May, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (5), 1245—1250 (1977) 1245

Adsorption of Benzoic Acid on a Mercury Electrode

Isao TANIGUCHI, Koji MACHIDA, Norio SATO, and Taro SEKINE
Department of Electronic Chemistry, Graduate School at Nagatsuta, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received August 23, 1976)

The differential capacity and the surface tension at the electrode-electrolyte interface of a dropping-mercury electrode were measured in 0.5 M H_2SO_4 and 0.5 M Na_2SO_4 solutions for various concentrations of benzoic acid. On the basis of the Frumkin-Damaskin theory, the adsorption of benzoic acid on mercury was studied in the acid solution, and the parameters involved in the F-D theory were determined: $A=1.6$ μJ cm^{-2} ($\Gamma_m=6.5\times10^{-10}$ mol cm^{-2}), $B_0=597$ l mol^{-1}, $a=-0.35-2.5\,E$/V, and $C'=5.95$ μF cm^{-2}. The experimental values of the capacity and the surface tension are in good agreement with the theoretical values calculated by using the parameters obtained. The absence of an anodic maximum in the capacity-potential curve in the presence of benzoic acid was determined to be associated with a strong repulsive force between the adsorbed molecules. The value obtained for the maximum surface excess of benzoic acid is explained in terms of adsorption of the acid molecules for a vertical orientation on the electrode surface. This conclusion was supported by comparing the B_0 value for benzoic acid with those for phenol and aniline. The adsorption of benzoic acid in neutral solutions is also discussed.

The adsorption of organic substances on mercury electrodes has been reported by many workers.[1,2] At present, two theories developed by Frumkin and Damaskin (F-D theory)[1] and by Bockris, Devanathan, and Müller (B-D-M theory)[3] are applicable for describing the effect of an electric field on the adsorption of organic substances on the electrode surface. The adsorption of aliphatic amines,[4] alcohols,[4,5] carboxylic acids,[6,7] aromatic amines,[8,9] and phenol[10] has been investigated on the basis of the F-D theory, since this theory gives a quantitative description of the relationship between the surface tension or the differential capacity and the electrode potential in the presence of organic substances. Good agreement between the theoretical and experimental results has usually been obtained. In addition to the above compounds, the adsorption of aliphatic ketones[11,12] was studied using a modified F-D theory.[7] However, only a few reports have been made on the adsorption of aromatic carboxylic acids. Blomgren *et al.*[13] have carried out the measurement of electrocapillary curves on a mercury electrode in 0.1 M HCl solutions containing benzoic acid at concentrations less than 10 mM with the results treated on the basis of the Langmuir isotherm. Therefore, a precise experiment is required to further clarify the adsorption behavior and to elucidate the reduction mechanism of benzoic acid.[14]

Here, the adsorption of benzoic acid on a mercury electrode in aqueous sulfuric acid and sodium sulfate solutions investigated by measuring the differential capacity at the electrode-electolyte interface and the surface tension of a dropping-mercury electrode are reported. The results are discussed on the basis of the F-D theory.

Experimental

The differential capacity of the double layer was measured by means of an AC impedance bridge possessing a large capacity to prevent DC flow through the bridge and having a choke to prevent AC flow through the DC polarization circuit. The measurements were carried out on a dropping-mercury electrode with a droplife of 11—13 s (rate of mercury flow: 0.629 mg s^{-1}), and at various frequencies (0.2—10 kHz, V_{pp}: 5 mV). In the case of benzoic acid solutions of more than 1 mM, the frequency dispersion of the capacity was not observed at the bottom of the capacity curves. At the peak of the curves, the capacity depends slightly on the frequency of the applied AC signal. The capacity at equilibrium was obtained from an extrapolation of the peak capacity to zero frequency as a function of the square root of the frequency, as described by Hansen *et al.*[15] When the electrode has a long droplife, the influence of diffusion on the measured capacity is negligible. The capacity at equilibrium obtained by extrapolation is nearly equal to the capacities measured at 0.5 or 1 kHz, and the curves measured at 0.5 and 1 kHz are considered to be the equilibrium curves for solutions of more than 10 mM of benzoic acid without introducing any appreciable error.

