

Adsorption of Naphthalene at Mercury/Aqueous Solution Interface

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The adsorption of naphthalene at the mercury/1*N* sodium sulphate solution interface has been studied by the capillary electrometer method. From the evaluated thermodynamic data like charge on the metal surface (q_M) and surface excess of organic compound adsorbed (Γ_{org}) and from the adsorption data obtained it has been shown that the adsorption of naphthalene, which is flat on the metal surface because of π -electron interaction with metal surface, obeys Frumkin's isotherm. The experimental variation of electrostatic free energy of adsorption with charge (q_M) has been compared with the theoretically evaluated variation obtained using the equation proposed by Devanathan and Tilak [*Indian J. Chem.*, 3(1965), 373]. Marked deviations are observed both on anodic and cathodic sides of electrocapillary maximum. Adsorption as well as free energy of adsorption is found to be maximum at q_M of +3 to +4 $\mu\text{C}/\text{cm}^2$.

ORGANIC molecules generally do not follow a standard pattern in their adsorption at the interface as the nature of active groups present in them influences their physical properties. Following the models for the structure of the electrical double layer in the presence of organic compounds put forth by several authors¹⁻⁷, Devanathan and Tilak^{8,9} have put forth a theory of adsorption of organic compounds and also proposed an equation for the evaluation of electrostatic free energy of adsorption. The validity of this equation has already been tested in the case of adsorption of aliphatic organic molecules like formaldehyde and formamide^{10,11}. The aim of the present study is to test the validity of this equation for the adsorption of naphthalene. The study of adsorption of naphthalene at both liquid¹²⁻¹⁴ and solid^{15,16} metal surfaces and from aqueous and non-aqueous solutions¹⁷⁻²⁰ has already been reported. The present study involves the evaluation of thermodynamic parameters like charge (q_M) and surface excess (Γ_{org}) from electrocapillary curves in the presence of various concentrations of naphthalene, application of a suitable isotherm and a comparison of experimental and theoretical values of electrostatic free energies of adsorption for various values of q_M .

Materials and Methods

The design of the capillary electrometer and the cell used for measurements have been described already^{10,11}. Hydrogen used for deaeration was obtained electrolytically and purified by passing through palladised asbestos. Mercury used for filling up the capillary electrometer was purified by electrolysis and distillation in the manner previously described²¹. All solutions were prepared using conductivity water. Sodium sulphate used was of AR (BDH) grade. Naphthalene used was a Baker and Adamson product. A mercury/mercurous sulphate electrode was used as the reference electrode. All the measurements were carried out in an air thermostat at $25 \pm 0.2^\circ\text{C}$. The mercury in the capillary electrometer was polarised at various values of potential by means of a Tinsley potentiometer, type, 3387 (B. H. Tinsley, London), powered by a 2V lead acid battery.

Results

Electrocapillary curves — Electrocapillary curves for 1*N* sodium sulphate in the presence of five different concentrations of naphthalene in water are illustrated in Fig. 1. All the runs were duplicated and the results are reproducible to ± 0.2 dyne at the electrocapillary maximum (e.c.m.) and ± 0.8 dyne at the extremes of the curves.

Charge on the metal surface — 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 the charge density are 0.15 $\mu\text{C}/\text{cm}^2$ around e.c.m. to 0.5 $\mu\text{C}/\text{cm}^2$ at the extremes of the curves. Values of q_M obtained in this way for different concentrations of naphthalene are plotted as a function of E in Fig. 2.

Surface excess of the naphthalene adsorbed — The surface excess of the neutral organic molecule adsorbed is a function of the rate of change of interfacial tension with concentration or activity of organic compound at a constant E . Values of surface excess (Γ_{org}) were evaluated by the graphical differentiation of the curve, interfacial tension versus $\log C$ at constant E . Values of Γ_{org} obtained for various concentrations of naphthalene, as a function of q_M is shown in Fig. 3.

