ADSORPTION OF ORTHO AND PARA METHOXY BENZOIC ACIDS AT THE MERCURY/SOLUTION INTERFACE

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Adsorption of ortho and para methoxy benzoic acids at the mercury/0.1N Na₂SO₄ solution interface has been studied using capillary electrometer. Electrocapillary curves have been obtained for various concentrations of these acids added to the base electrolyte (0.1N Na₂SO₄ solution). Various thermodynamic parameters, like charge on the metal surface (q^M) in the presence and absence of adsorbates, surface excess of organic molecules adsorbed (Γ org) and coverage (θ) have been evaluated. The adsorption data obtained for both the compounds have been tested both graphically and using a computer programme. It is found that both the compounds obey Temkin's adsorption isotherm. From isotherm intercepts, free energies of adsorptions have been evaluated at different values of q^M. The variation of free energy with electrode charge is due to the interaction of adsorbed dipole with the metal surface.

Key words: Adsorption, electrical double layer, o and p methoxy benzoic acids, electrocapillary curves

INTRODUCTION

Adsorption of organic molecules at the metal/solution interface is one of the important factors determining the kinetics and mechanism of electrode processes and offers a scope for further development of the theory of the electrical double layer. Adsorption is the competition for the sites on the metal surface between organic molecules and solvent molecules. The introduction of an electrical field arising from the charge imparted to the metal surface is solely responsible for the preferential adsorption of organic molecules towards the metal surface. With aqueous solutions at high field strength, water molecules are attracted more at the interface owing to their higher polarisability, thus displacing almost completely adsorbed organic molecules. It is also found that the substituent group present in the organic molecule influences the extent of adsorption of the organic molecule. In the present study, the adsorption of two different isomers of methoxy benzoic acid (ortho and para) have been examined with an idea of ascertaining whether the position of the substituent group (-OCH₃) in the isomers influences the extent of adsorption and the type of adsorption isotherm. The adsorption of o-, m- and p-isomers of toluidine on mercury from potassium iodide solutions has been studied [1] but no attempts have been made to compare the extent of adsorption of these isomers. The adsorption of o- and p- toluidine using Na₂SO₄ as the base electrolyte has also been studied [2], though not thoroughly. Literature survey reveals that adsorption of isomers of methoxy benzoic acid has not been investigated so far and hence the present study has been taken up.

EXPERIMENTAL

The design of the capillary electrometer is the same as that used earlier [3-5]. The design of the cell used for measurements is the same as used earlier [4, 6]. It consists of a main compartment, through which capillary electrometer can be inserted and two side connections, one leading to the reference electrode compartment through the water seal stop joint and the other to the hydrogen inlet. Purified hydrogen was used for deaeration. Mercury used was of analytical grade, further purified electrolytically and distilled in an all glass set up under reduced pressure. All solutions were prepared using conductivity water.

All the measurements were carried out in an air thermostat controlled at a temperature of 298 ± 0.2K. The mercury in the capillary electrometer was polarised at various values of potential applied to the mercury-mercurous sulphate electrode by means of a precision potentiometer in combination with a 6 volt lead acid battery.

RESULTS

Electrocapillary curves

Electrocapillary curves for 0.1M Na₂SO₄ in the presence of six different concentrations of ortho and para methoxy benzoic acids ranging from 2×10^{-3}M to 3×10^{-2}M for ortho isomer and 2×10^{-4}M to 3×10^{-3}M for para isomer are shown in Fig. 1(a & b). It is seen that ortho isomer is more adsorbing than its para isomer. All the runs are duplicated and the results are reproducible to ± 0.2 dynes at the e.c.m. and ± 0.8 dynes at the extremes of curves.

Charge on the metal surface (q^M)

Charge q^M on the metal surface was evaluated by the graphical differentiation of the electrocapillary curve at 50 mV intervals. The error limits for charge density are 0.15 $\mu C.cm^{-2}$ around e.c.m. to 0.5 $\mu C.cm^{-2}$ at extremes of the curves. Values of q^M obtained in such a way for different concentrations of ortho and para methoxy benzoic acids are plotted as a function of E and shown in Fig. 2 (a & b).