The surface tension of the mercury electrode was measured by the drop-time method.[16] The surface tension at the electrocapillary maximum was evaluated from the measured surface tension.[17,18]

All measurements were repeated at least three times and the average of the measured values is adopted as the final value. The uncertainty is within ±3%.

Benzoic acid (analytical GR reagent grade) was recrystallized twice from water. The test solution was freshly prepared before the measurements. The concentration of benzoic acid was determined by means of UV absorption at 230 nm. The solution in the cell was deaerated by bubbling for more than one hour with purified nitrogen that had been passed through a washing bottle containing the same solution.

The physical meanings of all symbols appearing in this paper are summarized as follows:

(Roman letters)

A	Constant equal to $RT\Gamma_m$ (μJ cm^{-2})
a	Interaction constant of adsorbed molecules; a is a function of E
a_0	Value of a at zero charge potential in the solution without benzoic acid
B	Equilibrium adsorption constant at potential E (l mol^{-1})
B_0	Value of B at zero charge potential in the solution without benzoic acid (l mol^{-1})
C	Differential capacity (μF cm^{-2})
C_0	Differential capacity of the solution without benzoic acid (μF cm^{-2})
C'	Differential capacity for full coverage of electrode with benzoic acid (μF cm^{-2})
$C^{\min}$	Minimum differential capacity of the capacity-potential curves in the presence of benzoic acid (μF cm^{-2})
$C^{\max}$	Peak capacity (μF cm^{-2})

c	Concentration of benzoic acid (mol l^{-1})
E	Electrode potential with respect to zero charge potential in the solution without benzoic acid (V)
ΔE	Width of the capacity peak (V)
E^{min}	Potential corresponding to the minimum capacity (V)
E^{max}	Potential corresponding to the maximum capacity (V)
E_{N}	Potential difference between the respective zero charge potentials for zero and full coverage of the electrode with benzoic acid (V)
E_{Z}	Shift of the zero charge potential for a given coverage (V)
K_0	Integral capacity in the solution without benzoic acid (μF cm^{-2})
q_0	Charge density of the electrode surface in the solution without benzoic acid (μC cm^{-2}); q_0 was determined by graphical integration of C_0
R	Gas constant (J K^{-1} mol^{-1})
r	Function of a for a given fraction of the peak height
T	Absolute temperature (K)
y	Relative concentration of benzoic acid, $c/c_{\theta=0.5}$
(Greek letters)	
β	Coefficient of the potential dependence of a (V^{-1})
Γ_{m}	Maximum surface excess of benzoic acid (mol cm^{-2})
γ	Interfacial tension of the solution with benzoic acid (10^{-5} N cm^{-1})
γ_0	Interfacial tension of the solution without benzoic acid (10^{-5} N cm^{-1})
θ	Surface coverage
θ^{max}	Value of θ at E^{min}
ν	Frequency (kHz)

Results

In Acid Solution. Examples of typical capacity-potential curves for 0.5 M H_2SO_4 solutions of various concentrations of benzoic acid are shown in Fig. 1. The capacity curves exhibit no anodic maximum. At high negative potentials, the capacity-potential curves and the electrocapillary curves approach the curve obtained for a 0.5 M H_2SO_4 solution without benzoic acid, and this indicates the desorption of benzoic acid from the mercury surface.

