

Properties of Monomolecular Layers on Solutions of Salts. I

By *A. Pankratov*

The object of the present study was to investigate the adsorption of ions on films of organic compounds as well as the influence of this adsorption on the forces acting between the molecules of the organic compound, and at the same time to verify to what extent the change in the concentration of the electrolyte in the underlying solution is connected with a change in the hydration of the polar groups. Systems in which chemical interaction between the polar groups and ions (true salt formation) could occur were excluded from our consideration.

The investigations of Langmuir¹, Adam², and Lyons and Rideal³ have shown that the limiting area per molecule of the film of palmitic acid depends on the pH of the underlying solution, increasing with a rise in the acidity. The increase of the area of the film on acid solutions was ascribed by Langmuir to an increase in the size of the polar groups due to the adsorption of hydrogen ions. According to Rideal and Lyons, the rising tendency of the film to expand upon the acidulation of the solution is connected with an increase in the tilt of the molecules of the film.

Talmud and Bresler⁴ have come to the conclusion that the increase in the area of the film which they observed when

¹ Langmuir, J. Am. Chem. Soc., **39**, 1848 (1917).

² Adam, Proc. Roy. Soc., A **99**, 336 (1921).

³ Lyons and Rideal, Proc. Roy. Soc., A **124**, 334 (1929).

⁴ Talmud and Bresler, Surface Phenomena, 1934, p. 24.

substituting salt solutions for water is due to the dehydration of the polar groups of molecules increasing the forces of repulsion between them.

In order to come nearer to the elucidation of the mechanism of these phenomena, it was necessary to relate the behaviour of the film not only with the nature of the underlying solution, but especially with the specific properties of the solution-air interface.

With this object, as suggested by A. Frumkin, the author has investigated the mechanical and electrical properties of monomolecular films on aqueous solutions of a series of inorganic salts.

Procedure and apparatus

The measurement of the surface pressure was made by the torsion balance method of Adam and Jessop⁵, and the measurement of the contact potential with the help of the radioactive air electrode of Guyot⁶ and Frumkin⁷. The design of the apparatus was in the main similar to that of Adam and Harding⁸, with the exception of some small modifications. The potential of the air electrode was controlled before and after each measurement with the help of the surface of a 0,01 *N* KCl solution which could be cleaned by overflowing, as described in the paper of Frumkin⁷.

The sensitivity of the Compton electrometer used by the author was 0,2 mV. The measurements were made at a temperature of 20°.

Reagents

All the salts used were "C. P." products of soviet origin. Previous to their use these salts had been twice recrystallized and ignited at melting temperature. The aqueous solutions of the concentration required prepared from them were three or four times filtered through a glass filter. By means of these operations the salts were purified from organic surface-active substances which could influence the properties of the films. The water used for

⁵ Adam a. Jessop, Proc. Roy. Soc., A 110, 423 (1926).

⁶ Guyot, Ann. physique, (10) 2, 501 (1924).

⁷ Frumkin, Z. physik. Chem., 116, 485 (1925).

⁸ Adam a. Harding, Proc. Roy. Soc., (A), 138, 411 (1932).

the preparation of the solutions had been twice distilled. As film-forming substances Kahlbaum's ethyl palmitate and cetyl alcohol were used.

Experimental results

The dependence of the two-dimensional pressure Δ and of the potential difference V on the area per molecule S was investigated on the following solutions. Cetyl alcohol: on distilled water, on 1 *N* solution of K_2SO_4 , 1 *N* KCl, 1 *N* NaCl, 3,3 *N* $CaCl_2$, 1 *N* KBr, 3,3 *N* KCl, 3,3 *N* NaCl, 3,3 *N* KBr, 8 *N* $CaCl_2$ and 3,3 *N* KJ. Ethyl palmitate: on distilled water, on 1 *N* K_2SO_4 , 3,3 *N* $CaCl_2$, 1 *N* KBr, 3,3 *N* KCl, 3,3 *N* NaCl, 3,3 *N* KBr, 8 *N* $CaCl_2$ and 3,3 *N* KJ.

The results are shown in a series of curves in Figs. 1 and 2⁹. The potentials are referred to the potential which the corresponding substrate gives in the absence of the film. The two films studied on distilled water give the lowest $\Delta-S$ and $V-S$ curves, and the films on 3,3 *N* KJ, the highest. All the other $\Delta-S$ and $V-S$ curves are situated between these two extremes in the order indicated above.

