Studies on the Gas Liquid Interface by Surface Potential Measurements. II. On the Solutions of Dicarboxylic Acids

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Molecules of polar-nonpolar substances on the surface of a solution will probably take particular orientation at the gas liquid interface. The orientation of such molecules will be greatly affected with the molecular configuration of the adsorbed substances. Many investigations on the structure of monolayer of insoluble heteropolar compounds or the orientation of the molecules on water have been reported by many investigators.(1) The measurement of the surface potential of monolayer is one of the useful methods for studying the structure or the orientation of the monolayers. The method will also serve as the most useful one for the investigation on the nature of adsorbed surface layer of solutions. Nevertheless, relatively few investigations have already been reported.(2) Previously, one of the authors measured surface potential of aqueous solutions of some fatty acids.(3) Then, it was found that the surface potential of aqueous solutions of monocarboxylic acids such as *n*-butyric, *n*-valeric and *iso*-caproic acid reverses the sign of the potential in the region of concentration of high dilution. It was concluded that this reversal of the sign of surface potential is probably caused either by the dissociation of adsorbing acid or by the particular orientation of the adsorbed fatty acid molecules. In order to clarify the cause of the sign reversal of potential at high dilution and to obtain some informations of the molecular orientation of the adsorbed layer, we have measured in the present experiments the surface potential of aqueous and acidulated solutions of some dicarboxylic acids such as oxalic, fumaric, maleic, succinic, adipic, suberic, azelaic, sebacic and $\gamma\gamma'$-sulfonyl dibutyric acids. These acids, investigated in our present experiments, have polar groups at both ends of linear molecule and may lie probably flat in the adsorbed layer in virtue of two polar groups at the ends. γ,γ'-sulfonyl dibutyric acid has one more polar group at the midst of the molecule. Among the acids investigated, oxalic, maleic, fumaric and succinic acids always gave negative surface potential all over the concentration range. Other acids than these showed reversal of sign of the potential in the region of concentration of high dilution as in the cases of monocarboxylic acids. If the solution were acidulated by addition of small quantity of hydrochloric acid, the potential of the solutions was shifted to more positive values than the values of respective aqueous solutions. These results can readily be interpreted from the viewpoint that negative surface potential is principally caused from adsorbed fatty acid anions. At relatively high concentration, if the chain length of acid is sufficiently long, bending of the hydrocarbon chain of such dicarboxylic acid at the middle of a molecule would be caused by hydrophobic nature of hydrocarbon chain. Consequently, the adsorbed layer will much resemble to the adsorbed layer of monocarboxylic acid as indicated in Fig. 1. It was found that the expected resemblance of the surface layer of dicarboxylic acid solution to that of monocarboxylic acid was in part realized with concentrated solution of sebacic acid. One of the strong evidences which has rendered us to believe that the reversal of sign of potential is not caused by molecular orientation but mainly by dissociation of acid, is the following fact. The sign reversal of the surface potential was observed even with acidulated solution of γ,γ'-sulfonyl dibutyric acid which has one more polar group at the midst of molecule, so that the molecule can not bend anyway and must always lie flat.

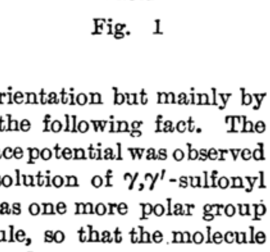

Fig. 1

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(1) N. K. Adam, " The Physics and Chemistry of Surfaces," 72-77, Oxford, (1941).

(2) Bichat and Blondlot, *J. phys. Radium*, **2**, 548 (1883); Kenrick, *Z. physik. Chem.*, **19**, 625 (1896); Frumkin, *ibid.*, **109**, 34 (1924); **111**, 190 (1924); Sawai, *Trans. Faraday Soc.*, **31**, 764 (1935).

(3) T. Isemura, "Gendai Koshitsugaku no Tembo (Perspectives in Colloid Science, in Japanese)," Vol. 1, 177, Tokyo (1948).

Experimental

The method used for measuring the surface potential is the vibrating plate method, which is the same as used in the previous work of our laboratory. The amplifier, which was constructed for present expriment, was a three stage amplifier of resistance coupling using valves 6C6, 6C6 and 42. The principle of measuring the potential is essentially the same as was originally devised by Zisman.(4) Surface tension was measured by a simple tensiometer of Du Nouy.