Surface excess of isomers adopted (Γ org)

The surface excess of the neutral organic molecules adsorbed is a function of the rate of change of interfacial tension with concentration of the organic compound at constant E and is calculated using the equation:

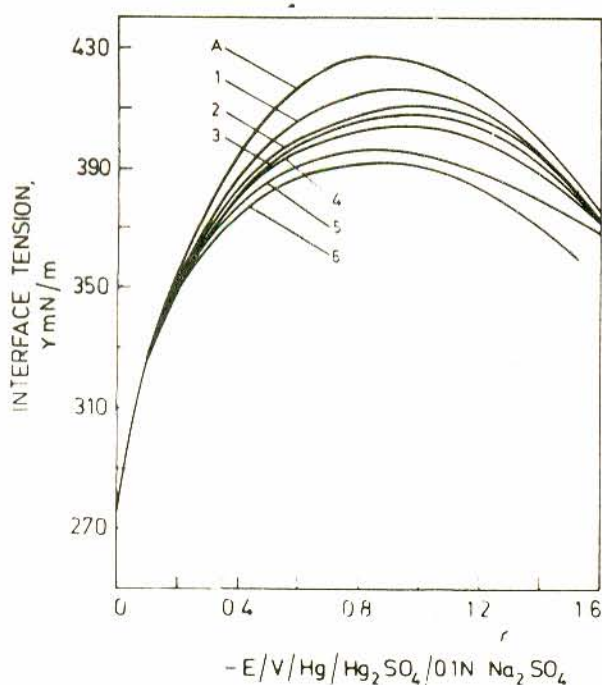$$\frac{d\gamma}{d\mu \, org} = \Gamma \, org \qquad \ldots (1)$$

Fig. 1(a): Electrocapillary curves for ortho methoxy benzoic acid
(A) 0.1N Na$_2$SO$_4$ (1) 2× 10^{-3}M (2) 5× 10^{-3}M (3) 8× 10^{-3}M (4) 1×
10^{-2}M (5) 2× 10^{-2}M (6) 3× 10^{-2}M
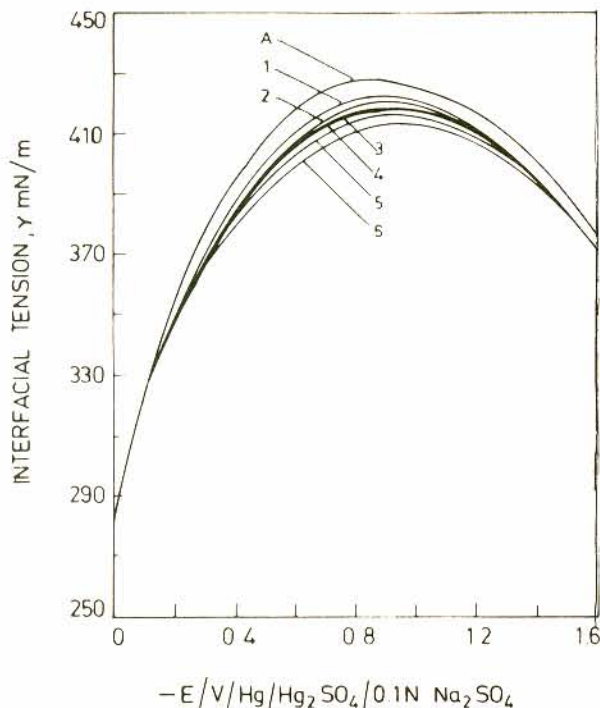
Fig. 1(b): Electrocapillary curves for para methoxy benzoic acid
(A) 0.1N Na$_2$SO$_4$ (1) 2× 10^{-4}M (2) 5× 10^{-4}M (3) 8× 10^{-4}M (4) 1×
10^{-3}M (5) 2× 10^{-3}M (6) 3× 10^{-3}M