In Fig. 3 are presented the curves relating the dipole moment to the area per molecule of cetyl alcohol, obtained on distilled water and 3,3 *N* KJ ($\bar{\mu}-S$ curves). In Fig. 4 are shown $\bar{\mu}-S$ curves obtained with the film of ethyl palmitate on distilled water and on 3,3 *N* KJ. On these two drawings, for the sake of comparison, the corresponding $\Delta-S$ and $V-S$ curves are also plotted.

The values of the dipole moment were calculated from the formula: $V = 4\pi n\bar{\mu}$ (n —number of molecules per $cm.^2$; $\bar{\mu}$ —vertical component of the dipole moment). Figs. 3 and 4 show that the effective dipole moment of the polar group immersed in a 3,3 *N* KJ solution is greater than in the case when this polar group is placed in distilled water.

The question as to the influence of the underlying solution on the surface pressure of the film will be discussed in the following

⁹ The curves obtained on 1 *N* and 3,3 *N* NaCl and on 3,3 *N* and 8 *N* $CaCl_2$ are omitted in Fig. 1 for technical reasons.

article; here we shall consider only the factors causing changes in the potential of the film.

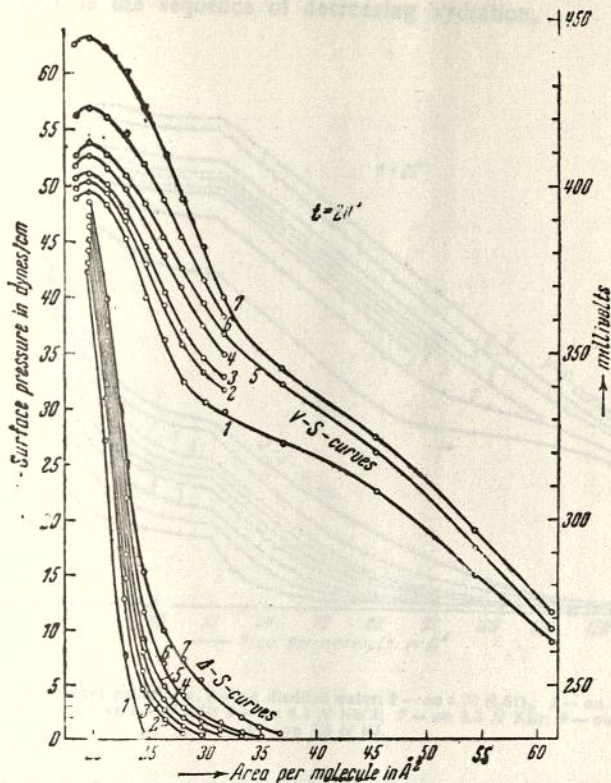


Fig. 1. Film of cetyl alcohol. 1 — on distilled water; 2 — on 1 N K_2SO_4 ; 3 — on 1 N KCl ; 4 — on 1 N KBr ; 5 — on 3,3 N KCl ; 6 — on 3,3 N KBr ; 7 — on 3,3 N KJ .

According to the investigations of A. Frumkin¹⁰ inorganic electrolytes charge the solution-air interface negatively. This is due to the fact that at this interface a prevailing adsorption of anions takes place. The increase in the adsorbability of anions is connected with a decrease in their hydration. According to the degree of their

¹⁰ Frumkin, Z. physik. Chem., 109, 34 (1924).

influence upon the increase of the negative charge of the surface the anions of the salts which we have used may be arranged in the following order: $\text{SO}_4'' < \text{Cl}' < \text{Br}' < \text{J}'$. This sequence at the same time is the sequence of decreasing hydration.

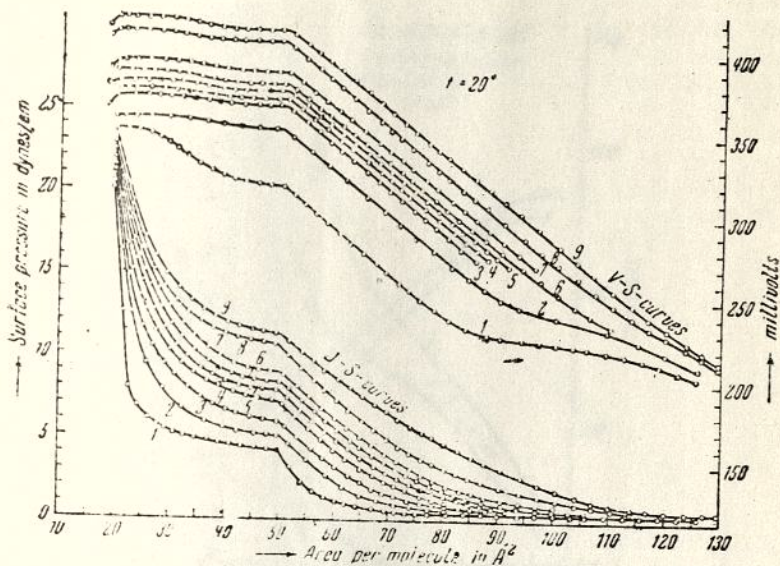


Fig. 2. Film of ethyl palmitate. 1 — on distilled water; 2 — on 1 N K_2SO_4 ; 3 — on 3,3 N CaCl_2 ; 4 — on 1 N KBr ; 5 — on 3,3 N KCl ; 6 — on 3,3 N NaCl ; 7 — on 3,3 N KBr ; 8 — on 8 N CaCl_2 ; 9 — on 3,3 N KJ .

