Properties of Monomolecular Layers on Solutions of Salts. II

By *A. Frumkin* and *A. Pankratov*

In comparing the $\Delta - S$ curves obtained in the preceding paper, one is struck by a considerable increase of the value of Δ at constant area when passing from water to solutions of salts, which naturally suggests the idea of an increase of repulsive forces as developed by Talmud and Bresler.

However, for a full understanding of the mechanism of the action of salts on films, the $\Delta - S$ curves are not sufficient. Thus, *e. g.*, introducing the assumption as to the dehydration of the polar groups, as is done by Talmud and Bresler, we assume a change in the character of the bond between the molecules of the organic substance and the underlying solution. With a smaller hydration this bond must weaken, which leads to an increase of the thermodynamic potential, at least for sufficiently dilute films in which the interaction between the molecules of the organic substance has no decisive influence. Therefore, in order to settle the question of the mechanism of the action of salts it is essential to know what points on the curves obtained with different solutions correspond to identical values of the thermodynamic potential. In order to find these points, in the first place the pressures were determined which correspond to the film that is in equilibrium with the solid substances.

The results of these measurements with ethyl palmitate are given in Table 1.

From the close agreement of the figures in the second (in the case of powder) and third column it follows that the pressures we observed actually corresponded to the equilibrium between the solid

Table 1

Substrate	Pressure of film obtained by bringing the surface into contact with ethyl palmitate in dynes/cm.		Final pressure obtained in compressing the film
Distilled water	Small particle	17,7	20,0
	Powder	20,7	
1 N K_2SO_4	Small particle	18,6	20,7
	Powder	21,2	
3,3 N KBr	Powder	23,2	22,8
8,0 N $CaCl_2$	Powder	23,2	22,9
3,3 N KJ	A few small particles	23,0	23,0

substance and the film, since they could be approached from two sides, starting both from the solid substance and from the film. In the case of cetyl alcohol similar results at room temperature cannot be obtained, since the numbers corresponding to column 2 are considerably smaller than those of column 3 and very strongly increase as the number of the particles of the alcohol placed on the surface is increased. It seems that the rate of spreading of the molecules of alcohol from the crystalline lattice on the surface is too slow. Therefore, further on we shall restrict ourselves to ethyl palmitate. The points on the $\Delta - S$ curves, corresponding to equilibrium with the solid substance (denoted by *1* in Fig. 1), may be considered as points of equal thermodynamic potential if we disregard the influence of water dissolved in the solid organic substance upon its activity. In order to find other points on the curves corresponding to equal values of thermodynamic potential, we shall use a method employed by A. Frumkin for the solution of a similar problem[1].

Let us denote by μ the thermodynamic potential of the film; by μ_0 and Δ_0 the values of potential and surface pressure, corresponding to the equilibrium with the solid substance. According to Gibbs' equation

$$d\mu = S d\Delta,$$

[1] A. Frumkin, Z. physik. Chem., **116**, 466 (1925).

whence

$$\mu_0 - \mu_1 = \int_{\Delta_1}^{\Delta_0} S d\Delta. \quad (1)$$

Thus, if the ordinate axis in the $\Delta - S$ diagram passes through the point $S = 0$, the area bounded by the $\Delta - S$ curve, by the straight lines $\Delta = \Delta_0$ and $\Delta = \Delta_1$, and the ordinate axis (Fig. 1), will directly give the value of $\mu_0 - \mu_1$. In this way calculations were made for ethyl palmitate on two solutions of salts N K_2SO_4 (Fig. 1, lower curve) and 3,3 N KJ (Fig. 1, upper curve); the points on

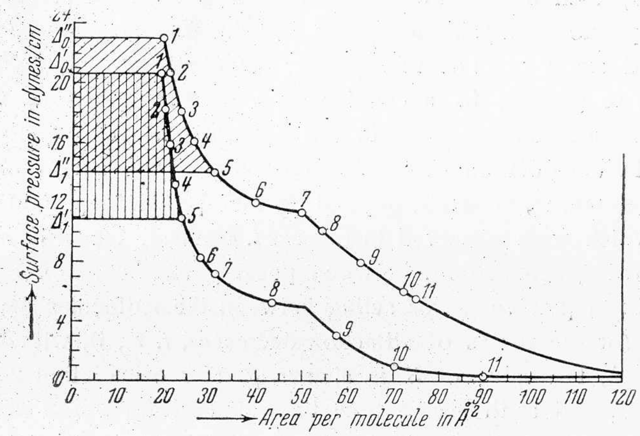

Fig. 1.

the $\Delta - S$ curves, in which the films possess an equal thermodynamic potential, are marked on the two curves by the same figures. This calculation brings us to the following result: for small values of S, the areas per molecule being equal, the thermodynamic potential of the film on KJ is higher than on K_2SO_4, but for large values of S the opposite is true, and the thermodynamic potential of the film on KJ is lower.