So values of surface excess were evaluated by graphical differentiation of the interfacial tension vs concentration curve at constant potential. Values of Γorg obtained for various concentrations of isomers as a function of q^M are shown in Figs. 3 (a & b).
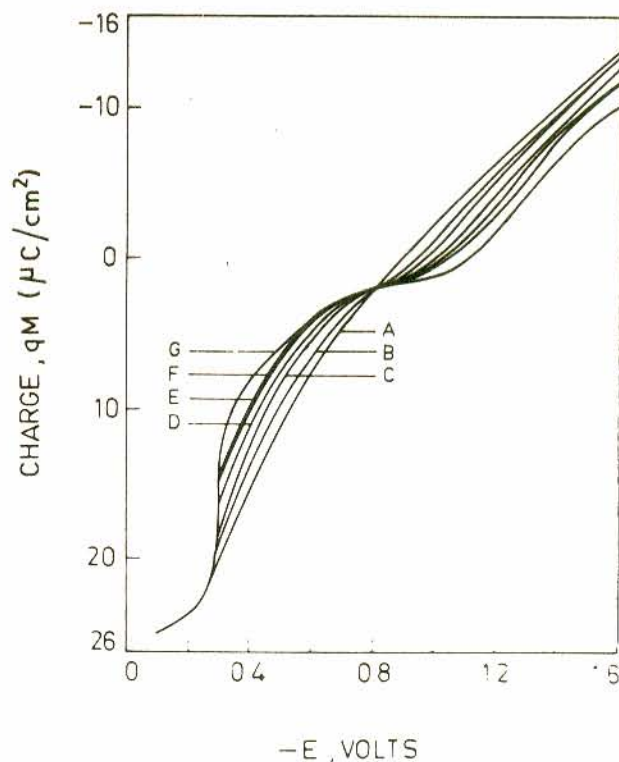

Fig. 2(a): Variation of q^M (μC.cm^{-2}) with E(volts) for ortho methoxy benzoic acid
(A to G Same as given in Fig. 1(a))
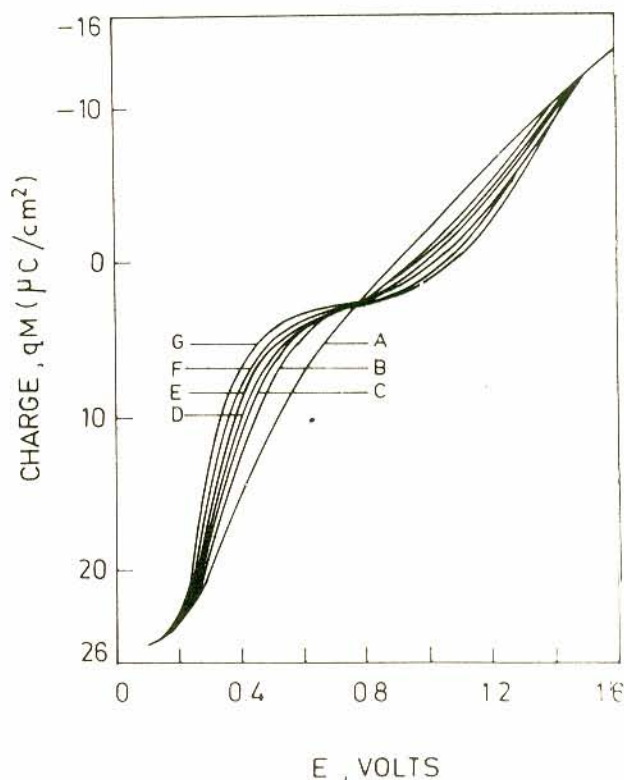

Fig. 2(b): Variation of q^M (μC.cm^{-2}) with E (volts) for para methoxy benzoic acid
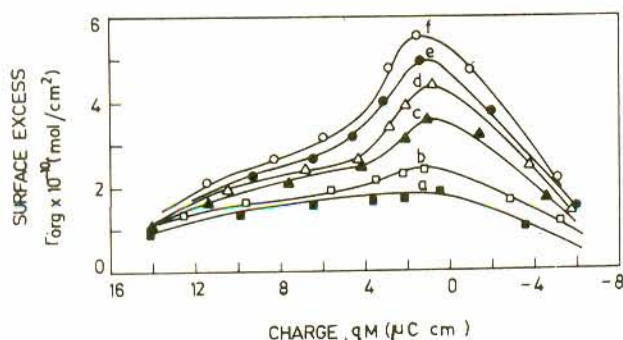(A to G Same as given in Fig. 1(b))

