

observed in the present work with α -spodumene, having maxima at 634 and 588 cm^{-1} , and the bands in the range 680–590 cm^{-1} exhibited by minerals also containing six-coordinate aluminium (topaz, kyanite, and beryl), may be related to one of the modes of the $\text{Al}_6\text{-O}$ stretching vibrations, in conformity with the above interpretation. This is evidently a different mode of vibration from the $\text{Al}_6\text{-O}$ vibration in the 920–850 cm^{-1} range.

β -Spodumene shows a band of moderate intensity with maxima at ~ 740 and $\sim 765 \text{ cm}^{-1}$. This band may represent one of the aluminium–oxygen stretching vibrations when aluminium has a coordination number of four.

In α -spodumene, in which aluminium has a coordination number of six, the Al-O distance is 2.07 Å according to the X-ray results³; when aluminium isomorphously replaces silicon, i.e. when it occurs in tetrahedra and has a coordination number of four, the Al-O distance decreases to 1.7 Å. Consequently, the frequency of the Al-O vibration should be greater when the coordination of the aluminium is four than when it is six. The transition from α - to β -spodumene is accompanied by the disappearance of the 634–588 cm^{-1} band and the appearance of a new band with maxima at ~ 765 –740 cm^{-1} , which is in qualitative agreement with the contraction of the Al-O bond when aluminium changes from sixfold to fourfold coordination.

Kolesova¹⁶ has recently ascribed the band in the 720–780 cm^{-1} range to a short "covalent" Al-O bond.

The spectra of minerals with sixfold coordination also contain bands of different types in this range. It must not be forgotten that one of the Si-O vibrations, which is well defined in cyclic silicates¹⁷, lies in this same region.

Our suggested interpretation of the 765–740 cm^{-1} band as one of the $\text{Al}_4\text{-O}$ vibrations is also confirmed, it seems to us, by the fact that the bands in this region observed with β -spodumene and with minerals containing aluminium in fourfold coordination, both observed in the present work and also known from the literature¹⁸, are very similar to one another. These bands usually occur in a region free from other bands, and their intensity is considerably less than that of the main band in silicates.

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SUMMARY

1. A study has been made of the infra-red absorption spectra in the range 3000–550 cm^{-1} of α -spodumene which has been subjected to different heat treatments. The spectral changes accompanying the conversion of α - into β -spodumene have been followed.
2. The characteristic features in the spectra of silicates having a definite coordination number make it possible to determine whether the coordination of the aluminium in any particular silicate is sixfold or fourfold. On this basis it has been shown that the aluminium in

β -spodumene has a coordination number of four. Thus in the α - β transition the aluminium changes its environment from six oxygen atoms to four.

3. A tentative interpretation of absorption bands of α - and β -spodumenes has been made.

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ADSORPTION OF IONS ON MONOLAYERS. IV. INTERACTION OF UNIVALENT AND BIVALENT MERCURY IONS WITH A MONOLAYER OF PALMITIC ACID

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It has been found¹⁻³ that the film of soap formed in a surface layer by interaction between molecules of a fatty acid and inorganic cations adsorbed from the underlying solution differs fundamentally in physicochemical properties from a monolayer of the fatty acid. The electrical characteristics of the surface layer also undergo considerable changes: i.e. the surface potential is different⁴⁻⁸. These investigations showed that the changes in surface potential depend on the concentration of the cation, on its charge, and on the pH of the underlying solution. This conclusion was based both on curves relating the two-dimensional pressure π and the surface potential ΔV with the surface area per molecule A , and on direct analytical

* The shape of the band illustrated in Fig. 2 may be somewhat distorted by the superposition of a weak band due to the oil.

determinations of the metal component in the monomolecular film removed from the solution surface. More recently, labelled atoms have been successfully employed to investigate the properties of monolayers and the changes occurring in them^{9,10}.

