Adsorption of Neutral Organic Substances Evaluated from Electrocapillary Curves and Double Layer Capacities

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Adsorption of neutral organic substances on mercury electrode was evaluated from both electrocapillary curves and differential capacities of the double layer. The results were compared for the adsorption of *n*-aliphatic alcohols, phenol, and *o*-cresol in 0.5 M H_2SO_4. There was some evidence that the electrode potential was more favorable than the charge on the electrode as an electrical variable in the adsorption of the *n*-aliphatic alcohols. However, the values deduced from the Frumkin model were generally larger than the θ's obtained from the electrocapillary curves. This discrepancy is probably due to the deviation from the two-condensers-in-parallel model, because, the two condensers were not independent in an actual system. Neither the two-condensers-in-parallel model nor the three-condensers-in-parallel model were applicable to the adsorption of aromatic compounds.

It is well known that there are two methods to evaluate the adsorption of organic molecules on mercury electrodes. One is purely thermodynamic, while the other, proposed by Frumkin[1] in 1926, is non-thermodynamic.

The surface excess Γ can be determined thermodynamically from the electrocapillary cruves; that is;

$$\Gamma_A = -(\partial\gamma/\partial\mu_A)_E \quad (1)$$

where γ is the interfacial tension at the mercury electrode-solution interface and μ is the chemical potential of the surface active organic molecules in the solution. The activity coefficient of organic substances in the electrolyte solution is assumed to be unity.

Frumkin's model treated the electrical double layer as a two-plate-condensers-in-parallel, which is strictly equivalent to a potential congruency isotherm at a constant amount adsorbed (Frumkin isotherm);

$$C_\theta = C_0(1-\theta) + C'\theta \quad (2)$$

where C_0 and C' are the differential capacities of the uncovered and fully covered electrode, respectively. The differential capacity of the electrode, C_θ, varies linearly with the surface coverage, θ. A potential-congruent isotherm leads to the equation for the charge on the electrode as a sum of the charges on the covered and uncovered parts of the electrode

$$q_\theta = q_0(1-\theta) + q'\theta \quad (3)$$

where q_0 is the electrode charge when $\theta=0$ and q' is the charge at $\theta=1$. Differentiation of Eq. (3) gives:

$$C_\theta = C_0(1-\theta) + C'\theta\,(q'-q_0)\mathrm{d}\theta/\mathrm{d}E \quad (4)$$

The capacity at a constant amount adsorbed Eq. (4) gives Eq. (2).

Breiter and Delahay[2] compared values of θ calculated from Eq. (3) with the thermodynamic surface excess for the adsorption of *n*-amyl alcohol from 1 M $NaClO_4$+ 0.001 M $HClO_4$ and found that the two sets of θ's are comparable but the values deduced from Eq. (3) are generally larger than the θ's obtained from the surface excess. The two methods for the evaluation of θ from the charge computed by graphical integration of the differential capacity curves at zero frequency and differential capacities compliment each other; *i.e.*, the differential capacity method (Eq. (2)) can be applied in the region of the adsorption maximum, in which the charge method becomes very uncertain. Hansen and his co-workers[3] confirmed that the double layer capacitance was linear in Γ for all the Γ's near the electrocapillary maximum for both the *n*-amyl alcohol- and phenol-containing systems in 0.1 M $HClO_4$. When the electrode charge was chosen as an independent variable, as has been shown by Parsons,[4] a charge-congruent isotherm is analogous to Eq. (3);

$$E_\theta = E_0(1-\theta) + E'\theta \quad (5)$$

where E_0 and E' are the potentials corresponding to $\theta=0$ and $\theta=1$ respectively at a constant charge. On differentiation, the differential capacity at a constant amount adsorbed is given by:

$$1/C_\theta = (1-\theta)/C_0 + \theta/C' \quad (6)$$

The charge congruent model shows a linear dependence of E on θ, as is shown by Eq. (5). On the other hand, in the case of the potential congruent model, the dependence of E on θ is not linear. This is shown by rewriting Eq. (2) as Eq. (7).