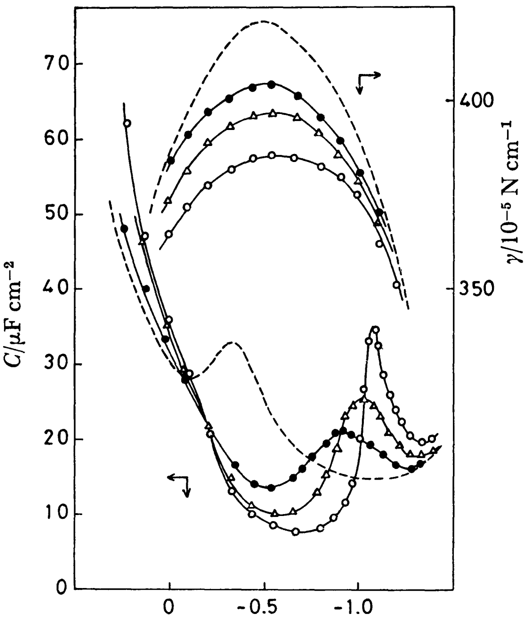


Fig. 1. Differential capacitance curves and electrocapillary curves at 1 kHz and 25 °C in solutions of 0.5 M H_2SO_4 at various concentrations of benzoic acid; ---: 0 mM, ●: 2.5 mM, △: 7.5 mM, ○: 15 mM.

To obtain the values of the constants characterizing the adsorption of benzoic acid on mercury, the results were treated on the basis of the Frumkin-Damaskin adsorption isotherm at the potentials corresponding to the maximum adsorption and the maximum capacity.

$$Bc = \frac{\theta}{1-\theta}\exp(-2a\theta). \tag{1}$$

The dependence of a on E was first evaluated as follows. Since the coverage is given in the potential region of maximum adsorption by

$$\theta = \frac{C_0-C}{C_0-C'}, \tag{2}$$

the attraction constant a was determined from the reduced adsorption isotherm[1,2]

$$y = \frac{c}{c_{\theta=0.5}} = \frac{\theta}{1-\theta}\exp[a(1-2\theta)]. \tag{3}$$

The value of C' was determined by extrapolating the plot of $1/C^{\mathrm{min}}$ against $1/c$ to $1/c=0$.[19] The extrapolation was made by the least-squares method for the data obtained in benzoic acid solutions of more than 7.5 mM. The results are shown in Figs. 2 and 3.

The values of a at the peak potentials were calculated from ΔE using[1,2,19]

$$f(a) = \lg\frac{1-r}{1+r} - \frac{ar}{2.3} = \frac{\Delta E}{2}\left|\frac{\partial \lg c}{\partial E^{\mathrm{max}}}\right|, \tag{4}$$

where r is a function of a for a given fraction of the peak height, that is,

$$r_{1/2} = \sqrt{\frac{2-a}{4-a}} \text{ and } r_{3/4} = \sqrt{\frac{2-a}{8-a}}, \tag{5}$$

with the subscripts indicating the function of a which should be used for r in Eq. 4 when ΔE is used either at one half or at three-quarters of the peak height. The values of a at the peak potentials were also determined from the slope of the curve of lg c vs. E^{max} using

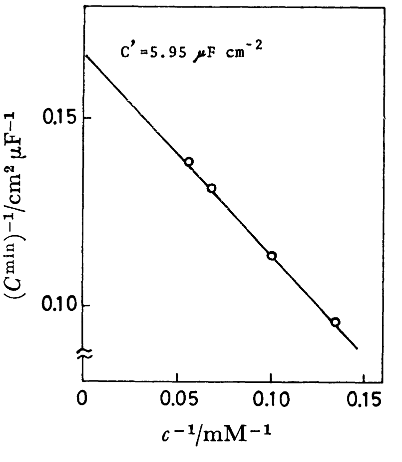


Fig. 2. The plot of the inverse of the minimum capacity against the inverse of the concentration of benzoic acid in 0.5 M H_2SO_4 solution.

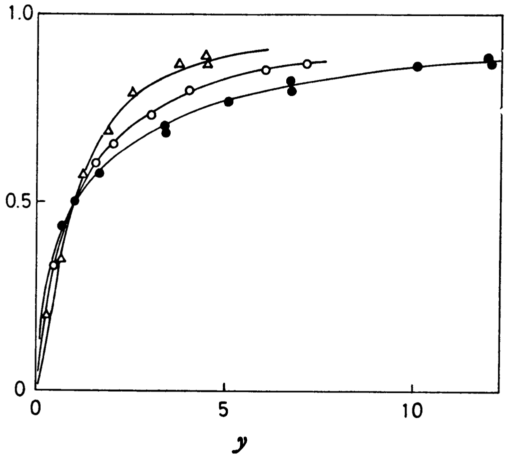


Fig. 3. Adsorption isotherm of benzoic acid in 0.5 M H_2SO_4 solution at −0.55 (●), −0.60 (○), and −0.66 (△) V *vs.* S. C. E. Solid lines are calculated from Eq. 3 with $a=-0.7$(at −0.55 V), −0.1(at −0.6 V), and 0.55(at −0.66 V).