Previous papers^{11,12} have analysed the more far-reaching interaction in the surface layer between molecules of palmitic acid and silver ions, which leads ultimately to the formation of a bimolecular film of silver palmitate. This process was found to occur at a rigidly defined ratio between the concentrations of silver and hydrogen ions in the solution.

The possibility of bimolecular films of fatty acids being formed at a water-air interface has been discussed in the literature on the basis of the experimental results obtained by Lyons and Rideal¹³, which pointed to the formation of a bimolecular film on a solution at pH 9 by the interaction of a monolayer of palmitic acid with alkali-metal ions. These workers thought of such a film as consisting of a lower layer of alkali-metal palmitate molecules and an upper layer of palmitic acid molecules. Objections to these conclusions, put forward by Adam and Miller¹⁴, were analysed by us¹¹, and shown to be unconvincing. The interesting case of the formation of a bimolecular film of cetyl stearate was pointed out by Trapeznikov¹⁵. From an analysis of the curves relating surface viscosity with area per molecule, he showed that at relatively high compressions of the monolayer the polar groups become detached from the surface of the water, so that two hydrocarbon chains of the ester become arranged one over the other.

In view of the above, we considered it essential to ascertain whether bimolecular films are formed by the interaction of monolayers of fatty acids with ions of other metals too, and to study their properties. In the present work an attempt was made to obtain bimolecular layers by the interaction of a monolayer of palmitic acid with univalent and bivalent mercury ions.

EXPERIMENTAL

Whether interaction occurred in the surface layer between fatty acid molecules and mercury ions in solution was assessed from the change in surface potential with time.

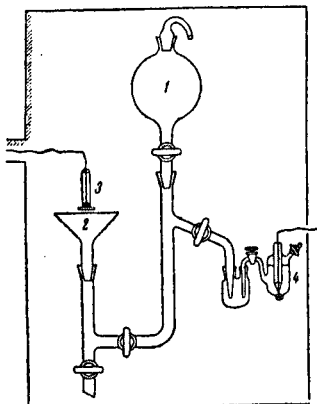


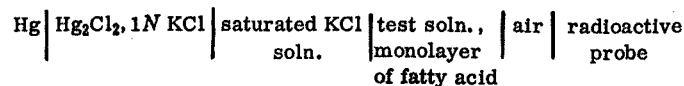
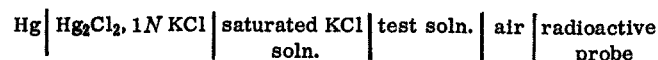
Fig. 1. Diagram of apparatus for measuring the surface potential of a monolayer.

The salts employed were mercurous perchlorate $\text{Hg}_2(\text{ClO}_4)_2$, and mercuric chloride HgCl_2 , both of which were carefully purified by recrystallisation. Solutions were made up with redistilled water. Benzene, used as solvent for the fatty acid, was free from thiophen, and was redistilled, the middle fractions being collected. A criterion of the purity of the benzene was the absence of any change in potential when an excess of it (relative to the amount used in an experiment) was spread on the clean surface of the solution.

Method

The surface potential was measured with the aid of a radioactive probe by the method of Guyot and Frumkin^{16,4} in the glass apparatus illustrated in Fig. 1. Solution from the reservoir 1 was transferred to the ground-in funnel 2, over which was placed the radioactive probe 3 connected with one of the plates of an electrometer, the other being earthed. The radioactive probe was a platinum disc 1 cm in diameter sealed into a glass tube; the lower face, turned towards the solution, was coated with polonium. The probe was fixed in a special holder by means of an amber collar. The surface was cleaned by allowing the solution to flow over the edge of the funnel for some time and then detaching the liquid from the probe by means of a glass rod coated with paraffin wax. A criterion of the purity of the surface was the closeness of the potential differences obtained in two or three successive measurements after the surface had been renewed. The solution in the funnel was earthed by means of a calomel electrode via a potentiometer. The whole apparatus, including the electrometer, was shielded electrostatically with an earthed metal-gauze screen.