Discussion

Electrocapillary curves — Figure 1 indicates that naphthalene is strongly adsorbed on the positive side of the electrocapillary maximum (e.c.m.) due to the interaction of π -electrons of the naphthalene adsorbed in a flat position and the positively charged metal surface. The extent of adsorption on the positive side of e.c.m. is more than in the case of benzene²². This, as shown by Gerovich and Rybalchenko¹⁴ and Frumkin²³, can be attributed to the fact that adsorption on a positively charged surface increases with an increase in the number of double bonds. Naphthalene gets desorbed as the mercury surface becomes negatively charged and also at extreme anodic polarisation owing to salting out effect.

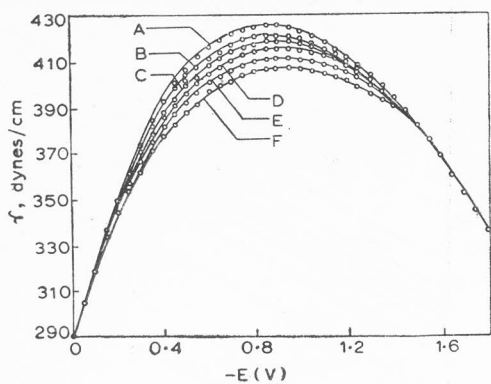


Fig. 1 — Electrocapillary curves of naphthalene in 1N sodium sulphate. [Curve A, 1N Na_2SO_4 alone curves, B—F, naphthalene conc. in the range $0.2687 \times 10^{-4} M$ to $1.3480 \times 10^{-4} M$]

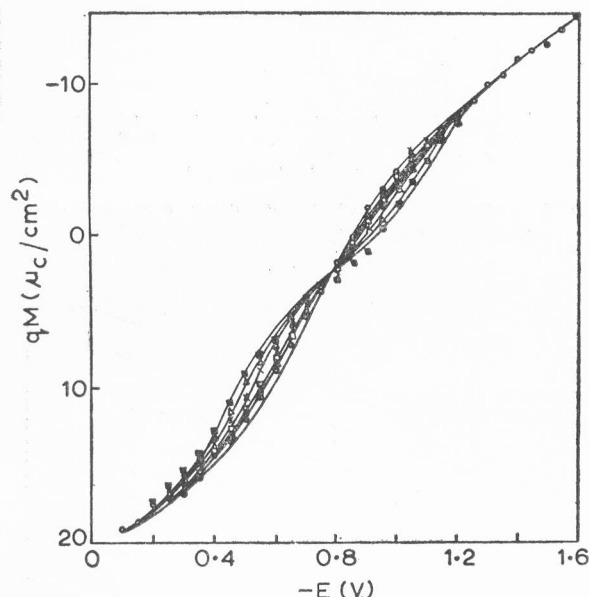


Fig. 2—Variation of q_M ($\mu\text{c}/\text{cm}^2$) with E (volts) for the adsorption of naphthalene on mercury [Naphthalene conc. in the range $0.2687 \times 10^{-4} M$ (\blacktriangle — \blacktriangle) to $1.3480 \times 10^{-4} M$ (\blacksquare — \blacksquare)]

Charge (q_M) versus potential ($-E$) curve—It is seen from Fig. 2 that curves for base solution alone and containing various concentrations of naphthalene added intersect one another at a potential of 780 mV, which is positive to e.c.m. and at a charge of $+3 \mu\text{c}/\text{cm}^2$, showing that maximum adsorption occurs at these values of potential and charge.

Surface excess versus charge curves—Figure 3 indicates that naphthalene is preferentially adsorbed on the positive branch and gets desorbed at extremes of potential. All the curves in Fig. 3 exhibit a maximum value of surface excess at a q_M value of $+4 \mu\text{c}/\text{cm}^2$. This is contrary to that observed in the case of adsorption of aliphatic organic molecules where maximum adsorption occurs at a charge of -2 to $-3 \mu\text{c}/\text{cm}^2$.