$$\frac{\partial E^{\max}}{\partial \lg c} = \frac{2.3(C_0-C')}{2-a}. \tag{6}$$

Since this treatment is applicable only to equilibrium capacity-potential curves, the data obtained at 0.5 and 1 kHz in benzoic acid solutions of concentration greater than 10 mM and those obtained by extrapolation to $\nu=0$ were used for the above calculation.

The values of a thus found are plotted against the electrode potentials in Fig. 4. When the values of a were assumed to be a linear function of E,

$$a = a_0 + \beta E, \tag{7}$$

thus (although some deviation was observed) the values of a_0 and β are found to be −0.35 and −2.5 V^{-1}, respectively.

Other parameters, such as E_N, A, and B_0, were evaluated using the following treatment. The value of E_N was determined from the electrocapillary curves[2,19] to be −0.05 V. The value of A was calculated from the following relation:[2]

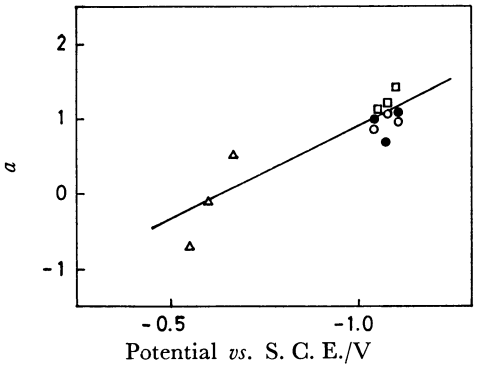


Fig. 4. Dependence of the attraction constant on potential in 0.5 M H_2SO_4 solution. The values of a were obtained from; △: the shape of the adsorption isotherm (Eq. 3), ○: the width of the capacitance peaks at half of their height (Eqs. 4 and 5), ●: the width of the capacitance peaks at three-quarters of their height (Eqs. 4 and 5), □: the slope of the curve of lg c *vs.* $E^{\max}$ (Eq. 6).

$$A = \frac{\gamma-\gamma_0}{\ln(1-\theta)+a\theta^2}. \tag{8}$$

The mean value of A was 1.60 μJ cm^{-2} in the 15 mM benzoic acid solution (Table 1). The value of B_0 was evaluated from[19]

$$\ln B_0 = -a_0 - \ln c + \frac{\int_0^{E^{\max}} q_0 \mathrm{d}E + C'E^{\max}(E_N - E^{\max}/2)}{A}. \tag{9}$$

The value of B_0 was also calculated by substituting the coverage θ and a into Eq. 1 for zero charge potential in the solution without benzoic acid (*i.e.*, −0.5 V *vs.* S.C.E.). The values of B_0 obtained by the different methods are in fairly good agreement with each other (Table 2).

Thus, the parameters were found to be $A=1.6$ μF cm^{-2}, $B_0=597$ l mol^{-1}, $C'=5.95$ μF cm^{-2}, $a_0=-0.35$, and $\beta=-2.5$ V^{-1}.

