SURFACE POTENTIAL DIFFERENCES OF UNIMOLECULAR FILMS OF FATTY ACIDS.

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Introduction.

The measurement of the surface potential difference between air and aqueous solutions of many electrolytes was first studied by Bichat and Blondlot⁽¹⁾ in 1883. Later Kenrick⁽²⁾ measured the electromotive force of the following type of cells coupled with various inorganic salt solutions:

n. KCl | solution A | air gap | solution B | n. KCl

where the solution A of a certain electrolyte was dropped from a jet placed at the upper part of the axis of the vertically suspended cylinder and insulated from the solution B by an air gap. The solution B of another electrolyte, or of the same electrolyte as A but of different con-

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(1) Bichat and Blondlot, *J. physiq.*, [2], **11** (1883), 548.

(2) Kenrick, *Z. physik. Chem.*, **19** (1896), 625.

centration, was flowed very slowly to cover the inner wall of the vertical cylinder. There was found a parallelism between the variation of the surface potential difference with the concentration of the solution of electrolyte and its surface activity.

Since Guyot(3) and Frumkin(4) succeeded independently in measuring the surface potential more accurately and quantitatively, devising an ingenious apparatus, many researches were carried out in this field by several investigators, such as Rideal,(5) Adam,(6) Fosbinde,(7) Zisman,(8) Harkins,(9) and their collaborators. In all these experiments of the above authors a platinum electrode coated with polonium or ionium was used as an ionizer of the air gap instead of Kenrick's dropping electrode, and from the measured surface potentials of the liquids the state of films of polar substances was discussed.

In the present experiment X-ray was used to ionize the air gap instead of radioactive elements. This method was already adopted in 1931 by Yoshikazu Tsunoda and one of the present authors for the study of the similar subject at the same laboratory. X-ray was emitted from an ordinary Coolidge tube and allowed to pass through the air space between the surface of the solution on which a film of fatty acid was spreaded and the platinum disk placed in the air parallel to this surface. Thus the potential differences between air and the films of stearic, oleic, and trichloroacetic acids on 0.02 N KCl aqueous solution were measured respectively. The results, however, were not published.

In the next year 1932 Hayato Shigeno(10) studied the unimolecular films of several fatty acids by the same method, simplifying the apparatus by using a glass dish instead of the funnel used by Tsunoda and others. The present study is to complete this X-ray ionization method by using the former apparatus with a few improved points.

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(3) Guyot, *Ann. physiq.*, [10], **2** (1924), 506.

(4) Frumkin, *Z. physik. Chem.*, **109** (1924), 34; *ibid.*, **116** (1925), 485; *ibid.*, **123** (1926), 321. Frumkin and Williams, *Proc. Nat. Acad. Sci.*, **5** (1929), 400.

(5) Schulmann and Rideal, *Proc. Roy. Soc.*, A, **130** (1930), 259, 270, 284. Lyons and Rideal, *ibid.*, **124** (1929), 323. Schulmann and Hughes, *ibid.*, **138** (1932), 430. Whally and Rideal, *ibid.*, **140** (1933), 484, 489, 497.

(6) Adam and Harkins, *ibid.*, **138** (1932), 411; *Trans. Faraday Soc.*, **29** (1933), 90, 837. Adam and Miller, *Proc. Roy. Soc.*, A, **142** (1933), 401.

(7) Fosbinder and Lessing, *J. Franklin Inst.*, **215** (1933), 425.

(8) Zisman and Yamins, *J. Chem. Phys.*, **1** (1933), 656.

(9) Harkins and Fischer, *J. Chem. Phys.*, **1** (1933), 852.

(10) H. Shigeno, the results were not published.

Experimental.

The measurement of the surface potential is based upon the principle of ionizing the air space between the platinum electrode and the fatty acid film on the KCl solution by X-ray, and the potential difference between the elctrode and the film is obtained by the compensation method by using Lindemann electrometer which is suitable for this experiment owing to its small capacity. The apparatus and the operation are as follows.