Coverage (θ) versus charge (q_M) curves—Coverage θ has been determined using the relation $\Gamma/\Gamma_M = \theta$,

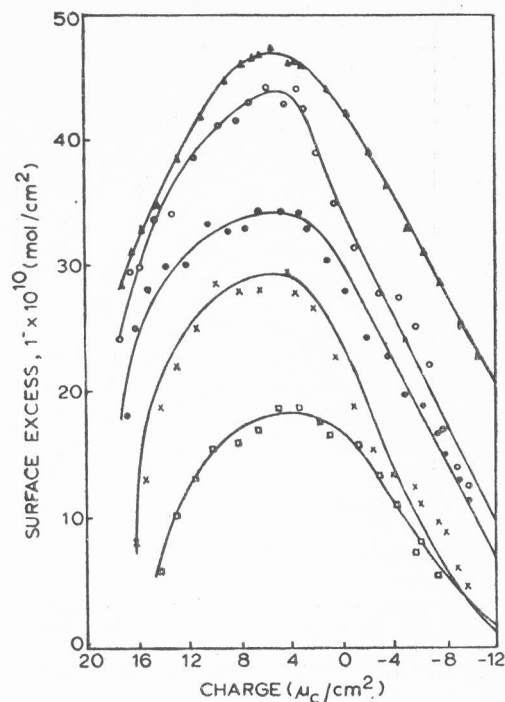


Fig. 3 — Variation of surface excess (Γ_{org}) with q_M ($\mu\text{c}/\text{cm}^2$) on the metal for the adsorption of naphthalene. [Naphthalene conc.: \blacktriangle — \blacktriangle , 1.3480×10^{-4} ; \circ — \circ , 1.074×10^{-4} ; \bullet — \bullet , 0.8061×10^{-4} ; \times — \times , 0.5374×10^{-4} ; and \blacksquare — \blacksquare , $0.2687 \times 10^{-4} M$]

being evaluated by plotting c/Γ against C , for $q_M = 0$ and measuring the initial slope of the linear plot obtained. The value of Γ_M obtained equal to $4.938 \times 10^{-10} \text{ mol}/\text{cm}^2$. Values of coverage evaluated in this way, have been plotted against the charge density q_M on the metal (Fig. 4). These curves exhibit a maximum value of coverage at $q_M = +4 \mu\text{c}/\text{cm}^2$.

Application of Frumkin's isotherm³—From the calculated values of coverage θ , it is possible to show that the adsorption of naphthalene obeys Frumkin's adsorption isotherm, which can be written as

$$BC = \theta/1 - \theta \exp. (-2a\theta) \quad \dots (1)$$

where a is the quantity characterising the interaction between the adsorbed particles and B is a constant determining the adsorption equilibrium at small coverage, i.e.

$$B = \exp(-\Delta G^\circ / RT) \quad \dots (2)$$

ΔG° in Eq. (2) represents the free energy of adsorption.

The applicability of this isotherm has been tested by plotting $(\log C - \log \theta/1 - \theta)$ against θ for various values of q_M . A family of parallel linear lines is obtained (Figs. 5 and 6), thereby proving that the system obeys Frumkin's isotherm. The intercepts of these linear plots give a measure of ΔG° of naphthalene.

Free energy of adsorption (ΔG°) as a function of q_M —The ΔG° of naphthalene on mercury surface has been evaluated from the found values of intercept and plotted against q_M (Fig. 7). The almost