The substances studied are oxalic, maleic, fumaric, succinic, adipic, azelaic, sebacic and $\gamma\gamma'$-sulfonyl dibutyric acids. The first four acids are the purest commercial samples available. Those acids were repeatedly recrystallized from adequate solvents. Agreement of melting points with literature was satisfactory, excepting maleic acid. Recrystallized maleic acid used in our present experiment melted sharply at 138°. This melting point does not agree with the literature. However, Mr. I. Moritani found that a single crystal of pure sample of maleic acid melts sharply at that temperature.(5) Suberic and azelaic acids were prepared by usual method of oxidation of castor oil with nitric acid. The obtained azelaic acid was finally recrystallized from benzene (m. p. 106–108°). Suberic acid was fractionally recrystallized using ether repeatedly (m. p. 138–140°). Sebacic acid was prepared also form castor oil by the procedure presented by Sugino and his collaborators,(6) and was recrystallized from 15% alcohol (m. p. 131°). γ,γ'-sulfonyl dibutyric acid was a pure sample which was given by Prof. S. Murahashi in this Institute.

All measurements were made at room temperature without special regulation of temperature. However, one series of experiments were made within a range of temperature as small as possible, and the variation of temperature never exceeded more than 2°.

Results

The surface potentials observed are shown in Fig. 2 and Fig. 3, and the surface tensions of respctive solutions are shown in Fig. 4. In these figures solid lines are the results for aqueous solutions and chain lines are the results for acidulated solution by 1/100 *N* hydrochloric acid. In Fig. 2, the curves for monocarboxylic fatty acids, *i. e.* butyric, valeric and *iso*-caproic acid which were already reported in the previous paper are also shown for comparison. Values of surface potential in relatively low concentration region of respective acids could not be determined as accurately as in rather concentrated region of the solutions. The parts of curves shown in dotted lines are the parts with somewhat less reliability than that of solid or chain lines. In these parts the potential fluctuated to some extent. Later the cause of the fluctuation of surface potential data in such concentration region will be thoroughly discussed.

Dicarboxylic acids which have relatively short carbon chain such as oxalic, maleic and fumaric acids gave always negative surface potential all over the concentration range examined up to saturation. With oxalic, maleic and fumaric acids, the potential reached to −140, −150 and −129 millivolts respectively at the concentration of nearly saturated solution. Succinic and

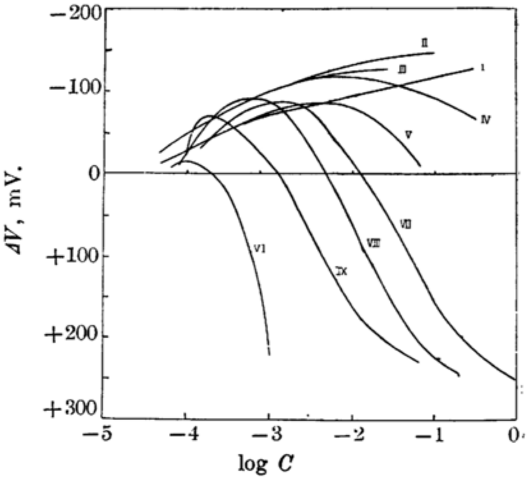

Fig. 2.— I, oxalic acid (11°C.); II, maleic acid (8°C.); III, fumaric acid (8°C.); IV, succinic acid (8°C.); V, adipic acid (10°C); VI, sebacic acid (10°C.); VII, n-butyric acid; VIII, valeric acid; IX, *iso*-caproic acid.

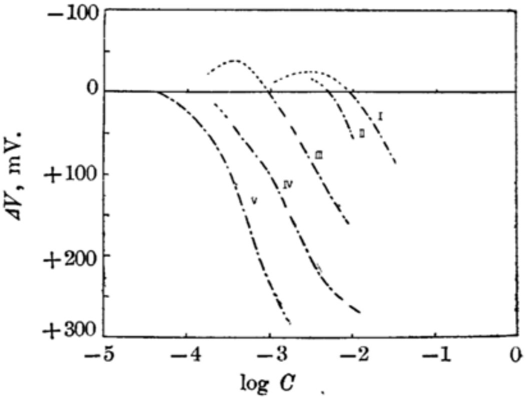

Fig. 3.— I, adipic acid (11°C.); II, $\gamma\gamma'$ sulfonyl dibutyric acid (14°C.); III, suberic acid (13°C.); IV, azelaic acid (14°C.); V, sebacic acid (17°C.).