At first a certain quantity of the substrate solution is poured into the glass dish (A) and mounted on the ebonite platform (E); it is raised to a certain height by the screw (S), so that the junction tip (T) of the connecting tube reaches the surface of the substrate solution and the width of the air gap between the platinum electrode and the solution is reduced to a few millimeters. The substrate solution in the dish (A) is connected to the calomel half cell (C) through the three way cock (K) and the reservoir (J) which contains 0.1 N KCl solution. The liquid junction is made in the three way cock by drawing the solution with the rubber tube (G). After the lid of the brass cover was shut, X-ray of a certain intensity is emitted through the slit into the air gap between the electrode and the solution, and the contact point (W) previously grounded is disconnected. Adjusting the potentiometer so that the needle of the Lindemann electrometer indicates its original position (zero point) which was found at the grounded needle, the potentiometer is read. The current of the Coolidge tube and the primary voltage of the high tension transformer are also observed. Thus the measurement of the surface potential (v) of the pure substrate solution is carried out.

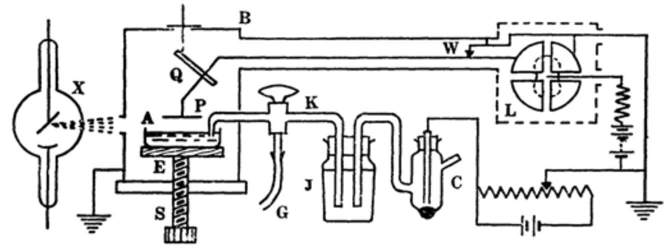

Fig. 1.

The vessel (A) is now carefully taken outside the brass cover and a few drops of the very dilute solution of the fatty acid in petroleum ether is dropped from the small capillary pipette previously calibrated. The petroleum ether is allowed to evaporate and the thin film of the fatty acid is made on the solution. The dish is again screwed up to the former position and the surface potential is measured as before. The difference of this value and the former gives the surface potential of the fatty acid film at the concentration known from the number of drops added.

Preliminary Experiment. (1) *The cleanness of the vessel* (A). The cleanness of the vessel is one of the most important factors to obtain reproducible results. Before every measurement all vessels are washed several times with sulphuric acid chromate mixture and then with ordinary water and finally rinsed with distilled water. In washing, good care must be taken not to touch the vessels with fingers by using two glass rods, otherwise fat on the skin spreads rapidly on the wet surface of the vessel and causes a great error in the measurement. The vessels thus washed are placed on sheets of filter paper and dried at room temperature overnight.

(2) *The effect of the width of the air gap.* The variation of the surface potential with the change of the distance between the platinum electrode and the surface of the solution was investigated. The most favourable distance for the measurement is 6–7 mm., and an increase of 10 mm. in distance gives 30–40 mv. increase in potential, i.e. the reading of the potentiometer increases as if a large resistance were put in the air gap.

(3) *The upper limit of the range of the X-ray radiation in the air gap.* The influence of the height of the X-ray radiation on the surface potential of the fatty acid film was investigated. It was found that when the upper range of the radiation is kept at a level the same as, or slightly higher than, that of the platinum electrode, the measured potenial difference is not altered, but when the holder of the electrode is illuminated the measured potential decreases about 10 mv. or more owing to the leakage between the electrode and the grounded brass box. Hence all experiments are carried out at the best condition of the X-ray radiation, i.e. the upper range being kept at the same height as the platinum electrode.

(4) *The decrease of the surface potential with time.* Although the vessel is sufficiently washed, the surface potential decreases gradually with time. But when the junction tip (T) is drawn out from the solution and again dipped into another position of the surface, the potential difference which was once decreased regains the value near the original one. This phenomenon is reproducible during at least half an hour.