$$E = (q+C'E_N\theta)/[C'\{C_0(1-\theta)/C'+\theta\}] \quad (7)$$

where the potential E is referred to the potential of zero charge for $\theta=0$ and E_N is the shift of the point of zero charge (p.z.c.) as θ changes from 0 to 1. Frumkin *et al.*[5] found that the experimental evidence of Eq. (7) holds at $q=0$ for the case of the adsorption of *n*-propanol and *n*-caproic acid on mercury, in which the θ's were evaluated by using both thermodynamic and differential capacitance methods. A direct comparison of Eqs. (3) and (5) was made by Dutkiewicz *et al.*[6] for simple aliphatic compounds with four carbon atoms. It was found that, for 1,4-butanediol and 2-butyne-1,4-diol, both equations, (3) and (5), fit equally well. On the other hand, neither equation can represent the data for *n*-butanol and diethyl ether. However, Frumkin *et al.*[5] showed that the isotherms obtained for *n*-butanol are congruent with respect to charge. The discrepancy between these results is probably due to the fact that Frumkin *et al.*[5] used Eqs. (3) and (5) for calculating the adsorption isotherm (or Eqs. (2) and (6) were used at the p.z.c.) in the θ *vs.* concentration of *n*-butanol plots both at E=const. and q=const. On the other hand, Dutkiewicz *et al.*[6] used the thermodynamical method to evaluate the surface excess. As has already been mentioned by Breiter and Delahay in their pioneer work[2] and in our previous work,[7] the surface coverages deduced from Eq. (3) are generally larger than the θ's obtained from Eq. (1) for *n*-amyl alcohol.

In the present work, (i) the reproducibility of the values is examined by comparing the results of previous works with those of the present work and (ii) the validity of Eq. (2) at a constant amount adsorbed is studied by a comparison of the values of θ directly obtained from Γ.

Experimental

The Lipmann electrometer used in the present experiment has been described previously.[8] The double layer capacitance was measured with a Yokogawa BV-Z-103-A universal bridge at 1000 Hz. The surface active organic substances were of an analytical reagent grade (Tokyo Kasei); no further purification was made. Solutions were made up of 0.5 M H_2SO_4 solution. The solutions were de-aerated with nitrogen purified by passing through a vanadous solution. The purified nitrogen was pre-saturated by passing it through a solution identical with that being studied and then to the cell. The radius of the capillary at the null point was determined by standardization against a solution of known surface tension.[9] All measurements were made at 25 ± 0.1 °C. The potentials were measured against a saturated calomel electrode.

Results and Discussion

n-*Amyl Alcohol.* Electrocapillary curves for the solutions of *n*-amyl alcohol and the interfacial tension *vs.* the logarithm of the concentration of *n*-amyl alcohol are shown in Figs. 1 and 2, respectively. Reproducibility of these electrocapillary curves was studied by comparing the results obtained independently by two persons with a different capillary. The difference between these results was, at most, 1.1 dyne/cm in the potential range between -0.4 and -0.8 V (*vs.* SCE). The surface excess of the alcohol was determined by graphical differentiation of the electrocapillary curves. The error in the surface excess was within 10%. The adsorption isotherm of *n*-amyl alcohol at the potential of electrocapillary maximum in 0.5 M H_2SO_4 is shown in Fig. 3; it is generally in accord with that obtained by Hansen *et al.*[3]

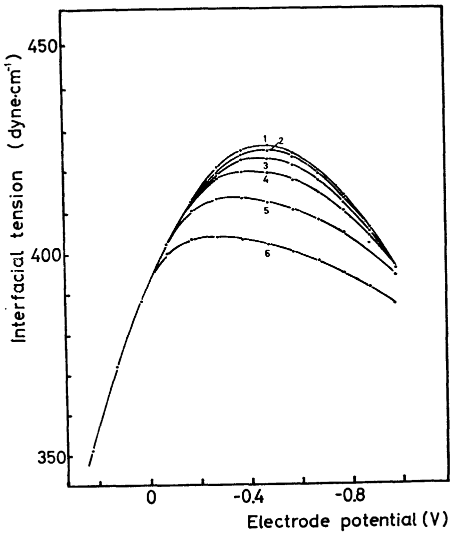

Fig. 1. Electrocapillary curves for *n*-amyl alcohol at various concentrations in 0.5 M H_2SO_4. (1) base solution; (2) 2.0 mM; (3) 5.0 mM; (4) 10 mM; (5) 20 mM; (6) 50 mM.