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(4) Zisman, *Rev. Sci. Instrument*, **3**, 7 (1932); Yamins and Zisman, *J. Chem. Phys.*, **1**, 656 (1933).

(5) Private communication.

(6) K. Sugino and collaborators, *J. Soc. Chem. Ind. Japan*, **44**, 706 (1941).

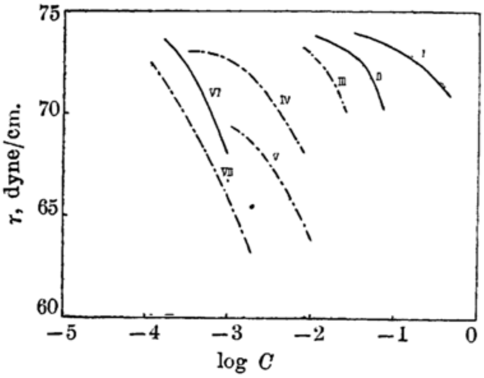

Fig. 4.— I, maleic acid (10°C.); II, adipic acid (9°C.); III, adipic acid+N/100 HCl (11°C.); IV, suberic acid+N/100 HCl (16°C.); V, azelaic acid+N/100 HCl (17°C.); VI, sebacic acid (10°C.); VII, sebacic acid+N/100 HCl (17°C.).

adipic acids in aqueous solution also gave always negative potential, however, the potential tends to be less negative if the concentration of the solution approaches to saturation. Sebacic acid gave negative potential in very dilute solution but changed the sign of potential in more concentrated solution. With this acid, surface potential curve plotted as a function of logarithm of concentration (mol/l.) of the acid was similar to the curves of monocarboxylic fatty acids which were mentioned above. The potentials were generally shifted to more positive values when hydrochloric acid was added to the solution and maximum negative potentials were markedly suppressed. Maximum surface potentials of various dicarboxylic acids were not similar as shown in monocarboxylic acid and the more positive potential was observed the longer the carbon chain of the acid. Maximum potential observed in our experiments for adsorbed layer of solutions was 280 mV. for 0.016 mol solution of sebacic acid at 17° acidulated with hydrochloric acid so as to become 0.01 N with respect to hydrochloric acid. The vertical contribution of surface moment of the adsorbed acid was calculated by Helmholtz equation,

$$\Delta V = 4\pi n\mu,$$

with the aid of Gibbs' adsorption formula and our surface tension concentration curves. In the above equation ΔV is surface potential, μ, the vertical contribution of dipole moment of the surface molecule and n, the number of adsorbed molecules per unit area. The vertical contributions of surface moments of suberic, azelaic and sebacic acids and their molecular area on the surface of solution at different surface potentials were tabulated in Table 1. The data of the area occupied and vertical component of dipole moment of adsorbed solute were shown as a function of surface potential and calculated assuming that both the activity coefficient and the dielectric constant were equal to unity.

Table 1

Molecular Area and Vertical Component of Dipole Moment with Respect to Surface Potential of Solutions of Dicarboxylic Acids.

(calculated as activity coefficient = 1 and dielectric constant = 1)

Surface potential ΔV (mV.)		280	240	200	160	120	80	40
Molecular area (Å^2.)	Suberic acid				124	140	206	310
	Azelaic acid		92	160	220			
	Sebacic acid	68	92	120	130	170	190	240
Vertical component of dipole moment per each polar group (Debyes)	Suberic acid				0.27	0.23	0.22	0.17
	Azelaic acid		0.30	0.37	0.47			
	Sebacic acid	0.25	0.30	0.33	0.28	0.27	0.20	0.12

Discussion

From the results just mentioned above, it will be noticed that the surface potentials of solutions of dicarboxylic acids near the concentrations of their saturated solutions became more positive value with increase of the length of hydrocarbon chain in the acid molecules. This is a remarkable difference between the results obtained with dicarboxylic acids and those with monocarboxylic acids. With monocarboxylic acids such as butyric, valeric and *iso*-caproic acids, solutions of these acids showed almost the same positive potential, *i.e. ca*, 240 mV. in the concentration ranges near saturation. If the solutions of dicarboxylic acids of moderate carbon chain length were acidulated with hydrochloric acid, the surface potential was generally shifted to more positive value. Then, the curves of surface potential versus logarithm of concentration were almost parallel as shown in Fig. 3, and from the figure it is obvious that about one third concentrated solution is sufficient to attain a certain value of surface potential if the acid has one more CH_2 group in the chain. This fact is analogous to that found with monocarboxylic acids in the previous investigation. The work of adsorption is increased in the cases of dicarboxylic acids also, by a constant amount for each CH_2 group added to the chain, so that the relation of every CH_2 to the water surface is the same, whatever its position in the chain.