Fig. 3(a): Variation of Γorg with q^M for the adsorption of ortho methoxy benzoic acid
(a to f) same as (1) to (6) given in Fig. 1(b)

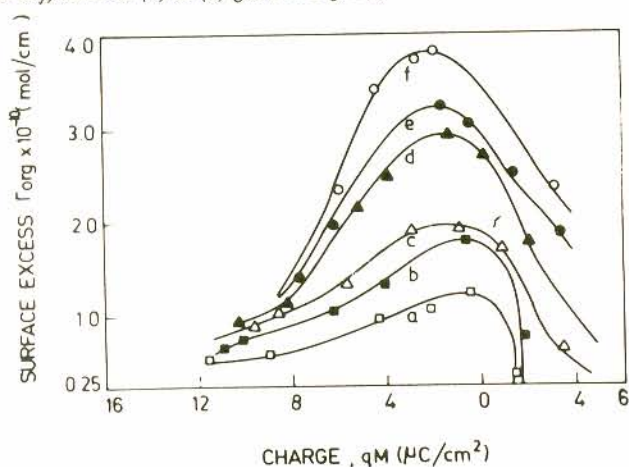*Fig. 3(b): Variation of Γorg with q^M for the adsorption of para methoxy benzoic acid*
(a to f) same as (1) to (6) given in Fig. 1(b)

DISCUSSION

Electrocapillary curves

Figures 1 (a & b) show that there is adsorption both on the positive and negative sides of the electrocapillary curve. In the case of positive side, there is adsorption of organic molecules at the extreme positive charge. It is possible that at high field strengths, water molecules are more polarisable than organic molecules and they can easily replace organic molecules from the metal surface [7]. Adsorption is found to be more near electrocapillary maximum, because at this point water molecules are loosely held to the metal surface because, $q^M = 0$. So organic molecules can easily replace water molecules near around e.c.m. and adsorption is found to be more in this region. It is also found that both the isomers adsorb to a lesser extent on the negative side of the electrocapillary curve, than on the positive side. This adsorption may be due to the fact that the -COOH group may get adsorbed on the negatively charged surface [8]. The adsorption on the positive side of electrocapillary curve may be due to the interaction of the delocalised π-electrons of the benzene ring with the positively charged metal surface [9-11].

Charge (q^M) vs (-E) curves

It is seen from Figs. 2 (a & b) that q^M-E curves for various concentrations of both the isomers intersect one another at a potential of 750 - 800 mV which corresponds to a charge of +2 to +3 $\mu C.cm^{-2}$. Similar behaviour has been observed for all aromatic organic molecules.

Surface excess (Γorg) vs q^M curves

Figures 3 (a & b) show that both the isomers get adsorbed on both the sides of electrocapillary curve. Surface excess is found to be considerably less on the extremes of both the sides of the curve, where they are found to desorb. Maximum values of surface excess is found near q^M of range +3 to +4 $\mu C.cm^{-2}$. This is in agreement with fact that q^M-E curves curves for different concentrations of both the isomers intersect one another at a charge of +2 to +3 $\mu C.cm^{-2}$. So for aromatic organic molecules, maximum adsorption occurs at a charge of +2 to +3 $\mu C.cm^{-2}$. It is also found that adsorption of ortho isomer is found to be more than the para isomer. The stronger adsorption of the ortho isomer may be due to the absence of intramolecular hydrogen bonding i.e. the methyl group of the methoxyl group cannot form a hydrogen bond with the adjacent COOH group [12]. The lesser electron releasing power of -OCH₃ group in the para position may be responsible for the lesser adsorption of this compound at the mercury surface. The difference in adsorbability can also be attributed to the difference in the dipole moments.

Coverage vs q^M curve

Values of coverage (θ) for the isomers adsorbed have been evaluated using the relation Γ/Γmax = θ where Γm is the maximum value of surface excess. The value of Γm is evaluated by plotting C/Γ vs C for $q^M = 0$ and measuring the initial slope of the straight line obtained. It is also evaluated using the area obtained from molecular models and the value has been found out to be 7.4×10^{-10} moles.cm^{-2} for ortho and 5.23×10^{-10} moles.cm^{-2} for the para isomer. Values of coverage have been evaluated for the adsorption of both the isomers using the above values of Γm.