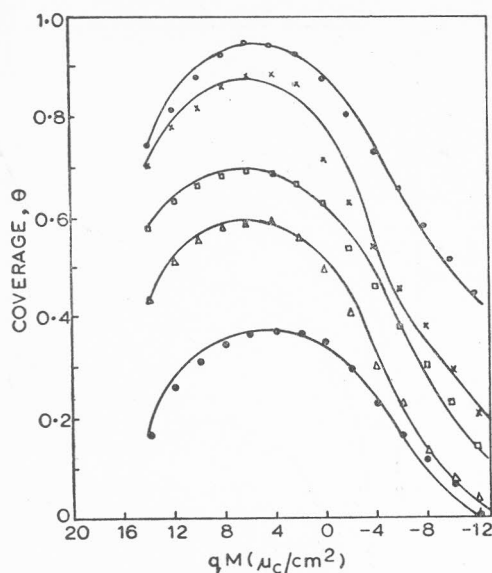


Fig. 4 — Variation of coverage (θ) with charge ($\mu\text{c}/\text{cm}^2$) on the metal for the adsorption of naphthalene [Naphthalene conc. : $\circ-\circ$, 1.3480×10^{-4} ; $\times-\times$, 1.074×10^{-4} ; $\square-\square$, 0.8061×10^{-4} ; $\triangle-\triangle$, 0.5374×10^{-4} ; and $\bullet-\bullet$, $0.2687 \times 10^{-4} \text{N}$]

constancy of free energy on the anodic side of e.c.m. can be explained as due to the interaction between π -electrons of the naphthalene nucleus adsorbed flat on the metal surface and positive charge on the metal surface. The decrease in ΔG° on the cathodic side shows the lack of interaction between the aromatic nucleus and negative charge on the metal surface. ΔG° shows a maximum value at a charge of $+4 \mu\text{c}/\text{cm}^2$ which is in keeping with the observation that maximum adsorption for naphthalene also occurs at this charge.

Evaluation of electrostatic free energies of adsorption of naphthalene — The metal/solution interface offers the possibility of studying the effect of electrical field on the chemical bond between the metal and neutral organic molecules. Neutral organic molecules like butanol gets adsorbed to the maximum at the metal surface with the hydrocarbon end near it when $q_M = 0$. When the field is increased, water molecules which have a high polarisability get adsorbed at the metal surfaces displacing organic molecules. In the case of thiourea, adsorption is maximum on the positively charged metal surface and it adsorbs with the sulphur atom in contact with the metal surface. In order to evaluate the role of electrical field in increasing the bond between sulphur atom and the metal, it is necessary to assess (i) magnitude of μ_F terms relevant to adsorption and (ii) the role of water in organic adsorption. Both these require a knowledge of the structure of the electrical double layer in the presence of organic compounds. The main feature of the theory put forth by Devanathan and Tilak^{8,9} is that water molecules are assumed to be adsorbed flat, unlike previous models which assume water molecules to be perpendicular with the dipole to or away from the metal surface. The electrostatic part of the free energy of adsorption can be written in the form

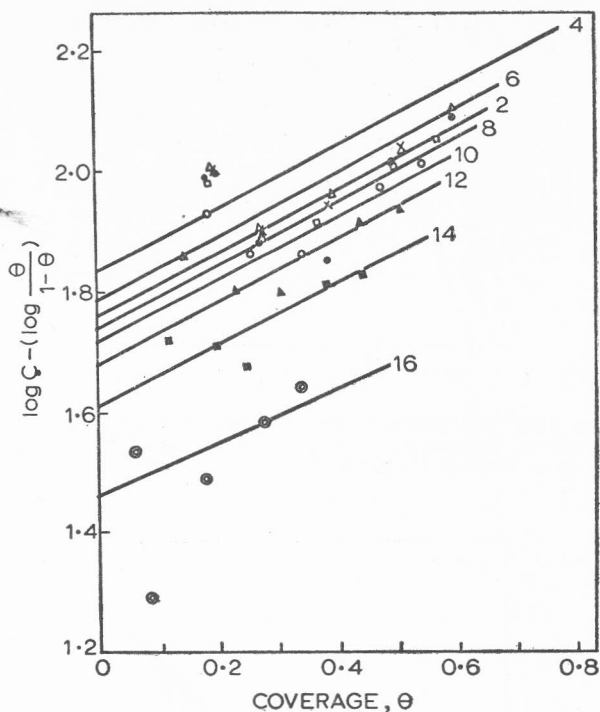


Fig. 5 — Plot of $(\log C - \log \theta/(1-\theta))$ vs θ at some anodic values of charge for the adsorption of naphthalene.