(5) *The influence of the hardness and the intensity of X-ray.* The intensity of X-ray is represented by the current of the Coolidge tube and its hardness is proportional to the voltage of the high tension side of the transformer. The effects of these factors on the surface potentials were examined by altering the current and the tension of the X-ray producing apparatus. It was found that there are no perceptible changes or deviations of the surface potential of fatty acid film, when the current of the Coolidge tube is 0.6–1.6 milliamp. and the primary voltage of the X-ray transformer is 70–85 v. Therefore all experiments were carried out at the following conditions: the current of the Coolidge tube about 1.0 milliamp. and the primary voltage of the X-ray transformer about 70 volts.

(6) *The sensibility of the Lindemann quadrant electometer.* The sensibility of the Lindemann electrometer used was already studied by Tsunoda and examined again before the experiment. It depends principally on the applied needle potential and the humidity of the atmosphere. The following results were obtained at the sufficiently good dryness.

Needle potential (v.)	43.5	42.0	40.5	38.6	36.7	34.8	33	31	30
Division/100 mv.	7.7	5.1	3.8	2.7	2.1	1.9	1.3	1.1	0.9

(7) *The concentration of fatty acids.* Fatty acids used for the experiment are myristic, palmitic, stearic, and oleic acids, having melting points 53.8, 60.8, 69, and 14°C. respectively. These acids are weighed and dissolved into purified petroleum ether and diluted further with 20 or 30 times of the same solvent in such dilution that the acid in one drop of the solution from the capillary pipette gives the surface concentration of about 1×10^{-10} g. mol/cm.^{2} after the evaporation of the solvent on the surface of the substrate solution. The volume of one drop from the pipette is about 0.01 c.c, The petroleum ether employed was a product from N. P. C. It was distilled three times and the fraction between 35 and 50°C. was collected.

Measurements and Experimental Results. All experiments were carried out under the following conditions: temperature 17–20°C., substrate solution 0.01 N KCl or 0.11 N HCl, current of Coolidge tube 1.0 milliamp., primary voltage of transformer 70 volts, and needle potential 42 or 43 volts.

The surface potential of the substrate solution is measured at first under the above conditions and by the experimental manipulations already described. A certain number of drops of petroleum ether solution of the fatty acid is then added on the substrate solution and the film of the fatty acid with a certain surface concentration is formed on the solution

Table 1.

Myristic acid			Palmitic acid		
Surface conc. ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution		Surface conc ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution	
	0.111 N HCl 17°C.	0.01 N KCl 18°C.		0.111 N HCl 18°C.	0.01 N KCl 17°C.
	Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)		Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)
0.93	66.6 35.5	—	1.76	191 176 164	119 111
1.87	103 75.5	—	2.64	210 221 234	166 124 123
2.80	98 136	42.5 50.5	3.52	230 242 248	188 190 172
3.74	138 138	49 64.7	4.40	276 270	222 200
4.67	205 194	106 105	5.28	304 304 283	245 218
5.60	243 228	160 164	6.16	305 338 335	245 255 256
6.54	313 270	177 204	7.04	337 337 338	251 261 257
7.47	325 302	236 268	7.92	348 350	262 256
8.41	323 345	268 275	8.80	358	263
9.43	360 360	268	10.56	335	265
12.14	353	271	11.44	—	262
14.01	360	270	13.2	—	257

Table 1 (*Concluded*).

Stearic acid			Oleic acid		
Surface conc. ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution		Surface conc. ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution	
	0.111 N HCl 18°C. Pot. dif. ΔV (mv.)	0.01 N KCl 18°C. Pot. dif. ΔV (mv.)		0.111 N HCl 17°C. Pot. dif. ΔV (mv.)	0.01 N KCl 17°C. Pot. dif. ΔV (mv.)
0.95	45 74	74 81	1.03	107 111	38 53
1.90	120 126	153 145 145	2.06	129 124 128	82 81
2.85	167	200 208 204	3.09	151 147 168	95 106 101
3.80	258 249	243 245 242	4.12	190 198 177	137 146 144
4.75	300 318	248 262	5.15	223 239 204	160 177 186
5.70	320 316	280 289 300	6.18	228 230 230	162 194 153
6.65	348 350	304 300	7.21	253 240	173 189 169
7.60	354 348	314 302	8.24	250 248	188 193
8.55	—	300	9.27	—	190
9.50	355	312 306	10.3	257 256 253	176 185
11.40	358	—	15.45	262 265 262	203 184

by allowing the petroleum ether to evaporate. Finally the surface potential of the film is measured under the same experimental conditions as in the former measurement.