After the potential difference at the solution-air interface had been measured, the solution of palmitic acid was added drop by drop by means of a micropipette connected with a special pump, and the potential difference at the monolayer-air interface was measured. The surface potential was found from the difference between the potential differences measured for the following two cells:



First of all, the limiting potential difference was measured when a dilute solution of palmitic acid was gradually applied to the surface of a solution containing no mercury ions, in order to determine the amount which corresponded exactly to saturation of the surface with the monolayer. In subsequent experiments involving mercury ions, this measured quantity of palmitic acid was applied rapidly to the surface of the solution, after which the change in potential with time was recorded.

RESULTS

Fig. 2 shows curves relating surface potential with time for a monolayer of palmitic acid on $10^{-4} N \text{ HClO}_4$ (pH = 4) and on the same solution containing $10^{-4} N \text{ Hg}_2(\text{ClO}_4)_2$.

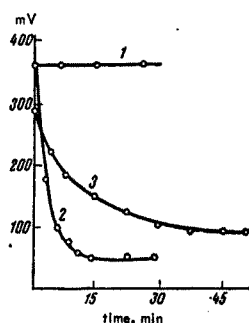


Fig. 2. Curves showing the change in the surface potential of a monolayer of palmitic acid with the time it has been in contact with the solution:
1) $10^{-4} N HClO_4$; 2) $10^{-4} N HClO_4 + 10^{-4} N Hg_2(ClO_4)_2$;
3) $10^{-6} N HgCl_2$ at pH = 5.9.

(curves 1 and 2 respectively). Comparison of these curves shows that the presence of mercurous ions in the solution produces a sharp drop in the surface potential of the monolayer, which reaches a constant value of 40–50 mV 10–15 min after the addition of the fatty acid. A fall in the value of ΔV of this magnitude up to 300–320 mV, is evidently a result of interaction between the mercurous ions and the molecules of palmitic acid, leading to breakdown of the monolayer, similar to earlier findings with silver ions.

The plots of ΔV against pH for three concentrations (10^{-5} , 10^{-4} , and $10^{-3} N$) of $Hg_2(ClO_4)_2$ in Fig. 3 shows that

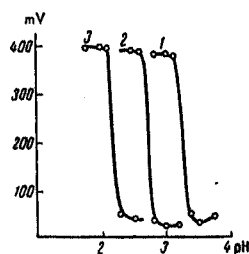


Fig. 3. Curves relating the surface potential with the pH of solution for three concentrations of $Hg_2(ClO_4)_2$: 1) $10^{-5} N$; 2) $10^{-4} N$; 3) $10^{-3} N$.

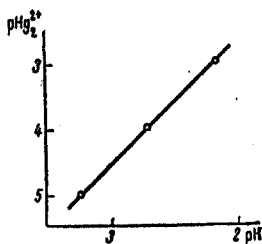


Fig. 4. Dependence of the critical concentration of Hg_2^{2+} ions on the pH of solution.

the fall in potential occurs at definite relative concentrations of mercurous and hydrogen ions in the solution and is localised within a very narrow pH range. For example, in a $10^{-3} N Hg_2(ClO_4)_2$ solution a sharp fall in potential is observed on passing from pH 2 to pH 2.25. Examination of the data shows that the minimum concentration of Hg_2^{2+} ions causing breakdown of the monolayer (the critical concentration) increases as the pH falls. A qualitatively similar relationship was observed earlier in the presence of silver ions, but with the difference that, at the same salt concentration, the pH values at which the effect occurs are displaced towards the alkaline side in the case of silver ions. Fig. 4 shows that a linear relation exists between the negative logarithm of the critical concentration of Hg_2^{2+} ions and the pH of the solution. At the same pH value, e.g. pH = 4, the concentration of mercurous ions causing breakdown of the monolayer is about 10^4 times as great as the critical concentration of silver ions.