With sufficiently large values of S the influence of the interaction between molecules decreases, and the behaviour of the film is determined mainly by its interaction with the underlying solution. The lower values of the potential on KJ in this region indicate a stronger bond with the substrate; we thus come to the conclusion that the salt which exercises a larger influence upon the equation of state, increases the attraction of molecules of the organic substance to water, *i. e.*, the work of adsorption from the gaseous state. This conclusion is in disagreement with the assumption of Talmud and Bresler who explain the action of salts by the dehydration of the polar group of the film. With a decrease of the area S per molecule, forces of interaction between molecules become more pronounced, the attraction between organic molecules on KJ being considerably weaker than on K_2SO_4. Talmud and Bresler explained this phenomenon by an increase in the dipole moment of the polar groups and, consequently, in the repulsion between them caused by their dehydration. From the aforesaid, another explanation of this phenomenon should be sought; the mechanism suggested by Talmud and Bresler in any case cannot play a dominating part. Previous to passing to a consideration of this question, we shall show that our conclusion as to the impossibility of explaining the change in the position of the Δ—S curves by the action of repulsive forces alone, does not depend on the special shape of the Δ—S curves which were observed in our case. Namely, let us demonstrate the following proposition. If, when passing from solution 1 to solution 2, the repulsive forces acting between the molecules of the film increase (or the forces of attraction decrease), *i. e.*, if, with an equal value of Δ, the value of S is always greater on solution 2 than on solution 1, and at the same time the value of Δ_0, corresponding to the film which is in equilibrium with the pure substance, is also greater on solution 2 than on solution 1, the work of adsorption A of the molecules of the film as gained when passing from some standard state on the surface of the solutions is larger for solution 2 than for solution 1. Further on we shall denote by indices $'$ and $''$, respectively, the values referring to solutions 1 and 2.

According to equation (1)

$$\mu_0' - \mu_1' = \int\limits_{\Delta_1'}^{\Delta_0'} S d\Delta; \quad \mu_0'' - \mu_1'' = \int\limits_{\Delta_1''}^{\Delta_0''} S d\Delta.$$

But according to the condition of equilibrium $\mu_0' = \mu_0''$ and, hence,

$$\mu_1'' - \mu_1' = \int\limits_{\Delta_1'}^{\Delta_0'} S d\Delta - \int\limits_{\Delta_1''}^{\Delta_0''} S d\Delta. \qquad (2)$$

Let us now take for the lower limit of integration such a large value of S, S_1, that the forces of interaction between the molecules could be disregarded, and the substance of the film would be governed by the law of ideal gases. Then

$$\Delta_1' = \Delta_1'' = \frac{RT}{S_1}, \qquad \mu_1' = -RT \ln S_1 - A' + \text{const.}, \qquad (3)$$

$$\mu_1'' = -RT \ln S_1 - A'' + \text{const.}, \qquad (3a)$$

A' and A'' representing the value of the work of adsorption from some standard state. Under this condition the value of the constant in equations (3) and (3a) does not depend on the nature of the solution, and from these equations and equation (2) it follows:

$$\mu_1'' - \mu_1' = A' - A'' = \int\limits_{\frac{RT}{S_1}}^{\Delta_0'} S d\Delta - \int\limits_{\frac{RT}{S_1}}^{\Delta_0''} S d\Delta = \int\limits_{\frac{RT}{S_1}}^{\Delta_0'} (S' - S'') d\Delta - \int\limits_{\Delta_0'}^{\Delta} S d\Delta. \quad (4)$$

According to our assumptions, at constant Δ, $S' < S''$ and moreover $\Delta_0'' > \Delta_0'$; therefore the right-hand side of equation (4) is always negative and, hence, $A' < A''$. In other words, from the fact that the equilibrium pressure Δ_0 is increased when passing to solutions of salts, it follows that the attraction of molecules of the organic substance to the surface of these solutions is greater than in the absence of salt. Let us try to explain the mechanism of action of these salts.