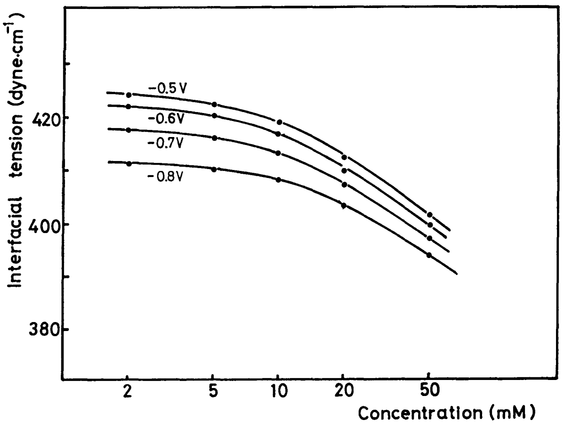

Fig. 2. Variation of interfacial tension with the logarithm of concentration of *n*-amyl alcohol at various electrode potentials in 0.5 M H_2SO_4.

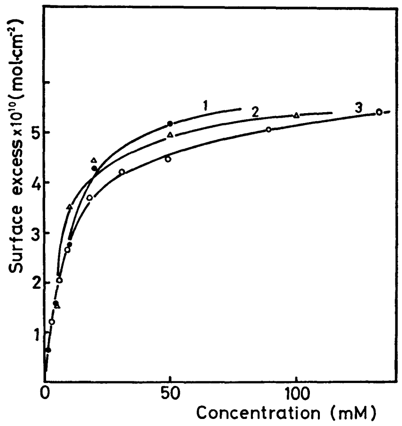

Fig. 3. Adsorption isotherms of *n*-amyl alcohol on mercury electrode calculated from the electrocapillary measurement at p.z.c. in the base solution. (1) present work I; (2) present work II; (3) Hansen *et al.*[3]

The adsorption isotherms determined by both electrocapillary and differential capacitance measurements at the potential of electrocapillary maximum for the base solutions are shown in Fig. 4. We should notice that the agreement between the isotherms evaluated by the same method is very good regardless of the type of supporting electrolyte in the solution. This is probably because neither sulfate ions nor perchlorate ions were adsorbed specifically on mercury electrode near the p.z.c. On the other hand, the isotherms obtained by the electrocapillary measurement agreed poorly with those determined by the differential capacitance method, as is shown in Fig. 4.

Equation (6) was tested by plotting the shift of the electrocapillary maximum against Γ (Fig. 5). In this

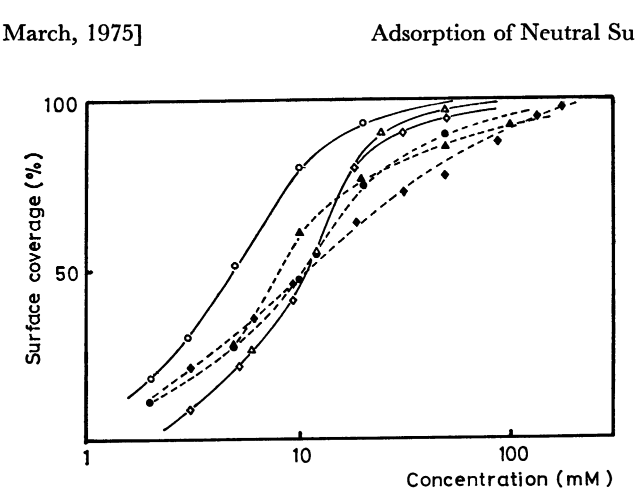

Fig. 4. Adsorption isotherms of *n*-amyl alcohol on mercury electrode. Dotted lines are calculated from the electrocapillary measurement and solid lines are from the differential capacity measurement at p.z.c. in the base solution. —●— present work I; —▲— present work II; —◆— Hansen *et al.*[3]; —◇— Hansen *et al.*[10]; —△— Breiter and Delahay[2]; —○— present work III.