The variation of more than 10 mv. is hardly found in the measured values of the substrate solution without the film. Variations of about

40 mv. are, however, often found in the case of the solution with fatty acid film on it. This large variation is generally found in the case of the small surface concentration giving non-uniform film on the whole surface. In the case of larger concentration probably giving an uniform film on the surface, there is scarcely found a variation over 10 mv. The difference between the mean value of the measured values of the solution with the film and that of the solution without the film is taken as the surface potential difference of the fatty acid film of the surface concentration evaluated from the number of drops added.

Such surface potential differences as the above-mentioned have been obtained from the experimental data for the four fatty acids and these values are shown in Table 1. The first column of the table indicates the surface concentrations of the fatty acid, and the second the surface potential differences in mv. The relations between the potential differences and the surface concentrations are shown graphically in Fig. 2–5. The abscissa of the graphs indicates the surface concentrations (n) in 10^{-10} g. mol/sq. cm., and the ordinate the potential differences (ΔV) in mv. The curve A is the relation obtained by using 0.11 N HCl as the substrate solution and the curve B is that by 0.01 N KCl.

(1) *Myristic acid.* Fig. 2 shows the relation between the surface potential difference of myristic acid film on the solution and its surface concentration. The curve drawn with the dotted line in the figure was plotted with the data obtained by Harkins⁽¹¹⁾ for the same acid film. Although these data were obtained by Harkins by using 0.01 N HCl as the substrate solution and by an entirely different method, the resulting curve C shows good agreement with curve A. It is found that the two curves A and B are parallel with each other and have almost uniform inclinations.

The following well-known formula of Helmholtz is now applied to this case:

$$\Delta V_1 - \Delta V_2 = 4\pi(n_1 - n_2)\bar{\mu} ,$$

where ΔV represents the surface potential difference, n the number of molecules on 1 sq. cm., and $\bar{\mu}$ the mean vertical component of dipole moment. From this formula it may be seen that $\bar{\mu}$ indicates the slope of the ΔV–n-curve, namely the inclination of the (surface potential)—(surface concentration)-curve.

From the fact that two curves A and B are parallel and have the same inclination, it may be considered that the mean vertical component

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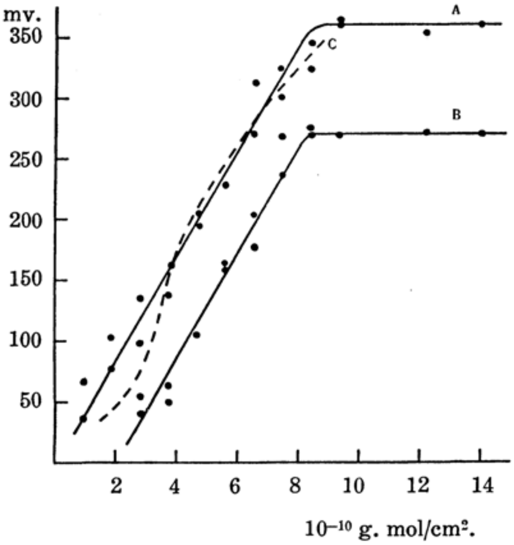
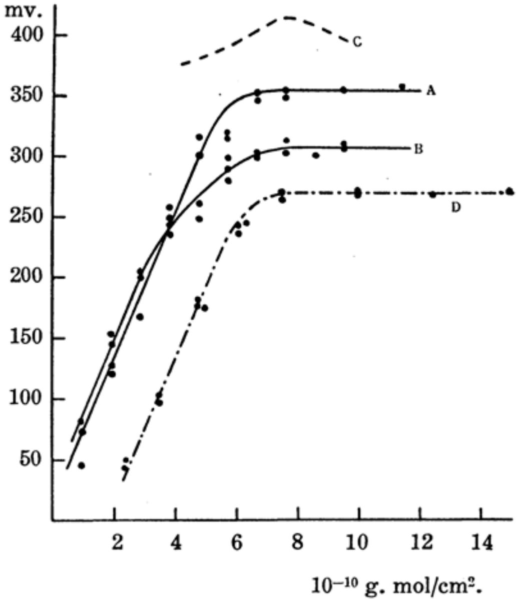
(11) Harkins, *J. Chem. Phys.*, **1** (1933), 858.