In the previous paper, we inferred that the reversal of sign of surface potential that was observed at high dilution of solution may be the characteristic phenomena for the adsorbed layer of gaseous film type, caused either by molecular orientation, that is lying flat on the surface, or by the dissociation of adsorbed acids. Since the acids investigated in the present work are dicarboxylic and have two polar groups at both ends of the molecule, two water soluble polar groups would naturally make the molecule lie flat, if the surface potential is defined principally by the orientation of the adsorbed molecules, the potentials of solutions of these acids will not reverse the sign at all, and change steadily to a saturation value. With oxalic, maleic and fumaric acids, which have relatively large dissociation constants, this is the case. With dicarboxylic acids of longer chain than adipic acid, however, the reversal of the sign of the potential was observed just as with monocarboxylic fatty acids. Thereupon, these facts cannot be attributed simply to the change of orientation of the adsorbed molecules. Further, if the reversal of potential was caused by the orientation, the calculated vertical contribution of the dipole moment of the molecules of dicarboxylic acids, which lie on the surface of solution, should be independent of the concentration of the solution and of the length of carbon chain of the acids. These inferences were not supported with our experimental results. On the other hand, if we assume the reversal of surface potential are caused by the dissociation of the acid, the experimental results will be explained without any difficulty. In acidulated solutions, the dissociation of dicarboxylic acids will be suppressed and the potential of the surface was shifted to more positive values in comparison with that of non-acidulated solutions. In very dilute range of concentration of the solution, number of molecules of adsorbed acid might be relatively few and a large proportion of the adsorbed acid should be ionized. Hence, surface potential of the solution may be reversed the sign.

These inferences would readily be comprehended by comparing the surface potential curves in Fig. 2 and Fig. 3 with dissocation constants of respective acids tabulated in Table 2. Except oxalic, maleic and fumaric acids which have relatively high dissociation constants, all acids investigated have the first dissociation constants of the order of magnitude of 10^{-5}. With the aid of Ostwald's dilution law, the degree of dissociation of dilute solutions of various concentrations can readily be calculated and rough estimate at two different dissociation constants would have values as shown in Table 3. Since hydrochloric acid is practically dissociated completely in 1/100 N solution, the dissociation degree of the acids, having dissociation constant of the order of magnitude of 10^{-5}, will be as much as 3×10^{-3}.

Table 2

Dissociation Constants at 25°C.

Acids	k_1	k_2
Oxalic acid	3.8×10^{-2}	
Succinic acid	6.5×10^{-5}	2.3×10^{-6}
Fumaric acid	9.3×10^{-4}	1.8×10^{-6}
Maleic acid	1.2×10^{-2}	3.9×10^{-7}
Adipic acid	3.8×10^{-5}	2.4×10^{-6}
Suberic acid	3.0×10^{-5}	2.5×10^{-6}
Azelaic acid	2.6×10^{-5}	2.7×10^{-6}
Sebacic acid	2.8×10^{-5}	2.6×10^{-6}
n-Butyric acid	1.5×10^{-5}	
n-Valeric acid	1.5×10^{-5}	
iso-Caproic acid	1.5×10^{-5}	

(cited from the Beilstein's Handbuch.)

Table 3

Degree of Dissociation Calculated from Ostwald's Dilution Law

Dissociation constant	Concentration, N				
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
1.5×10^{-5}	0.012	0.038	0.12	0.31	0.68
2.5×10^{-5}	0.016	0.046	0.14	0.39	0.77

Surface potential changed its value to some extent with time after making surface on the solution according to the kind and concentration of acid. The values plotted in Figs. 2 and 3 were those within one minute after making new surface. The potentials in the range of negative value tend to more negative value with time. It has already been pointed out by some authors that surface tensions of solution of certain substances changed with time,(7) and at least five minutes were required to attain steady values of surface tension with all aliphatic acids above n-butyric acid. Time required to obtain equilibrium surface tensions

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(7) H. H. King, *Kansas State Agr. Col., Agr. Exp. Station Techn. Bull.*, No. 9, (1922); Addison, *Nature*, **156**, 600 (1945).