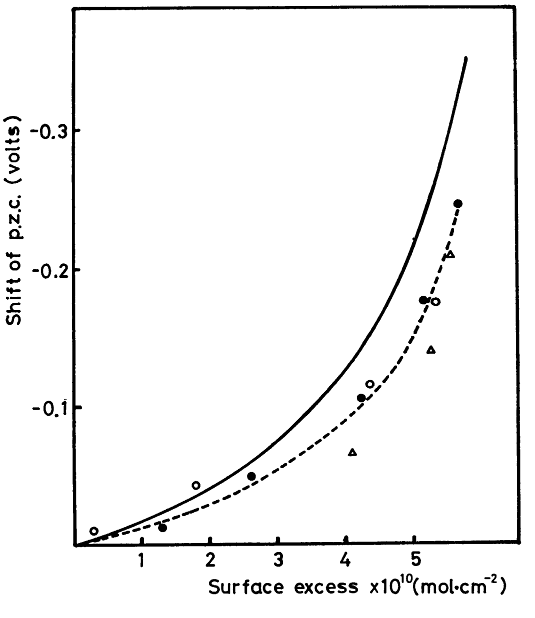

Fig. 5. Dependence of p.z.c. on amount of adsorbed *n*-amyl alcohol. Solid line is calculated from the data taken from ref. (2) and dotted line is calculated from the present work. (△) Breiter and Delahay[2] (differential capacity measurement); (●) present work (electrocapillary curve); (○) present work (differential capacity measurement).

case, the surface excess was evaluated by using the Gibbs equation (Eq. (1)) for the electrocapillary measurements and by using Eq. (2) for the differential capacitance measurements. The experimental values of the electrocapillary measurements agreed well with the calculated values using Eq. (7), where the parameters were $C/C'=4.03$ and $E_N=0.245$ V. The values obtained by the differential capacitance measurement, however, showed a systematical deviation from the calculated curve (*i.e.*, from the values determined by the electrocapillary measurement). That is, at lower concentrations of *n*-amyl alcohol the coverage evaluated by the differential capacitance measurement showed a smaller value than that evaluated by the electrocapillary measurement. On the other hand, at higher concentrations of the alcohol it showed a larger value; agreed with the statement of Breiter and Delahay.[2] This result also agreed with the observation by Frumkin *et al.* for *n*-butyl alcohol.[5]

The systematic deviation of the measured values, as determined by means of the differential capacitance measurement, from those of the calculated values by using Eq. (7) can be explained as follows. When the surface excess of the adsorbed species is small, the adsorbed molecules can move rather freely and they are not necessarily oriented perpendicularly to the electrode. Some of them may be flat, some in a vertical position, and some in intermediate position. The center of the dipole of these adsorbed molecules (the -OH group) is, as the average, closer to the electrode surface than that of the perpendicularly oriented molecules. The contribution to the displacement of the p.z.c. by these molecules becomes larger than that by the perpendicularly oriented molecules. That is, the capacitance of the condenser filled with randomly oriented molecules, C_l', must be greater than that filled with molecules with a fixed orientation (perpendicularly oriented to the electrode), C'. Accordingly, C_0/C_l' with the configuration of the low coverage type becomes smaller than C/C' for the saturated adsorption. This leads to a negative deviation of the measured values from the calculated values according to Eq. (7).