Assignment of isotherms

Isotherms have been assigned to both the systems by (i) using a recently developed computer programme [13] and (ii) using the graphical method. In the computer programme, input parameters are coverage (θ) and concentration (C) at different values of q^M and output parameters are (i) slope which gives the interaction parameter (ii) correlation coefficient which gives the best fit of all isotherms under study and (iii) intercept which gives the free energy of adsorption. It is seen from this study that Langmuirs'isotherms which give a maximum value of correlation coefficient of 96% will be the best fit for the adsorption of both the compounds. But slope values obtained for different charges are far different from unity and therefore Langmuirs' isotherm cannot be applied in both the cases. Then, the next choice is Temkin's isotherm [14] which gives the correlation coefficient of 92%. Other isotherms give considerably lower values of correlation coefficients and they cannot be used to characterise the adsorption of these isomers. So the best choice for adsorption of isomers is Temkin's isotherm. This fact is again proved when the isotherm is tested graphically. When coverage (θ) is plotted against log C for different values of q^M, a set of straight lines have been obtained (Figs. 4(a & b) and 5 (a & b)) both at positive and negative values of charges (q^M) for the isomers. This clearly shows that the adsorption of both the adsorbates obey Temkin's isotherm. From these plots, values of gradients and intercepts are noted for each value of q^M. Intercepts are related to the free energy of adsorption, thereby proving clearly that the adsorption of both the isomers obeys Temkin's isotherms.

Free energy of adsorption as a function of q^M

The free energy adsorption of ortho and para isomers of methoxy benzoic acid is evaluated from isotherm intercepts at all values of q^M using the Temkin's equation [14]

$$\theta = \frac{RT}{a_\pm} \ln(\beta a_\pm) \qquad \ldots (2)$$
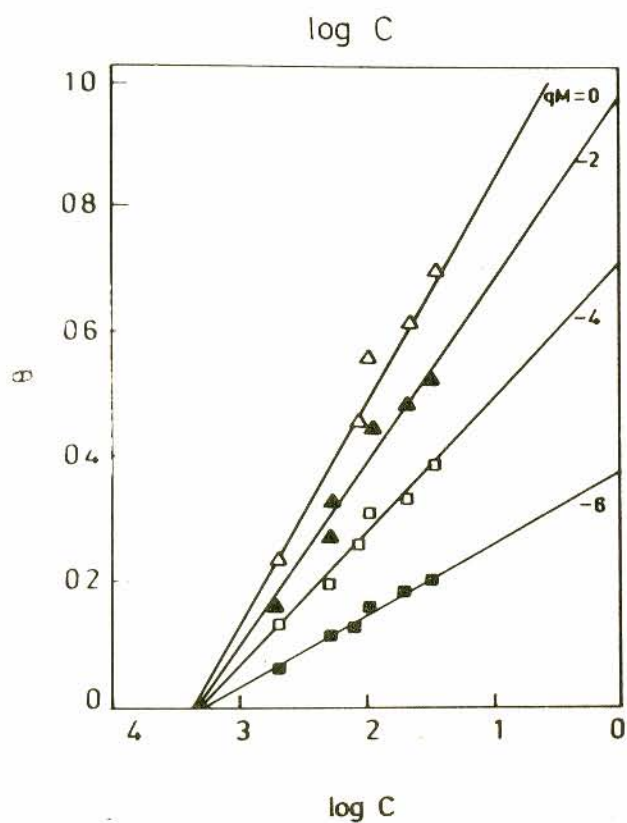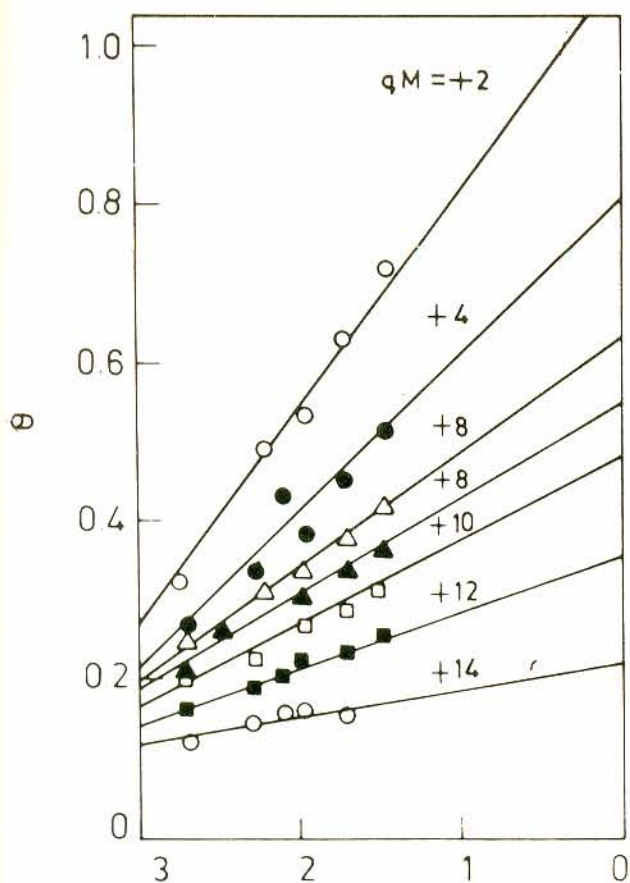
where