Table 1. Value of A calculated from Eq. 8 using the data for the 15 mM benzoic acid solution

E *vs.* SCE V	$\gamma-\gamma_0$ 10^{-5} N cm^{-1}	θ	a	A μJ cm^{-2}
−0.55	−34.0	0.865	−0.23	1.56
−0.60	−33.0	0.856	−0.10	1.64
−0.70	−30.0	0.861	0.15	1.61
			mean	1.60

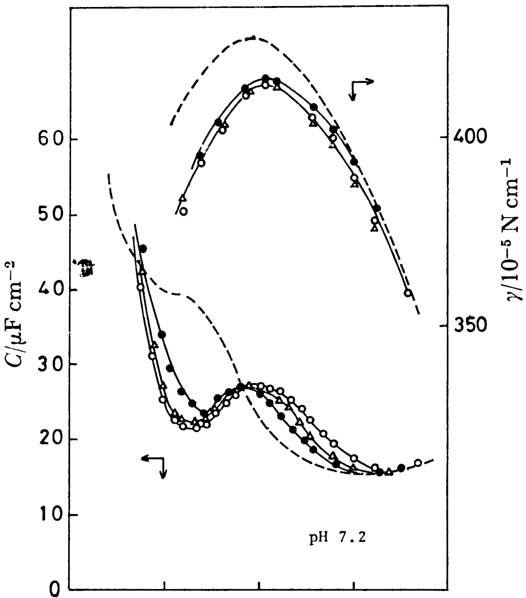
Table 2. Estimate of the B_0 value

Benzoic acid concentration	B_0 l mol^{-1}	
mM	From Eq. 9	From Eq. 1
15.0	596	598
17.8	578	617
	mean 597	

In Neutral Solution. The capacity-potential curves and electrocapillary curves in 0.5 M Na_2SO_4 solutions containing various amounts of benzoic acid are shown in Fig. 5 (The pH value of the solution was adjusted to 7.2 by adding an NaOH solution). Small peaks (or humps) were observed around −0.5 V (*vs.* S.C.E.) for the capacity-potential curves. A decrease in surface tension due to adsorption of benzoate anions was observed for a positively-charged surface, while for a negatively-charged surface the surface tension and the capacity approached the values obtained in a 0.5 M Na_2SO_4 solution without benzoic acid. Thus, the hump appearing in the capacity curve is regarded as the adsorption-desorption peak of the benzoate anion.

Discussion

The adsorption of benzoic acid in acid sulutions is now considered in detail. At negative potentials, an attractive force is observed between the adsorbed acid molecules. The attractive force changes to a repulsive force as the potential becomes positive (Fig. 4). A similar change in a with the potential has been



Potential *vs.* S. C. E./V

Fig. 5. Differential capacitance curves and electrocapillary curves at 1 kHz and 25 °C in solutions of 0.5 M Na_2SO_4 at various concentrations of benzoic acid; ---: 0 mM, ●: 5 mM, △: 15 mM, ○: 50 mM. The pH value of the solution was adjusted to 7.2 by adding an NaOH solution.

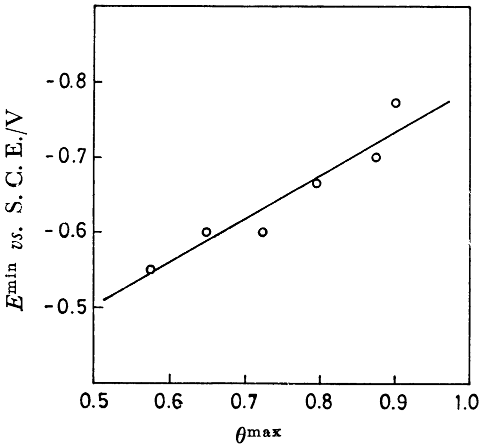


Fig. 6. Variation of the potential of minimum capacity with the coverage. Solid line indicates the theoretical dependence of $E^{\min}$ on $\theta^{\max}$ calculated from Eq. 10 by assuming the value of K_0 of 20 μF cm⁻².

observed for pyridine ($\beta=-2.8\,V^{-1}$)[1,20] and phenol ($\beta=-2.05\,V^{-1}$).[10] When the value of a is considerably negative, no peak is observed in the capacity-potential curves.[19,21] It is also considered that the strong repulsion between the adsorbates observed for positive potentials causes appreciable desorption of the adsorbed benzoic acid in spite of the increase in the π-electron interaction between the adsorbed molecules and the positively-charged surface. These considerations are consistent with the experimental results for a positively-charged surface: no anodic maxima in the capacity-potential curves were observed and the degree of decrease of the surface tension became smaller with increasing potential, as is shown in Fig. 1. The potential $E^{\min}$ shifted to more negative potentials with increasing benzoic acid concentration (Fig. 1). The degree of this shift was explained using the negative β value ($-2.5\,V^{-1}$) obtained in this study according to the following relation[19] (Fig. 6)

$$\frac{\partial E^{\min}}{\partial \theta^{\max}} = \frac{2A\beta}{K_0 - C'}. \tag{10}$$