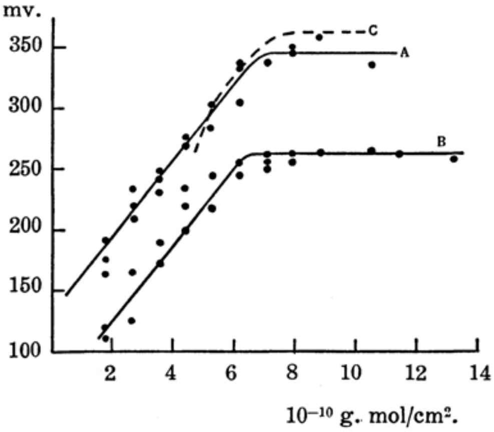
Myristic Acid

Fig. 2.



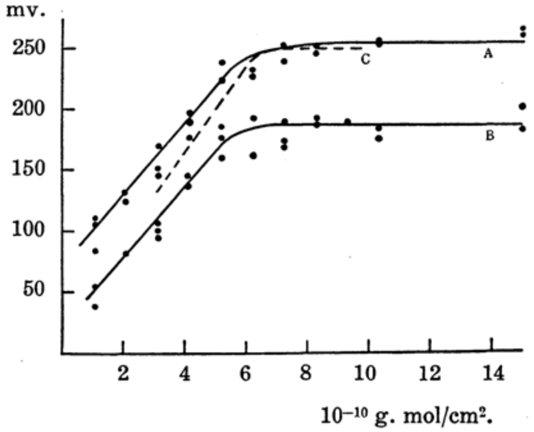
Stearic Acid

Fig. 4.



Palmitic Acid

Fig. 3.



Oleic Acid

Fig. 5.

of dipole moment $\bar{\mu}$ of myristic acid has the same value and alter neither with the surface concentration nor with the substrate solution.

(2) *Palmitic acid.* The results obtained with palmitic acid are plotted in Fig. 3. There is also parallelism between curves A and B and the coincidence of A and C.

(3) *Stearic acid.* Fig. 4 shows the curves for stearic acid. Curve D drawn with a chain line was plotted with the data obtained by Y. Tsunoda(10) with 0.02 N KCl as the substrate solution. Comparing these four curves, if the values of curves A and D are correct, those of B and C are a little higher and if B and C are correct, A and D are a little lower. The slopes of curves A, B, and D, however, are almost similar to one another.

(4) *Oleic acid.* Fig. 5 shows the curves for oleic acid. If a curve be drawn with the data obtained by Y. Tsunoda with 0.02 N KCl as the substrate solution, it falls nearly on curve B, although the former is not drawn in the figure. It is found that curves A and B are parallel as before and curve C falls nearly on A. It is very remarkable in this case that the maximum surface potential attainable is about 100 mv. less than those of the former three fatty acids.

Assuming the surface potentials of the fatty acid films of the same surface concentration are nearly proportional to their length of the molecules or their dipole moments, and basing on the fact that the saturated surface potential of oleic acid film is about 100 mv. less than that of stearic acid with the same number of carbon atoms (18) in the molecule, it may be considered that the vertical length of the former on water is smaller than that of the latter by the amount corresponding

Table 2.