$$\beta = \frac{\text{delta}}{1000\,\text{max}}e^{-}\Delta G^{\circ}a \pm /RT \qquad \ldots(3)$$
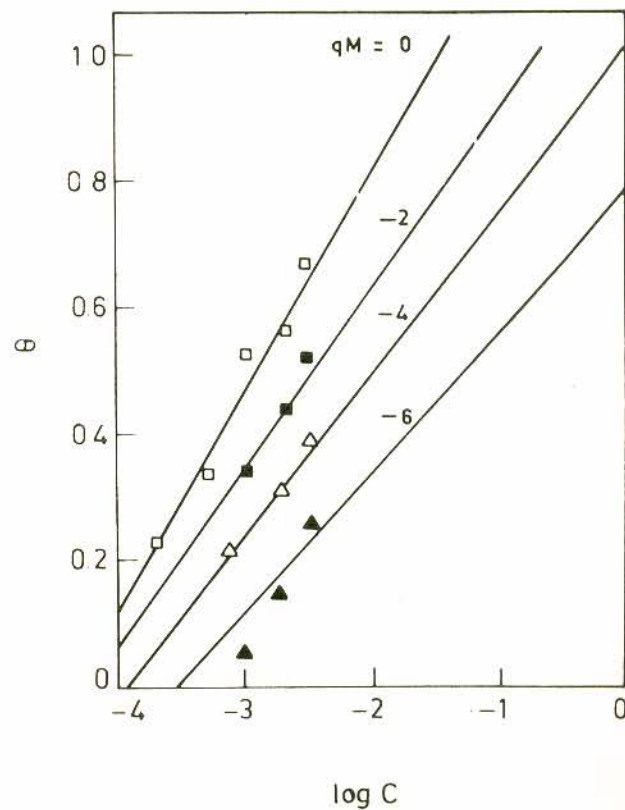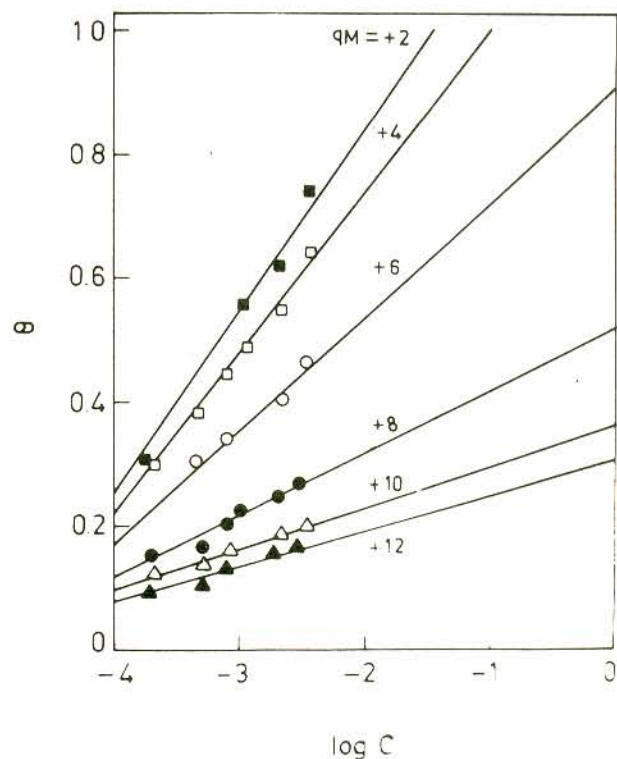

