods of estimation use a temperature extrapolation to a range where definite changes in the physical state of the polymer may take place. We have no reason to think that the adsorption layer has a physical state different from that of the surface layer of the solid polymer. We believe that at the same temperature in the state of saturation the adsorption layer has a structure which is identical to the structure of the surface layer of solid polymer independent of the phase state, whether crystalline or amorphous. To find the value γ_{lim} it is sufficient to estimate the preexponential factor and knowing γ_0 to calculate γ_{lim} without extrapolation.

III EXPERIMENTAL RESULTS

To prove Eq. (16) we have studied solutions of some oligodiethylenglycoleadipinates of different molecular weight in formamide as a solvent. These compounds are low molecular weight polymer liquids at room conditions. This gives the possibility of the direct determination of their surface tension by the suspended drop method[17].

Some results of γ_{lim} determination using Eq. (16) and by the suspended drop method are given in Table I. The data in Column 2 have been calculated using the least squares method. It is seen that γ_{lim} coincides with the value of γ_{LV} and the divergence does not exceed experimental error. The study of the temperature dependence of surface tension in the same system completed earlier[18] shows that not only the surface energy of solution but

TABLE I

Comparison of experimental and calculated values of the surface tension for oligomers

Mol. wt.	γ_{lim},dyn/cm	γ_{LV},dyn/cm
800	45.9 ± 0.7	44.8 ± 0.5
2100	41.8 ± 1.1	41.5 ± 0.5
4800	40.4 ± 0.2	39.7 ± 0.5

the change in the surface entropy has a tendency to reach a limiting value (Figure 1). This shows that when solution concentration increases the degree of molecular orientation in the adsorption layer also reaches a definite limit. This is another confirmation of the validity of the extrapolation method that we have proposed above.

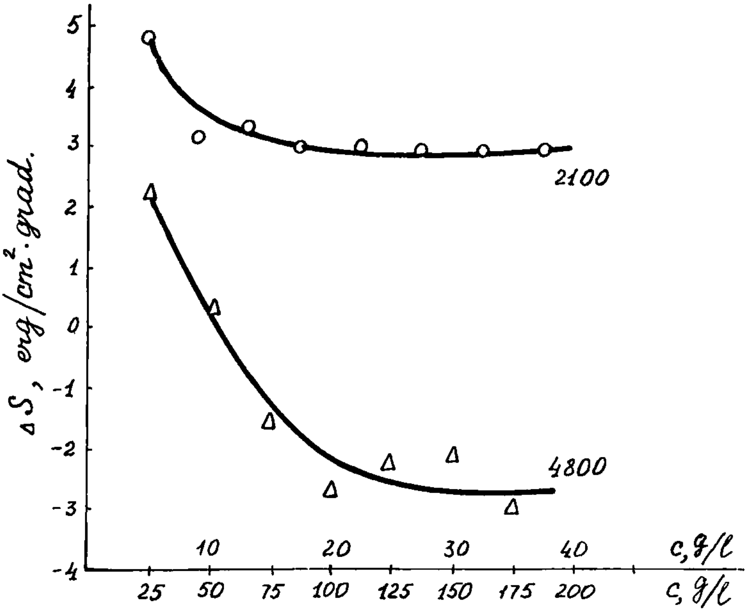

FIGURE 1 The change in the surface entropy for polydiethyleneglycoladipate solution at 20°C.

○ — $\overline{M}_n = 2100$
△ — $\overline{M}_n = 4800$

There are some essential consequences from the Eq. (16). The first derivative of γ is

$$\frac{d\gamma}{dc} = -b(\gamma_o - \gamma_{\text{lim}}) \exp(-bc) \tag{17}$$

where $b = K/(\gamma_0 - \gamma_{\text{lim}})$. Taking into account Eq. (16) we have

$$\frac{d\gamma}{dc} = -b(\gamma - \gamma_{\text{lim}}) \tag{18}$$

It is seen that the function and its first derivative are connected by a linear relationship. Then we have a simple method for the verification of the validity of the equation for a different system. Figure 2 shows the concentration dependence of the surface tension for the system epoxy resin–acetone[19].