Fatty acid	M.p.	Mean vert. comp. dipole moment ($\bar{\mu}\times10^{-19}$ e.s.u.)	Saturation point		
			Subs. sol.	Area (sq. Å per mol.)	Pot. dif. (mv.)
Myristic acid $CH_3(CH_2)_{12}COOH$	53.8	1.89	HCl KCl	19.6 20.0	360 270
Palmitic acid $CH_3(CH_2)_{14}COOH$	60.8	1.37	HCl KCl	26.4 28.3	340 260
Stearic acid $CH_3(CH_2)_{16}COOH$	69	2.68	HCl KCl	27.0 27.0	350 310
Oleic acid $CH_3(CH_2)_7CH{=}CH{\cdot}(CH_2)_7COOH$	14	1.27	HCl KCl	27.0 30.0	250 190

to this value. This can be explained from the fact that oleic acid has a double linkage in the central part of the molecule and is folded at this point. The mean vertical component of dipole moment ($\bar{\mu}$) is calculated from Helmholtz's formula for the four fatty acids and shown in Table 2. The value for stearic acid is about 2.7×10^{-19} e.s.u., while that of oleic acid is ca. 1.3×10^{-19} e.s.u. and about half that of stearic acid.

Discussion.

The characteristic values calculated from the measured results of the four fatty acids are summarized in Table 2. The third column of the table is the mean vertical component of dipole moment ($\bar{\mu}$) calculated from Helmholtz's formula. The fifth and sixth columns are the area per molecule in sq. Å and the surface potential at the saturation point respectively. It is found that there is always a saturation curve in the (surface potential)—(surface concentration)-curve of the fatty acids. The break point on the curve, i.e. the starting point of the saturation is nearly similar for all the acids and is about 27 sq. Å per molecule and this is the value of the order of a molecular dimension. From this fact it may be considered that at this break point the unimolecular film of fatty acids is established, and in the range of larger area per molecule than that of the break point, i.e. in the inclined part of the curve, the film is in the expanded state and the potential difference changes nearly proportional to the surface concentration. And in the range of smaller area per molecule than the break point, i.e. in the horizontal part of the curve, the film is in the condensed or liquid state as former investigators already described. At extreme concentration, the film is transformed into solid state and sometimes it is considered that small crystals of fatty acid are locally floating on the film.

The maximum or saturation potentials of the saturated fatty acids are almost nearly equal, about 350 mv., but in fact there should be a certain difference in potentials, i.e. about 20–30 mv. for one carbon atom in fatty acid as stated by Harkins and others. Comparing the mean vertical component of dipole moment of fatty acids, that of stearic acid with the largest number of carbon atoms is greatest in value and that of oleic acid is nearly half that of stearic acid, since the length of the molecule of the former is shortened owing to the fold at the point of the double linkage at the central part of the molecule in spite of the same number of carbon atoms.

The value of palmitic acid is less than that of stearic acid. However the value for myristic acid and that for palmitic acid are reversed if the numbers of carbon atoms in them are compared.

One of the authors studied on the similar subject by using a different method of ionizing the air gap at the Physico-chemical Laboratory of University College, London, with the encouragement of Prof. F. G. Donnan to whom he wishes to express his cordial thanks.

Summary.

(1) Gas—liquid interfacial potential difference of fatty acid film was measured by using the method of ionizing air gap between the electrode and the surface of the liquid with X-ray.

(2) Various factors which affect the measurements were studied at first.

(3) Under the most favourable conditions the measurements of the surface potentials were carried out with four fatty acids, i.e. myristic, palmitic, stearic, and oleic acids.

(4) The surface potential difference attains a maximum or a saturation value at a certain definite surface concentration. This value is nearly equal for three saturated fatty acids and is about 350 mv. The value for oleic acid, however, is about 240 mv.

(5) The (surface potential)—(surface concentration)-curves were plotted and the mean vertical component of dipole moment was calculated for these fatty acids by applying Helmholtz's formula.

(6) The break point of the curve or the saturation point of fatty acid is nearly similar for four acids, and the area occupied by a molecule at this point is about 27 sq. Å.

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