At higher coverages, on the other hand, the positive deviation of the measured values suggests a larger value for C_{0h}/C' than for C_0/C', where C_{0h} is the double layer capacitance of the uncovered part of the electrode at a higher coverage. The capacitance of the condenser filled with water molecules in the presence of a large amount of the adsorbed *n*-amyl alcohol, C_{0h}, is con-

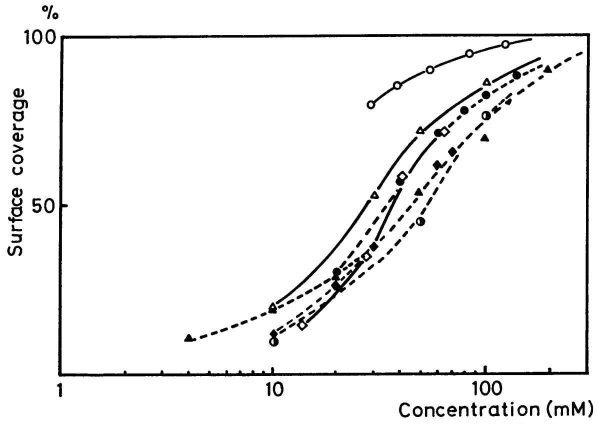

Fig. 6. Adsorption isotherms of *n*-butyl alcohol on mercury electrode at p.z.c. in the base solution. Dotted lines are for the electrocapillary measurement and solid lines for the differential capacity measurement. —▲— present work I; —◆— present work II; —●— Frumkin *et al.*[5]; —◑— Blomgren *et al.*[12]; —△— present work III; —◇— Biegler and Laitinen[13]; —○— Sathyanarayana.[14]

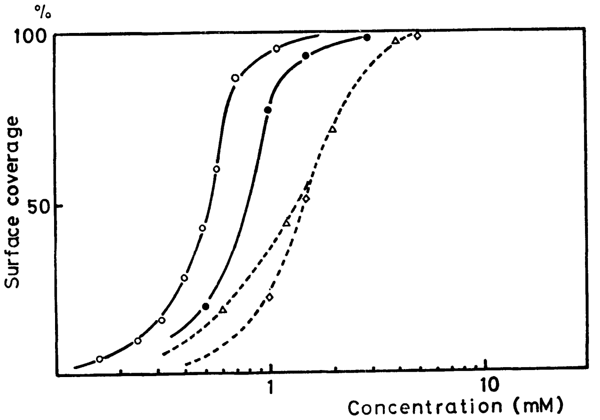

Fig. 7. Adsorption isotherms of *n*-hexyl alcohol on mercury electrode at p.z.c. in the base solution. Dotted lines are for the electrocapillary measurement and solid lines for the differential capacity measurement. —△— present work I; —◇— present work II; —●— present work III; —○— Ohsumi.[15]

sidered to be larger than that at the electrode without an adsorbed species on the electrode. At the electrode with higher coverages by *n*-amyl alcohol, the hydrocarbon end is in contact with the electrode surface and the molecule is normal to the surface. The inductive effect by the oriented alcohol molecules may influence the orientation of water molecules at the electrode surface. As in the case of the repulsive interaction between the dipoles at the electrode surface,[11] this effect causes an increase in the capacitance of the condenser filled with water molecules from C_0 to C_{0h}.

The adsorption isotherms for *n*-butyl alcohol and *n*-hexyl alcohol are shown in Figs. 6 and 7. These isotherms also showed the same tendency as in the case of *n*-amyl alcohol. The negative deviation from Eq. (7) at lower coverages decreased with an increase in the chain length of the alcohol molecule, and the positive deviation increased with the chain length. This behavior can easily be explained by the arguments used in the case of *n*-amyl alcohol. The plot of the shift of the p.z.c. against the surface excess of the alcohol showed an excellent agreement with Eq. (7) for both *n*-butyl and *n*-hexyl alcohols when the surface excess was determined thermodynamically.

Phenol. The adsorption isotherms of phenol from 0.5 M H_2SO_4 solution at the potential of electrocapillary maximum of the base solution are shown in Fig. 8, together with the adsorption isotherms obtained by Hansen *et al.*[3] and by Blomgren *et al.*[12] All of these isotherms were determined from the electrocapillary measurements, and they showed a good agreement between them. The adsorption isotherms for phenol