increases very rapidly with chain length of acids. Of course, the cause for the change of surface potential with time might be the same with that for surface tension and attributed probably to slow adsorption of solute. Ions of acids are exceedingly more soluble than undissociated molecules. The latter will immediately be adsorbed. While, ions which have hydrocarbon of moderate length and are considerably soluble in the solution, would be adsorbed very slowly. The rate of adsorption of ions must be slower than that of undissociated molecules and depends on the length of hydrocarbon chain. If such ions of moderate hydrocarbon chain reached to surface, they would be captured by surface layer and partly cambined with hydrogen ion and converted into undissociated molecule according to relatively high concentration of such weak acid in the surface phase. Nevertheless, actual concentration of negative ions is gradually increased and surface potential effectively changes to more negative. With acids of sufficiently long chain, solubility of those acids would be decreased markedly and the acids might be often practically insoluble, and the adsorbed layer, which covers the surface of solution completely or surface monolayer closely packed, would be made exclusively of undissociated molecules. Hence the surface potential is positive and has no bearing on time. The surface films of insoluble fatty acids such as stearic and myristic acids, of which dissociation constants are the order of magnitude of 10^{-13}, give generally positive surface potential. Even with such acid of low dissociation constant as myristic acid, however, the change of sign of surface potential was observed recently by Guastella and Michel(8) at extremely dilute surface concentrations. They found with myristic acid that surface potential changes to negative for molecular area from 1000 to 30000 Å.^{2} They concluded that the results obtained by them at high dilution appear to indicate that the molecules of myristic acid turn their negative pole upwards. On the other hand, with the concentrated solution of acids which have moderate length of carbon chain and show some solubility, surface layer is completely covered with preferentially occupied undissociated molecules and leaves no space for belated ions. Under these circumstances also, the potential is always positive and does not change with time.

Each molecule of sebacic acid, dicarboxylic acid of ten carbon atoms, occupied an area of 68 Å.^{2} on the surface of its $10^{-3}\,N$ solution, whose surface potential of which was 280mV. Calculated from these figures, the vertical component of dipole moment assigned to each polar group was 0.25 D. U. This is nearly identical with the value of vertical contribution of dipole moment of monocarboxylic acid at higher concentration or of monolayer of insoluble saturated fatty acid. In this case the molecule may be anchored by two carboxylic groups at both ends, neverthless, the hydrophobic hydrocarbon chain is repellent to aqueous phase. So that, the molecule probably bends somewhat at the middle of the molecule as shown in Fig. 1. This conclusion is not strange at all. J. T. Davies measured force area and surface moment area curves for the monolayers of some long chain diesters containing the same number of carbon atoms.(9) A plot of areas at the same surface pressure against the number of carbon atoms in each end chain was drawn. He found a maximum close to the point where the number of carbon atoms in the end chains is equal to the number in the middle of the molecule. These results together with our own concerning with sebacic acid are both equally understood, if the molecule is considered to bend at its middle. It must be emphasized, however, that the reversal of the sign of surface potential of dicarboxylic acid is not always connected with the bending of molecule. This will be clearly understood by the fact that γγ'-sulfonyl dibutyric acid, which has one more polar group of hydrophilic nature in the middle of molecule and for that reason cannot bend the chain molecule, reversed the sign of the surface potential at high dilution. For these reasons, it is believed that the reversal of sign of surface potential would be caused mainly by the dissociation of some weak acid. Some aliphatic non-ionizable substances are to be investigated.

Summary

Surface potentials of solutions of some dicarboxylic acids were measured by vibrating plate method. Dicarboxylic acids of short chain such as oxalic, maleic, fumaric and succinic acids gave always negative potential. However, dicarboxylic acids of moderate chain length gave positive potential at high concentration. While, with these acids, the potential changed to more negative at high dilution as in the cases of monocarboxylic acids. The values of potential were shifted to more positive values when the

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(8) J. Guastella and Michel, *Research (London), Suppl., Surface Chemistry*, 127 (1949).

(9) J. T. Davies, *Trans. Faraday Soc.*, **44**, 909 (1948).

solutions were acidulated by hydrochloric acid. Such reversal of sign of surface potential might be attributed mainly to the dissociation of the acid and not to the molecular orientation. Molecule of sebacic acid adsorbed on the surface of nearly saturated solution bends probably its hydrocarbon chain at the middle of the molecule and it behaves as two adsorbed molecules of monocarboxylic acid in regard to molecular area and surface moment.

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