Fig. 4: Plot of θ against log C at (a) some positive values of the charge and (b) for the adsorption of ortho methoxy benzoic acid

Fig. 5: Plot of θ against log C at (a) some positive values of the charge and (b) some negative values of charge for the adsorption of para methoxy benzoic acid

Hence δ is the thickness of the mono molecular layer of adsorbate obtained in cms from the molecular model. $RT/a\pm$ and $\ln \beta$ are the slope and the intercept obtained from the graphical plots of θ vs log C.

Values of $-\Delta G$ were plotted against q^M for both the systems (Figs. 6 a & b.) Free energies of adsorption of both the isomers on the mercury surface was evaluated from the values of intercepts obtained from the plots of Temkin's isotherms for different values of positive and negative charges. Variation of free energies of adsorption with charge q^M for both the isomers can be explained in the following way.

Adsorption is found to be considerably less at extremes of both charges. At extreme field strength water molecules are more polarisable than organic molecules and they will replace organic molecules from the metal surface. Adsorption is found to decrease with decrease in positive charge on the metal surface. Adsorption is found to be maximum for both the compounds at a charge of $+2$ and $+3 \mu C.cm^{-2}$. Free energy is found to decrease with increase of negative charge and at extremes of negative charges both the adsorbates are completely desorbing as in the case of extreme positive charges.

CONCLUSIONS

The study of adsorption of isotherms of methoxy benzoic acid at the mercury/solution interface leads to the following conclusions: The adsorption is found to be more for the ortho isomer. The adsorption for both the isomers can be well described by Temkin's isotherm, irrespective of the position of $-OCH_3$ group in the benzene ring. Also the variation of free energy of adsorption with charge is similar to that observed for aromatic compounds and free energy of adsorption has a maximum value at a charge of $-2\mu C.cm^{-2}$.

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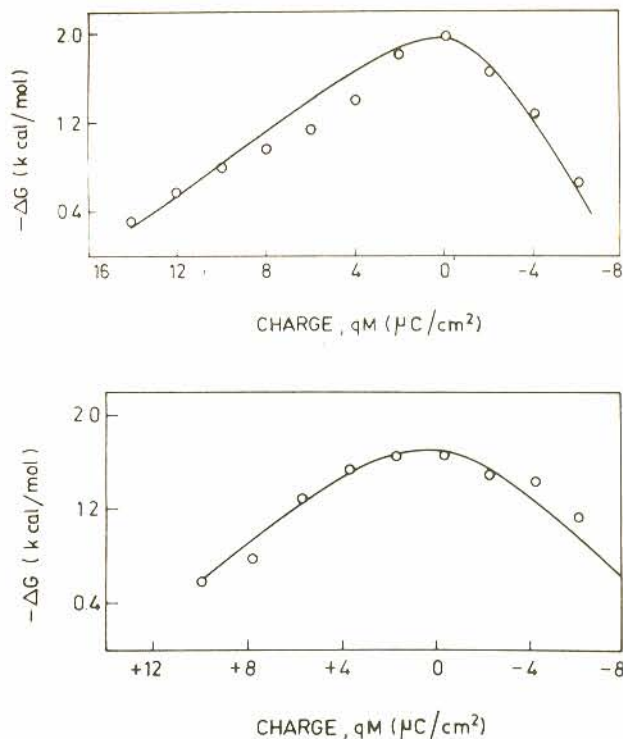4. P Peries, M.Sc. Thesis, University of Ceylon (1954)

Fig. 6: *Plot on the variation of free energy of adsorption with the charge at the interface for (a) ortho methoxy benzoic acid and (b) for para methoxy benzoic acid*

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