All the salts investigated charge the surface of water negatively. If as the zero potential that of an interface air/N K_2SO_4 be arbitrarily chosen, then, according to the measurements of Pankratov and earlier data of Frumkin[2], for the solutions of salts investigated by the authors values of potential difference air/solution are obtained as shown in the second column of Table 2. In the third column of this table changes of the potential difference air/solution are given when passing from a film of ethyl palmitate (at maximum compression) on N K_2SO_4 to similar films on the other solutions investigated; in the fourth column the same data are presented for cetyl alcohol.

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2 A. Frumkin, Z. physik. Chem., **109**, 34 (1924).

The data of the second column of Table 2 show the following. The order in which the solutions are arranged according to their action upon the surface pressure of the film (see preceding paper) fully coincides with the order in which their capacity to impart a negative potential to the surface of water increases, *i. e.*, in which the adsorption of anions increases. This makes it easy to explain the increase in the work of adsorption when passing from solutions of K_2SO_4 to solutions of, *e. g.*, KJ by an electrostatic interaction between the dipoles of the molecules of the organic substance which are turned with their positive end towards air and ions of the double layer on the surface of the solution in which the external sheet is formed by negative charges. Such an interaction should at the same time increase also the adsorption of the salt. An examination of the figures in the third and fourth columns of Table 2 at first sight seems to contradict this conclusion. In fact, as may seem from these figures, the shift of the potential to the negative side caused by the adsorption of the salt (columns 3 and 4), in the presence of the film is considerably smaller than in its absence and in some cases

Table 2

Solution	Potential difference at the interface air/solution in mV, referred to the p. d. air/1 N K_2SO_4		Potential difference air/ethyl palmitate on solution referred to p. d. air/ethyl palmitate on N K_2SO_4	Potential difference air/cetyl alcohol on solution referred to p. d. air/cetyl alcohol on N K_2SO_4
	Frumkin (standard solution N Na_2SO_4)	Pankratov		
1 N K_2SO_4	0	0	0	0
1 N KCl	—5	—9	—	—7
1 N NaCl	—5	—10	—	—7
3,3 N $CaCl_2$	—12	—12	0	—8
1 N KBr	—13	—14	3	—6
3,3 N KCl	—12,5	—16	4	—5
3,3 N NaCl	—15,5	—18	6	—4
3,3 N KBr	—31	—30	3	—8
8 N $CaCl_2$	—67	—65	—12	—28
3,3 N KJ	—82	—75	—15	—32

disappears altogether. However, in reality it would be incorrect to make hence the inference that the adsorption of salt in the presence of the film decreases or disappears altogether. This will be readily seen from a comparison of the values of surface tension of different solutions in the presence of the film and without the latter.

Let us denote the surface tensions of two solutions in the absence of a film by σ' and σ''; in the presence of a film in equilibrium with the solid substance these values will be expressed by $\sigma' - \Delta_0'$ and $\sigma'' - \Delta_0''$. As was shown by one of the authors[2], the value of $\sigma' - \sigma''$ with equal concentrations of the solutions is positive if electrical measurements show that in the second solution a stronger penetration of anions into the surface layer is observed. In the same case, according to the data given in the preceding paper and in Table 2, $\Delta_0'' > \Delta_0'$ and, hence, $(\sigma' - \Delta_0') - (\sigma'' - \Delta_0'') > \sigma' - \sigma''$. The left-hand part of this relation gives the change of surface tension when passing from solution 1 to solution 2 in the presence of the film; the right-hand part expresses the same change without any film. Thus, the change in the surface tension and, hence, also in the adsorption of ions, is actually larger in the presence of the film than without it[3].

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[3] The influence of the film upon the adsorption of ions may be more precisely stated using the formula of Gibbs for a two-component system (Γ — amount adsorbed per cm.^{2}):

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2,$$

where the subscript 1 refers to the salt, and the subscript 2, to the organic substance.

From this formula it follows:

$$\left(\frac{\partial \Gamma_1}{\partial \mu_2}\right)_{\mu_1} = \left(\frac{\partial \Gamma_2}{\partial \mu_1}\right)_{\mu_2}.$$

If a comparison is made of two Δ—S curves obtained on the solutions of the same salt of different concentration it will be readily seen that the value of Γ_2 at constant μ_2 with an increase of μ_1 at first increases and then begins to fall; hence, it follows that a similar dependence must exist between Γ_1 and μ_2, *i. e.*, the substance of the film brought onto the surface of the solution in increasing quantities at first causes an increase in the adsorption of the salt, and then its decrease. The total effect, caused by the equilibrium film as shown in the text compared with the initial state remains positive.