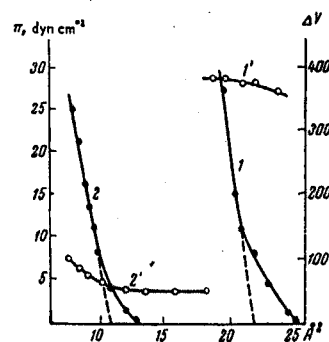


Fig. 5. Curves relating the surface potential ΔV and surface pressure π with the area per molecule in a film of palmitic acid. $HClO_4$ solution at pH = 3.2: 1) pressure; 1') potential. The same solution containing $10^{-4} N Hg_2(ClO_4)_2$: 2) pressure; 2') potential.

A monolayer of palmitic acid on solutions containing mercuric ions Hg^{2+} also showed a similar fall in surface potential. However, comparison of curves 3 and 2 in Fig. 2 shows that the rate of change of surface potential, which characterises the kinetics of the process occurring in the surface film, is less with mercuric ions, and the absolute value of the potential established at the end of this process is greater. Also, the pH range within which this effect is observed is wider for mercuric than for mercurous ions at the same concentration.

In order to determine the mechanism of the reaction occurring in the surface film, as well as the structure of the film which is formed, a study was undertaken of the variation of the surface pressure and the surface potential with the area per molecule of palmitic acid on solutions containing and not containing mercurous ions, using the technique previously described⁶. A difference in procedure was that a known quantity of a benzene solution of palmitic acid, corresponding to complete coverage of the surface with a monolayer, was applied to a solution of mercurous perchlorate, which was then allowed to stand for 30 min, sufficient time for the surface reaction to go to

completion, after which the film was compressed, and the surface potential and the surface pressure were measured as functions of the area per molecule. The results of these measurements for a solution of pure perchloric acid of pH 3.2 and for the same solution containing $10^{-4} N$ $Hg_2(ClO_4)_2$ are illustrated in Fig. 5. Comparison of curves 1 and 2 for π plotted against A shows that, following breakdown of the monolayer, compression leads to the production and growth of a surface pressure at areas per molecule which are considerably lower than that corresponding to a monolayer. Extrapolation of the linear portions of the curves, representing the solid condensed state of the film, to zero pressure gives values of this area of 21.4 and $10.6 \text{ \AA}^2$ respectively for the two solutions. It thus appears that the occurrence of the surface reaction between molecules of palmitic acid and mercurous ions has approximately halved the area per molecule. Examination of the curves for ΔV plotted against A shows that compression of the layer formed after reaction with Hg_2^{2+} ions to an area per molecule of $10.5 \text{ \AA}^2$ involves no appreciable change in the surface potential, which remains at about 50 mV. On further compression a slight increase in potential is observed, reaching a value of 100 mV at an area of $8 \text{ \AA}^2$.

Similar curves for π plotted against A were obtained on compressing an expanded monolayer of palmitic acid on solutions containing mercuric ions. It is seen from Fig. 6 that the areas per molecule for films on a solution of $10^{-5} N$ $HgCl_2$ at pH 5.9 and on a solution at the same pH but containing no mercury ions are 12.5 and $22.0 \text{ \AA}^2$ respectively. In this case an increase in surface potential is observed at relatively low compressions, but it does not reach values approaching that of a monolayer of fatty acid even on compression to extremely low areas.

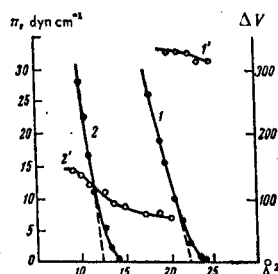


Fig. 6. Curves of π and ΔV plotted against A for a palmitic acid film. Pure water: 1) pressure; 1') potential. $10^{-5} N$ $HgCl_2$ solution: 2) pressure; 2') potential.

TABLE 1. Dependence of A and ΔV on the quantity of palmitic acid applied to a $10^{-4} N$ $HgCl_2$ solution at pH = 5.9.