In analysing our data it will be noted that according to the degree of their influence upon the growth of the surface pressure and the positive potential of the film at constant area, the anions are arranged in the same order: $\text{SO}_4'' < \text{Cl}' < \text{Br}' < \text{J}'$ ¹¹. Thus, comparing the authors' experimental results with the data of A. Frumkin, the following conclusion may be made. With a decrease in

¹¹ In the same sequence increases, according to Gorter (Proc. Ac Wet. Amsterdam, 35, 838, 1932; 37, 20, 1934), the spreading action of anion in the case of protein films on acid solutions.

the hydration of anions there takes place an increase in their adsorption on the solution-air boundary and in the negative charge of this boundary. The increase of the surface pressure and of the contact potential of the film must be closely connected with the growth of this surface adsorption of the ions of the substrate.

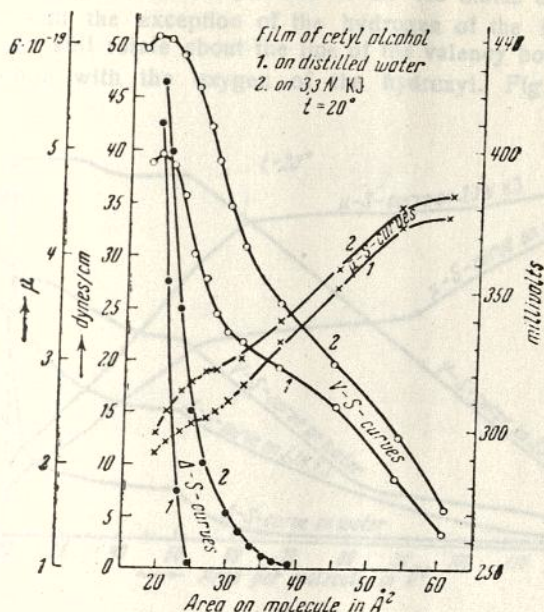


Fig. 3.

This relation is due to the interaction between the ions of the solution and the polar groups of molecules of the film. A similar assumption is expressed also by Schulman and Rideal¹².

Adam and Harding⁸ suggest that if the dipole moment of the carboxyl group in vacuum or in a non-polar medium is equal to $14 \cdot 10^{-19}$ e. s. u., whereas, when immersed in an electrolyte,

¹² Schulman and Rideal, Proc. Roy. Soc., A 130, 259, 284 (1931).

the effective moment is equal only to $2,3 \cdot 10^{-19}$, this difference must be caused by the influence of the ions of the solution upon the polar group. Thus, if the hydrocarbon part of the molecule of a fatty acid is located vertical to the surface of the solution, and the double bond $C=O$ coincides with the surface (see Fig. 5), the given condition fixes the position of all the atoms of the carboxyl group, with the exception of the hydrogen of the hydroxyl. This atom can still rotate about the line of the valency bond, connecting the carbon with the oxygen of the hydroxyl. Fig. 5 shows two

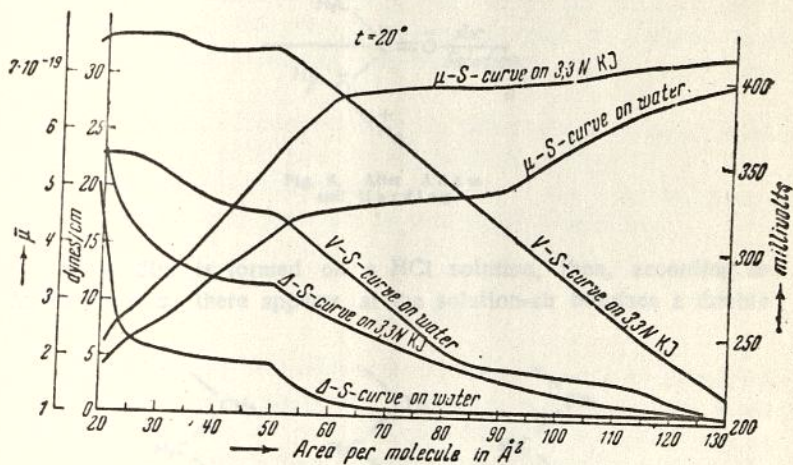


Fig. 4.