The experimental results were compared with the calculated capacity-potential curve and electrocapillary curve in order to examine whether or not the adsorption of benzoic acid follows the F-D theory over the entire potential region. The curves relating the capacity and the surface tension to the potential were calculated using

$$C = C_0(1-\theta) + C'\theta + \frac{[q_0 + C'(E_N - E) + \beta A(1-2\theta)]^2 h}{A}, \tag{11}$$

where

$$h = \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}, \tag{12}$$

and

$$\gamma = \gamma_0 + A[\ln(1-\theta) + a\theta^2]. \tag{13}$$

The value of θ appearing in Eqs. 11 and 13 was evaluated as follows.[2,19] The value of B was first determined using

$$B = B_0 \exp\left[-\frac{\int_0^E q_0 \mathrm{d}E + C'E(E_N - E/2)}{A}\right]\exp(-\beta E), \tag{14}$$

for a given potential, and then θ was calculated from Eq. 1 for a given concentration of benzoic acid. As is shown in Fig. 7, good agreement is obtained between the calculated values and experimental results for the capacity and the surface tension over the potential region investigated. The discrepancy observed for positively-charged surfaces in the capacity-potential curves is probably due to the π-electron interaction. However the agreement between the experimental electrocapillary curve and the calculated curve shows that the interaction is probably rather small.

When benzoic acid molecules are adsorbed on the electrode in either the vertical or the flat orientations, the two-condensers-in-parallel model (F-D theory) may be applied. If benzoic acid molecules are adsorbed on the electrode for both orientations, the three-condensers-in-parallel model would be applicable.[2] Both the two- and three-condenser models were tested by plotting the shift of the zero charge potential, E_z, against the coverage. For the two-condenser model, E_z is a function of θ:[2]

$$E_z = \frac{E_N\theta}{(C_0/C')(1-\theta)+\theta}. \tag{15}$$

On the other hand, the relationship between E_z and θ derived for the three-condenser model is[2,22]

$$E_z = \frac{E_{N1}\theta[(E_{N2}/E_{N1})(1-\theta)+\theta]}{(C_0/C')(1-\theta)+\theta}, \tag{16}$$

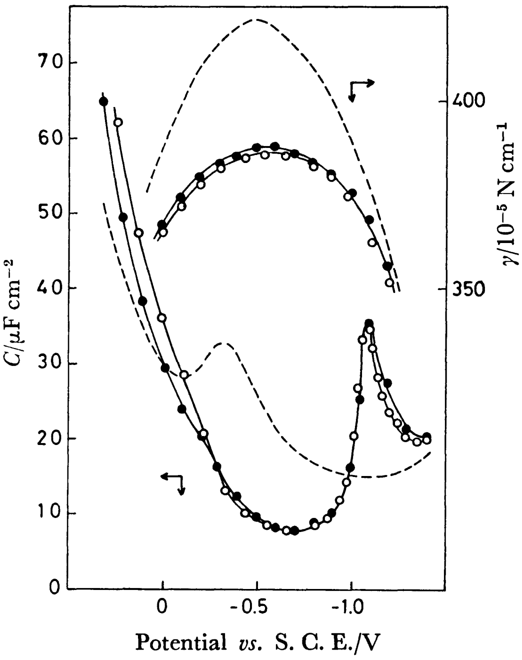


Fig. 7. Differential capacitance curves and electrocapillary curves in 0.5 M H_2SO_4 solution (broken line) containing 15 mM of benzoic acid. ○: experimental results at 1 kHz, ●: calculated from Eqs. 11 and 13.

where E_{N1} and E_{N2} are the shifts of the zero charge potential when the electrode is fully covered by adsorbed molecules in the vertical and flat orientations, respectively. E_{N2} was calculated to be -0.72 V from[2)]

$$\beta = \frac{-C'(E_{N1}-E_{N2})}{A}, \tag{17}$$

assuming $E_{N1}=E_N=-0.05$ V.