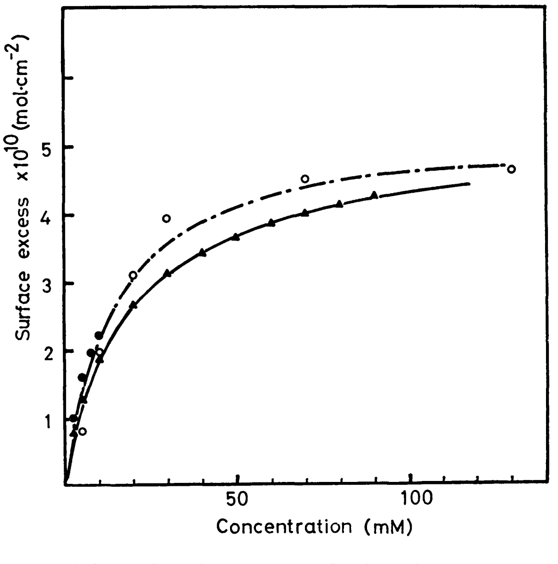

Fig. 8. Adsorption isotherms of phenol on mercury electrode at p.z.c. in the base solution calculated from electrocapillary curves. —○— present work; —▲— Hansen *et al.*[3]; —●— Blomgren *et al.*[12]

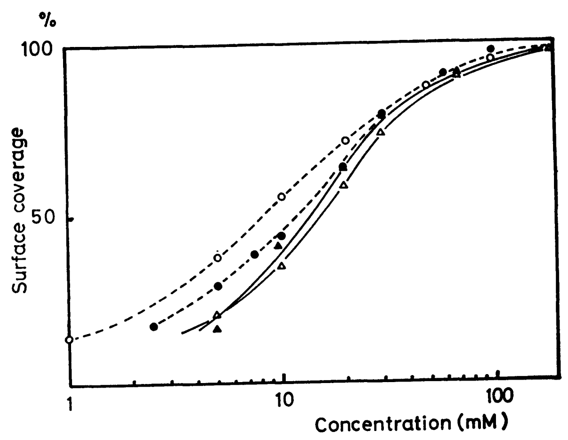

Fig. 9. Adsorption isotherms of phenol on mercury electrode at p.z.c. in the base solution. Dotted lines are for the electrocapillary measurement and solid lines for the differential capacity measurement. —▲— present work I; —●— Hansen *et al.*[3]; —△— present work II; —○— Hansen *et al.*[3]

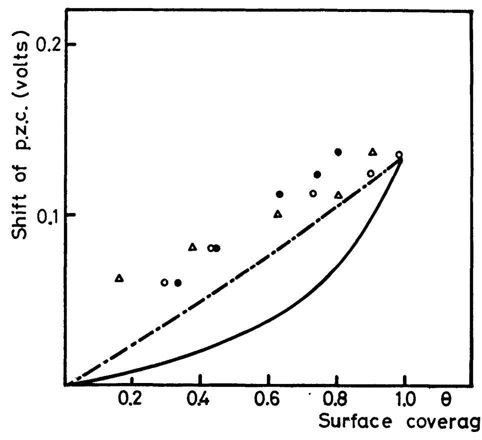

Fig. 10. Dependence of p.z.c. on amount of adsorbed phenol. The solid line is calculated from the present work and the dotted line corresponds to the three condenser model (*cf.* text). (△) present work and (○) Hansen *et al.*[3] for the electrocapacillary measurement; (●) Hansen *et al.*[3] for the differential capacity measurement.

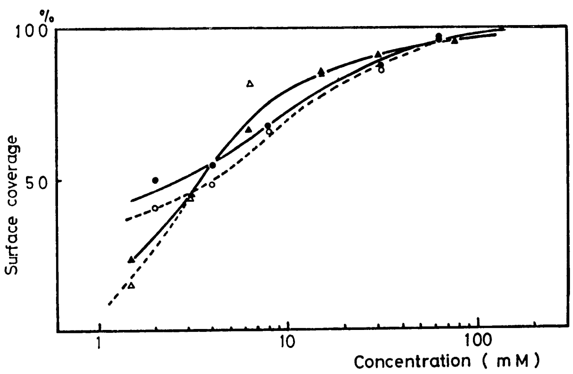

Fig. 11. Adsorption isotherms of *o*-cresol on mercury electrode at p.z.c. in the base solution. Dotted lines are for the electrocapillary measurement and solid lines for the differential capacity measurement. —○— present work I; —△— Manohar and Sathyanarayana[19]; —●— present work II; —▲— Manohar and Sathyanarayana.[19]