extreme positions of the hydrogen atom in which the vertical component of the dipole moment of the polar group has a maximum and a minimum. In the case when the hydrogen is in the α position, the vertical component is equal to $-4,2 \cdot 10^{-19}$. If the hydrogen is shifted in the β position, the value of the vertical component increases, with a change of sign, up to $13,2 \cdot 10^{-19}$ e. s. u. The vertical component equal to $2,3 \cdot 10^{-19}$, as observed by the contact potential method, corresponds, according to the authors named, to a position of the hydrogen atom when the latter has rotated from the α position through 75° . The possibility of rotating not only single atoms but also more complex structures, as, e. g., the short alkyl

chain of ethyl palmitate, is pointed out also by Alexander and Schulman¹³.

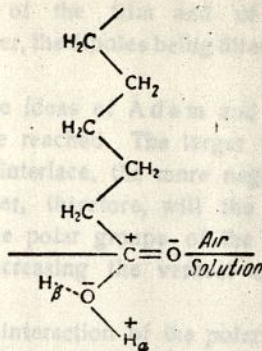


Fig. 5. After Adam and Harding.

If the film is formed on a HCl solution, then, according to A. Frumkin, there appears at the solution-air interface a double

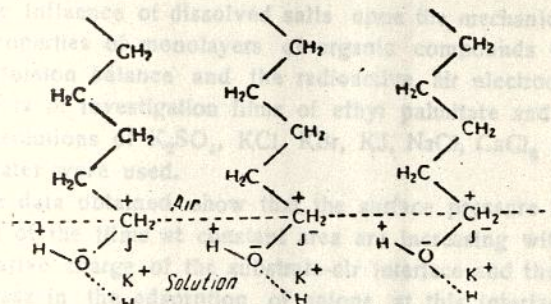


Fig. 6.

electric layer with the chlorine ions turned to the air phase, due to which the surface of the solution is charged negatively. Therefore,

¹³ Alexander a. Schulman, Proc. Roy. Soc., A 161, 115 (1937).

the hydrogen of the polar group, immersed in the HCl solution, will be attracted according to Adam and Harding, nearer to the β position. Systems are formed consisting of dipoles of the polar groups of the film and of dipoles of ionic pairs from the double layer, the dipoles being directed oppositely with regard to sign.

Extending these ideas of Adam and Harding the following conclusions may be reached. The larger the adsorption of anions at the solution-air interface, the more negative the charge of this surface, the stronger, therefore, will the atoms of hydrogen (or alkyl groups) of the polar groups of the film be attracted to the β position, thus increasing the vertical component of the dipole moment.

A scheme of interaction of the polar groups of cetyl alcohol with the double ionic layer of KJ is given in Fig. 6.

The order of arrangement of all the $V-S$ curves given in Figs. 1 and 2 fully corresponds with these conclusions.

Conclusions

The influence of dissolved salts upon the mechanical and electrical properties of monolayers of organic compounds was studied by the torsion balance and the radioactive air electrode methods. As objects of investigation films of ethyl palmitate and cetyl alcohol on solutions of K_2SO_4 , KCl, KBr, KJ, NaCl, $CaCl_2$ and on distilled water were used.

The data obtained show that the surface pressure and contact potential of the films at constant area are increasing with a rise in the negative charge of the substrate-air interface and therefore with an increase in the adsorption of anions at this interface. In other words, the less hydrated the anions of the solution are, the better they are adsorbed at the solution-air interface and the more negative the charge of this surface, the stronger is the influence of the latter upon the increase of the contact potential and the surface pressure of the film.

The increase of the vertical component of the dipole moment of the polar groups is probably a result of the rotation of the

hydrogen or of the alkyl radical of the latter to a higher position (Fig. 6); this rotation is caused by an electrostatic interaction with anions adsorbed from the solution.

In conclusion I wish to express my gratitude to Prof. A. Frumkin for his guidance during this research.

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Properties of Monomolecular Layers on Solutions of Salts. II

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In comparing the Δ — δ curves obtained in the preceding paper, one is struck by a considerable increase of the value of Δ at constant δ when passing from water to solutions of salts, which rather strongly supports the idea of an increase of repulsive forces as developed by Talmud and Brasler.

However, for a full understanding of the mechanism of the action of salts on films, the Δ — δ curves are not sufficient. Thus, in explaining the assumption as to the dehydration of the polar groups, as is done by Talmud and Brasler, 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 thin 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 I.

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