The experimental results for the relation between E_z and θ are shown in Fig. 8, together with the theoretical curves given by Eqs. 15 and 16. The two-condenser model is more successful in explaining the experimental results.

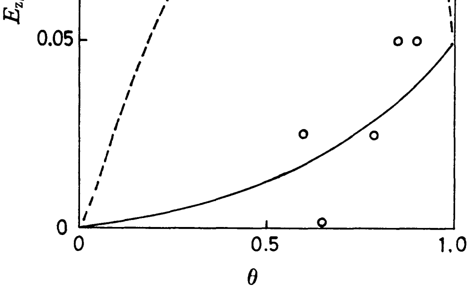


Fig. 8. Dependence of the point of zero charge on surface coverage with adsorbed benzoic acid in 0.5 M H_2SO_4 solution. Solid and broken lines are calculated from Eqs. 15 and 16.

From the above arguments, it is concluded that the adsorption of benzoic acid molecules follows the F-D theory of the two-condenser model and that the values of the parameters obtained are reasonable.

Orientation of Adsorbed Molecules. The orientation of the adsorbed benzoic acid molecules on the electrode surface can be discussed on the basis of the values of A, because A is related to the maximum surface excess. The experimental value of A corresponds to a maximum surface excess of 6.5×10^{-10} mol cm^{-2}. In the case of monolayer adsorption, the area occupied by one molecule of benzoic acid is calculated to be 26 Å^2 (1 Å=0.1 nm). According to the Fisher-Taylor-Hirschfelder model,[13)] one molecule of benzoic acid occupies 56 Å^2 for flat orientation and 20 Å^2 for vertical orientation. The area estimated from the A value indicates that for adsorption, benzoic acid has a vertical orientation.

The vertical orientation of the adsorbed benzoic acid molecules is also supported by the value of B_0 as follows. The value of B_0 is related to the standard free energy of adsorption, $-\Delta G_A^\circ$, by[2)]

$$-\Delta G_A^\circ = RT\ln(55.5\,B_0/1\ \mathrm{mol}^{-1}). \tag{18}$$

The calculated $-\Delta G_A^\circ$ value is 26 kJ mol^{-1} (6.2 kcal mol^{-1}). The value of B_0 (597 l mol^{-1}) obtained is less than that of phenol[10)] (1640 l mol^{-1}) for the flat orientation and is larger than that of aniline[9)] (191 l mol^{-1}) for the vertical orientation. The $-\Delta G_A^\circ$ and B_0 values decrease when the π-electron interaction between the adsorbate and the electrode decrease, and the specific interaction between functional groups and a mercury surface is considered to result in a change in orientation from flat to vertical. Taking into account the specific interaction of functional groups of aliphatic compounds with a mercury surface (the order of specific interaction has been reported to be -OH<-COOH<-NH$_2$),[7)] the decrease of B_0 values in the order, phenol>benzoic acid>aniline, is explained reasonably well in terms of the change in orientation from flat to vertical. Since some phenol molecules can undergo adsorption in the vertical orientation,[15,22)] benzoic acid is expected to be adsorbed in the vertical orientation. This is because benzoic acid has a greater possibility of existing in the vertical orientation than phenol, because of its smaller value of B_0 and the stronger interaction of a carboxyl group with a mercury surface than a hydroxyl group. This conclusion agrees with that derived from the evaluation of the maximum surface excess.