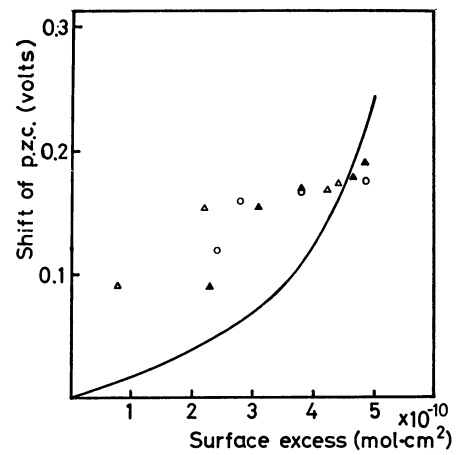

Fig. 12. Dependence of p.z.c. on amount of adsorbed *o*-cresol. (○) present work I; (△) Manohar and Sathyanarayana[19] (electrocapillary measurement); (▲) Manohar and Sathyanarayana[19] (differential capacity measurement).

calculated by using Eq. (2) at the p.z.c. for the base solution are shown in Fig. 9. The surface coverages determined by the electrocapillary measurement coincided with those determined by the differential capacitance measurement. This agreement has also been reported by Elliott.[17]

The two-condensers-in-parallel model was tested by plotting the shift of the potential of zero charge against Γ, as is shown in Fig. 10. The plots were far from this model. The shift of the electrocapillary maximum was nearly linear with respect to the surface excess of phenol. Similar behavior was also observed in the case of *o*-cresol in 0.5 M H_2SO_4, as is shown in Figs. 11 and 12. The surface excess evaluated from Eq. (2) coincided with the values evaluated thermodynamically. The two-condensers-in-parallel model was also inapplicable to this model, as is shown in Fig. 12.

The displacement of the potential of zero charge with respect to the surface excess was analyzed by using a three-condensers-in-parallel model[17] (the orientation of the adsorbed aromatic molecule changes from flat to vertical upon an increase in the concentration of the adsorbed species). The shift of the potential of zero charge is given by:

$$E = \theta E_{N1}\frac{(E_{N2}/E_{N1})(1-\theta)+\theta}{(C_0/C')(1-\theta)+\theta} \tag{8}$$

where E_{N1} and E_{N2} are, respectively, the shift of the potential of zero charge upon transition from the base solution to $\theta_1=1$ (when the electrode is fully covered by the vertically oriented molecules) and to $\theta_2=1$ (when the electrode is fully covered with the molecules of a flat orientation). E_{N2} was calculated by using this equation[17]

$$\beta = -\frac{C_1(E_{N1}-E_{N2})}{A} \tag{9}$$

where C_1 is the differential capacitance when $\theta_1=1$. The parameters used for the calculation were $\beta = -2.05\ \mathrm{V}^{-1}$,[18] $A=1.22\ \mu\mathrm{J/cm}^2$ ($A=RT\Gamma_{\mathrm{max}}$, $\Gamma_{\mathrm{max}}=4.93\times10^{-10}\ \mathrm{mol/cm}^2$), $C_1=7.00\ \mu\mathrm{F/cm}^2$, and $E_{N1}=-0.140$ V. The calculated $E_{N2}=-0.498$ V. The plot of the three-condensers-in-parallel model is shown in Fig. 10. The plot showed a linear dependence of the displacement of the potential of zero charge on Γ. The three-condensers-in-parallel model does not explain the large displacement of the p.z.c. at lower coverages of the electrode with phenol. As has been stated by Damaskin,[17] the shape of the E *vs.* θ curve varies with the values of (E_{N2}/E_{N1}) and (C_0/C_1); that is, its convex or concave side is turned toward abscissa axis. Equation (8), however, does not explain the large shift of the p.z.c. at low θ values regardless of the values of (E_{N2}/E_{N1}) and (C_0/C_1). This has also been reported by Damaskin on the basis of their data.[18] *o*-Cresol behaved much like to phenol.

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