Palmitic acid applied, $g \times 10^{-6}$	Mean area per molecule, $\text{\AA}^2$	ΔV after application, mV	ΔV after decay, mV
13.0	22.0	290	73
19.5	14.0	200	103
22.1	12.4	150	109
23.4	11.6	109	109
24.0	11.4	109	109
13.0	22.0	300	300

Note: The last line of the table gives values of the area and the potential measured under similar experimental conditions on a solution of the same pH (5.9) but in the absence of mercuric ions.

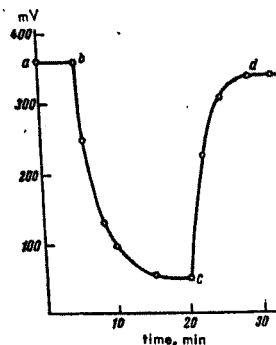


Fig. 7. Curve showing the change in the surface potential of a film of palmitic acid on a $10^{-3} N$ $HClO_4$ solution (pH = 3.2); point b corresponds to introduction of $Hg_2(ClO_4)_2$ to a concentration of $10^{-4} N$ beneath the monolayer; point c corresponds to acidification of the solution below the monolayer to pH = 2.

Some light is thrown upon the structure of the resulting surface film by results obtained for the variation of the surface potential with area per molecule of palmitic acid when it is freely applied to a $10^{-4} N$ $HgCl_2$ solution at pH 5.9. A certain amount of a benzene solution of palmitic acid was rapidly applied to the above solution in the funnel until a meniscus was formed, which corresponded to saturation of the surface with a monolayer. After the potential had fallen to some constant value, more palmitic acid was applied until a new meniscus was formed, and measurements were made of the maximum value of the surface potential, representing a state in which the surface layer is in equilibrium with a slight excess of palmitic acid, and of the value to which it fell after the meniscus had disappeared. It is evident from Table 1 that four successive applications were sufficient for complete saturation of the surface. Calculation of the area per molecule based on the total quantity of palmitic acid applied gives a value of $11.6 \text{ \AA}^2$, corresponding, as in the other experiments cited above, to half the area per molecule which characterizes a monolayer of a fatty acid.

The data in the table show also that as a new layer is formed the extent of change of the surface potential becomes less and less, and with amounts of palmitic acid corresponding to saturation of the surface the potential reaches a constant value of 109 mV.

The experimental results thus show that, under the influence of Hg_2^{2+} and Hg^{2+} cations adsorbed from the solution, a monolayer of palmitic acid undergoes changes resulting in the formation of a new film. To ascertain the nature of this film, it was important to investigate the reversibility of the process. For this purpose a monolayer was applied to a solution of perchloric acid at pH = 2.9, the surface potential being 360 mV, and below it was introduced a solution of $Hg_2(ClO_4)_2$ to yield a concentration of $10^{-4} N$, which produced a sharp drop in the surface potential. After the potential had become constant, the solution under the monolayer was acidified to pH 2, as a result of which a rapid increase in potential was observed to a value close to the original. Section ab of the curve in Fig. 7 represents the

TABLE 2.

$p\text{Hg}_2^{2+}$	pH	k'
3	2.17	1.34
4	2.70	1.40
5	3.25	1.50
		$k'_{av} = 1.42$

constant potential of the monolayer on a solution of pH 2.9 in the absence of mercurous ions, point *b* corresponds to the instant at which $\text{Hg}_2(\text{ClO}_4)_2$ was introduced below the monolayer, and the subsequent fall in potential along section *bc* represents the breakdown of the monolayer. At point *c* the solution under the monolayer was acidified to pH 2, producing the increase in potential along section *cd* of the curve. This result provides evidence of the re-establishment of the monolayer, and hence of the reversibility of the process.

DISCUSSION

The experimental results reported above establish that interaction between molecules of palmitic acid and Hg_2^{2+} and Hg^{2+} ions adsorbed in the surface film leads to a breakdown of the monolayer and the formation of a new film characterised by the parameters $A = 10.6 \text{ \AA}^2$ (half the value in the monolayer) and $\Delta V = 100 \text{ mV}$.