In the neutral solution (0.5 M Na_2SO_4, pH 7.2), the value $a<-4$ obtained from the shape of the hump indicates that there is a strong repulsive force between the adsorbates in the potential region of the hump. Since the pK_a of benzoic acid is 4.2,[23)] the adsorbed species at pH 7.2 should be the benzoate anion. The repulsive force may be caused by the Coulombic interaction between adsorbed benzoate anions, because no strong repulsive force was observed in the acid solution. The low and broad humps in the capacity-potential curves due to desorption extend to -0.25 V (*vs.* S.C.E.), and this fact indicates that desorption occurs even on a positively-charged surface because of the significantly large repulsive force between the adsorbed anions. The capacity-potential curves and electrocapillary curves are almost independent of the concentration of benzoate anion. These phenomena suggest that the adsorbed anions covered the electrode surface almost completely in the solution of a low concentration of benzoic acid.

References

1) A. N. Frumkin and B. B. Damaskin, "Modern Aspects of Electrochemistry," Vol. 3, ed by J. O'M. Bockris and B. E. Conway, Butterworths, London (1964), pp. 149—223.

2) B. B. Damaskin, O. A. Petrii, and V. V. Batrakov, "Adsorption of Organic Compounds on Electrodes," Plenum Press, New York (1971), Chaps. 2—4.

3) J. O'M. Bockris, M. A. V. Devanathan, and K. Müller, *Proc. R. Soc. London, Ser. A*, **274**, 55 (1963).

4) R. Lerkkh and B. B. Damaskin, *Russ. J. Phys. Chem.*, **38**, 631 (1964); *ibid.*, **39**, 112 (1965).

5) B. B. Damaskin, A. A. Survila, and L. E. Rybalka, *Elektrokhimiya*, **3**, 146, 927, 1138 (1967).

6) V. K. Venkatesyan, B. B. Damaskin, and N. V. Nikolaeva-Pedrovich, *Russ. J. Phys. Chem.*, **39**, 63 (1965).

7) B. B. Damaskin, A. N. Frumkin, and A. V. Cizov, *J. Electroanal. Chem.*, **28**, 93 (1970).

8) B. E. Conway and R. G. Barradas, *Electrochim. Acta*, **5**, 319, 349 (1961).

9) B. B. Damaskin, I. P. Mishutushkina, V. M. Gerovich, and R. I. Kaganovich, *Russ. J. Phys. Chem.*, **38**, 976 (1964).

10) B. B. Damaskin, V. M. Gerovich, I. P. Glakikh, and R. I. Kaganovich, *Russ. J. Phys. Chem.*, **38**, 1351 (1964).

11) O. Fischer, S. Standara, and J. Totusek, *Collect. Czech. Chem. Commun.*, **39**, 924 (1974).

12) O. Fischer and S. Standara, *Collect. Czech. Chem. Commun.*, **39**, 1965 (1974).

13) E. Blomgren, J. O'M. Bockris, and C. Jesch, *J. Phys. Chem.*, **65**, 2000 (1961).

14) I. Taniguchi, A. Yoshiyama, and T. Sekine, *Denki Kagaku*, in press.

15) R. S. Hansen, D. J. Kelsh, and D. H. Grantham, *J. Phys. Chem.*, **67**, 3216 (1963).

16) R. S. Perkins and T. N. Andersen, "Modern Aspects of Electrochemistry," Vol. 5, ed by J. O'M. Bockris and B. E. Conway, Plenum Press, New York (1969), p. 219.

17) L. I. Antropov and S. N. Banerjee, *J. Indian Chem. Soc.*, **35**, 531 (1958); *ibid.*, **36**, 451 (1959).

18) R. I. Kaganovich, V. M. Gerovich, and T. G. Osotova, *Dokl. Akad. Nauk SSSR*, **155**, 893 (1964).

19) B. B. Damaskin, *Russ. J. Phys. Chem.*, **37**, 1341 (1963).

20) L. D. Klyukina and B. B. Damaskin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **N6**, 1022 (1963); *Chem. Abstr.*, **59**, 7013h (1963).

21) B. B. Damaskin, *Dokl. Akad. Nauk SSSR*, **144**, 1073 (1962).

22) K. Niki, *Bull. Chem. Soc. Jpn.*, **48**, 997 (1975).

23) L. A. Flexser, L. P. Hammet, and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).