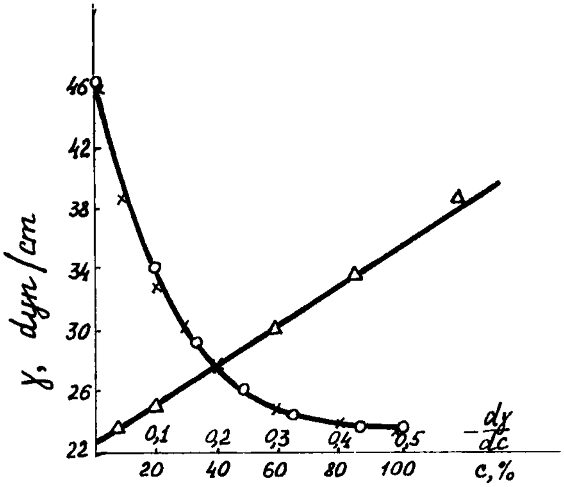

FIGURE 2 The concentration dependence of surface tension for epoxy resin solution (from Ref. 19).

△ — values dγ/dc
○ — experimental points
× — calculated points

The points obtained by graphical differentiation really fall upon the curve in the whole range of concentration. Taking values of b from the slope and the value γ_{lim} from the intercept, the surface tension γ for different concentrations have been calculated. It is seen (Figure 2) that the calculated values fall satisfactorily upon the experimental curve and maximum divergence does not exceed 0.6 dyn/cm.

Similar results were obtained when some data from the investigation of water solution of fatty acids were treated by our method. For this system we have found two values of γ'_{lim}—for plane orientation of acid molecules at the interface (γ'_{lim}) and for vertical orientation (γ''_{lim}). For the series of acids the following values of γ'_{lim} and γ''_{lim} have been found:

$$\gamma'_{\text{lim}} = 40 \pm 4 \text{ dyn/cm} \quad \text{and} \quad \gamma''_{\text{lim}} = 26 \pm 1 \text{ dyn/cm}.$$

Keeping in mind that the surface tension of these acids[22] has the same value as γ''_{lim} we can say that our suggestions as to the physical meaning of the constant γ_{lim} are valid.

The validity of the Eq. (16) follows also from the fact that on the basis of this equation it is possible to explain some empirical equations which are used for the description of the concentration dependence of the surface tension of surfactant solutions. We can represent Eq. (16) in the following form:

$$\gamma_0 - \gamma = (\gamma_0 - \gamma_{\text{lim}})(1 - \exp\{-Kc/(\gamma_0 - \gamma_{\text{lim}})\}) \tag{19}$$

and make an expansion into a MacLaren series taking only the first power term (for low concentration). Then we obtain

$$\gamma_0 - \gamma = Kc \tag{20}$$

in accordance with the experimental data of Traube[20,30]. If we take Eq. (16) in the form

$$\ln \{1 - [\gamma_0 - \gamma]/[\gamma_0 - \gamma_{\text{lim}}]\} = -bc \tag{21}$$

and make a series expansion taking only terms of power two, we can, after rearrangement, obtain the equation

$$\gamma_0 - \gamma = \tfrac{1}{2}(\gamma_0 - \gamma_{\text{lim}}) \ln (1 + 2bc) \tag{22}$$

By comparing this equation with the empirical equation of Szysckowski

$$\gamma_0 - \gamma = \gamma_0 B \ln \left(1 + \frac{c}{A}\right) \tag{23}$$

we can attribute the following physical meaning to the constants of Eq. (23):

$$B = \frac{\gamma_0 - \gamma_{\text{lim}}}{2\gamma_0} \tag{24}$$

$$A = \frac{1}{2b} \tag{25}$$

This allows us to explain some peculiarities of the constants of Eq. (23). For example, the fact that the constant B is roughly equal for each homologous series can be explained, as it is seen from the identity (24), by equal values of γ''_{lim} for a series of normal fatty acids investigated. The correlation given below

$$\frac{1}{A_1} : \frac{1}{A_2} = b_1 : b_2 = k_1 : k_2 \tag{26}$$

shows why the ratio of constants A corresponds to the Traube rule. The comparison of the constant values, for example, for *n*-butyric acid[20,21], given in Table II, shows the validity of Eqs. (24) and (25).

TABLE II

The experimental and calculated values of constants A and B

Constant	Calculated	Experimental
A	0.080	0.068
B	0.198	0.200

The results described above include only experimental data for liquid oligomers of different molecular weight. Nevertheless, we can assume the validity of our method for solid polymers also as there cannot be an essential difference in the molecular structure of oligomers and polymers. Additional data will be published later.

CONCLUSIONS

On the basis of our experimental data and some data given in the literature we can conclude that the proposed Eq. (16) correctly describes the real concentration dependence of the surface tension for solutions of surfactants and surface active polymers. Calculation according to Eq. (16) make it possible to determine the surface tension of the polymer solute.

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