The apparent disagreement between the results of comparison of the electric potentials and surface tensions of films on different solutions is explained very easily if we consider that the effective dipole moment of the organic substance is influenced by the underlying solution. Namely, as shown in the preceding paper, the presence of adsorbed anions makes this moment more positive. Therefore the adsorption of anions, which in itself leads to a negative charge of the surface, simultaneously increases also the positive potential depending on the molecules of the organic substance. As a result of this, the total effect of adsorption of ions upon the potential, in spite of a greater value of this adsorption, in the presence of the film is found to be less than in its absence and may even have the opposite sign.

In the preceding paper it was shown in detail how this increase of the dipole moment in the case of cetyl alcohol might be accounted for. Without having recourse to any special mechanism it may be stated in a more general way that the presence of anions in the external part of the surface layer must favour the appearance of such configurations of polar groups of organic molecules which give a higher positive potential difference. The increase of the effective dipole moment must lead to an increase of repulsive forces between the polar groups of the adsorbed molecules. A quantitative calculation of this effect is difficult, since it is not clear what value should be taken for the dielectric constant of water in considering the interaction between the dipoles on its surface, and therefore it is uncertain to what extent the expansion of the film observed on solutions of salts may be fully accounted for by a repulsion between the dipoles. In any case, it should be borne in mind that the presence in the surface layer of additional adsorbed ions also causes the appearance of repulsive forces both of electrostatic and of osmotic nature and, hence, also leads to an expansion of the film. As a result of an increase of the repulsive interactions at a certain compression of the film the presence of the adsorbed salt in the interface becomes disadvantageous from the standpoint of the thermodynamic stability of the film.

It should be noted that the assumption of an interaction between the dipoles of the polar groups of molecules and the adsorbed ions is not necessary in order to account for the increase in the work

of adsorption of organic molecules and in the repulsive forces between them. The same effects will be obtained if in the presence of the film the adsorption of ions will for some other reason, *e. g.*, due to van der Waals's forces between the anion and the hydrocarbon chain, be larger than on the clean surface of the solution. The last remark is essential, since Harkins and Morgan[4] observed on solutions of $CaCl_2$ a stabilization of layers of such compounds as phenanthrene, which do not contain polar groups. There is no doubt that this phenomenon belongs to the same group as those studied by us.

From Table 2 it follows that the sequence of expanding action of the salts on the film is at the same time the sequence in which the negative charge of the surface increases. We have not, however, included in this table pure water which is in this sense an exception. In fact, the potential which is observed on the surface of pure water as compared to the potential, for instance, of the solution of K_2SO_4 is more negative by about 25 mV, as it follows from the detailed yet unpublished measurements of M. Gerovich in this laboratory and has been confirmed in the research of Pankratov. On the other hand the whole behaviour of the film on pure water forces us to place water at the beginning of our series of solutions. The origin of those drops of potential which are observed with very dilute solutions of salts ("pure water") cannot as yet be considered as quite elucidated. It is beyond doubt, however, that here we have to do with phenomena different from those observed with higher concentrations. The question as to the electrical properties of films on dilute solutions of salts undoubtedly deserves further detailed study.

Conclusions

The action of salts increasing the surface pressure of films of organic substances is the more pronounced, the higher the negative charge on the surface of the solution of the salt, *i. e.*, the more the anion of the salt penetrates into the surface layer. The observed change of the dependence of the surface pressure on the area per molecule may be explained, as shown by a thermodynamic analysis

[4] W. D. Harkins a. J. Morgan, Proc. Nat. Acad. Sci., **11**, 637 (1925).

of the curves of surface pressure and of the values of the film pressure in equilibrium with the pure organic substance, if we assume that when passing from water to solutions of salts both the work of adsorption and the repulsive forces between the molecules of the film increase. These phenomena may be accounted for by the electrostatic interaction between the ions of the double layer charging the surface negatively and the dipoles of the molecules which give a positive potential difference. This interaction causes an increase in the work of adsorption both for the salt and for the organic substance and an increase in the effective dipole moment of the molecules. The latter, as well as the additional adsorption of ions, causes an increase of the repulsive forces in the surface layer. The same assumptions explain also the observed dependence of the effective dipole moment of the organic molecules on the presence of salts in the solution. In order to account for the increase of the surface pressure of the film in equilibrium with the solid substance it is sufficient to assume that the adsorption of ions of salts in the presence of the film is increased, independently of the mechanism of the adsorption interaction.

Electrochemical Laboratory,
Moscow State University.

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