From the fact that the cross-sectional area of the hydrocarbon portion of a fatty acid molecule in a monolayer (with close packing) cannot be smaller than $20 \text{ \AA}^2$, as many investigators have shown, it follows that in the present case formation of the new film results in half the molecules of palmitic acid being in some way removed from the monolayer. Here this cannot be due to dissolution of a proportion of the molecules of palmitic acid in the bulk of the solution, as pointed out by Adam and Miller¹⁴ in an analysis of the reasons for the breakdown of a monolayer of fatty acid on solutions at pH 9. It is also readily seen that the destruction of the monolayer cannot be due in this case to further aggregation with formation of a two-dimensional colloid, which Talmud¹⁷ observed when a monolayer of myristic acid interacts with certain cations, as a result of which the surface of the solution was almost completely freed from the film.

Analysis of the results obtained shows convincingly that we are dealing here with the formation in the surface layer of a bimolecular film of mercury palmitate. The process may be imagined as occurring in two stages, the first consisting in the formation of mercury palmitate by a chemical reaction occurring in the surface layer, and the second in the association of the palmitate molecules, under the influence of the strong electrostatic interaction of their polar groups, into micelles consisting of two molecules of soap oriented in such a way that one of the hydrocarbon chains is directed into the solution. Such an orientation can obviously be achieved when the electrostatic forces operative between the polar parts of the molecules are either greater than or equal to the adsorption forces tending to push the hydrophobic portions of the molecules out to the surface.

If such a view of the process, involving the conversion of a monolayer into a bimolecular film under the influence of mercury ions, is correct, then the number of palmitic acid molecules oriented in the monolayer should fall to half, and there should also be a considerable drop in the surface potential as a result of the balancing of the charges of polar groups pointing in opposite directions. The experimental results reported above confirm such a hypothesis. As has been shown experimentally, formation of a bimolecular film of mercury palmitate is a reversible process occurring at a constant ratio of the concentration of mercury ions to the hydrogen ion concentration of the solution. This suggests that at constant surface pressure and temperature a two-phase equilibrium is established in the surface layer:



In other words, this can be regarded as an example of a heterogeneous equilibrium in which the immiscible layers form the condensed phases.

The equilibrium constant of such a heterogeneous reaction is defined as

$$K = \frac{[\text{H}^+]^2}{[\text{Hg}_2^{2+}]} \quad \text{or} \quad -\log K = k' = 2\text{pH} - p\text{Hg}_2^{2+}.$$

It is seen from Table 2 that the value of k' , calculated for three values of the critical concentration of Hg_2^{2+} ions within the range 10^{-5} – 10^{-3} N , is satisfactorily constant (1.42).

Thus a shift in equilibrium towards the formation of a bimolecular film can obviously be achieved when $k' < 1.42$, whereas transition to a stable monomolecular layer should occur when $k' > 1.42$. In fact, as follows from the results reported above, such a conversion of a bimolecular into a monomolecular film, and conversely, is produced by appropriate change in the pH of the solution under the film.

In conclusion we should like to thank Academician A. N. Frumkin for discussing the results of the present work.

SUMMARY

1. The surface reaction between a monolayer of palmitic acid and mercurous and mercuric cations has been investigated by means of measurements of the surface potential and the surface pressure.
2. Under the influence of mercury ions adsorbed in the surface layer the monomolecular film of palmitic acid is converted into a bimolecular film of mercury palmitate. The equilibrium constant for this phase transition has been determined.
3. The mechanism of formation of the bimolecular film and the nature of its orientation at the interface have been discussed on the basis of an analysis of the curves for π and ΔV plotted against A .

* The authors probably mean that formation of a monolayer is favoured by a decrease in pH or an increase in $p\text{Hg}_2^{2+}$ (Ed. of Translation).