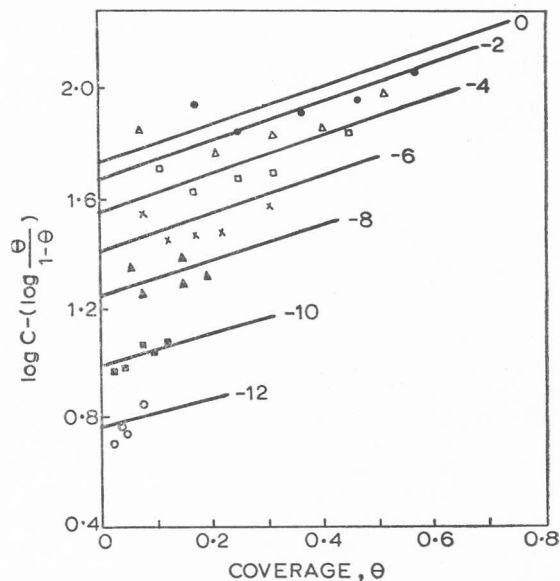


Fig. 6 — Plot of $(\log C - \log \theta/(1-\theta))$ vs θ at some cathodic values of charge for the adsorption of naphthalene.

$$\Delta G_E = 2\pi t q_M 2 \left(\frac{A_0}{\epsilon_0} - \frac{A_0}{\epsilon_w} \right) + 4 \pi q_M \left(\frac{\mu_0}{\epsilon_0} - \frac{n\mu_w}{\epsilon_w} \right) \quad \dots (3)$$

where t is the thickness of water molecules, A_0 the area of the organic molecule, ϵ_w the dielectric constant of water, ϵ_0 the dielectric constant of the organic group within the first water layer and n the number of water molecules replaced by organic molecule. Equation (3) permits an absolute accuracy

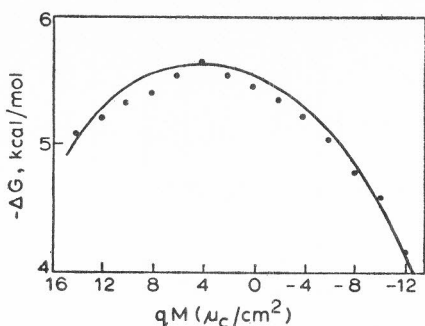


Fig. 7 — Plot of variation of the free energy of adsorption of naphthalene (ΔG°) with the charge q_M on the metal surface.

lation of the electrostatic free energy of adsorption, since it contains no unknown or adjustable parameters.

Electrostatic free energies of adsorption have been evaluated using the Eq. (3) and by considering that the molecule lies flat on the metal surface. So the area of the molecule in flat position has been obtained using catalin models. Naphthalene gets adsorbed to the metal due to π -bonding. The effect of π -electrons has been demonstrated from a comparative study of conjugated unsaturated hydrocarbons and their hydrogenated derivatives¹²⁻¹⁴. These effects can be quantitatively formulated by considering the polarisability of π -electrons. Hence the π -bond contribution ($\alpha\pi$) towards the free energy from six π -electrons is $8\pi^2 q_M^2 \alpha\pi / \epsilon kT$. Here ϵ is the dielectric constant of the vacuum. Since benzene adsorbs flat, π -electrons interact with the metal directly. The π -electron contribution to the free energy of adsorption has been included on both sides of e.c.m. The values of t , A_0 , μ_w , ϵ_w and n used in the evaluation of ΔG_E are given in Table 1.

Figure 8 shows a comparison between experimental and theoretical values of electrostatic free energies of adsorption. Marked deviations are observed at high field strengths both on the anodic and cathodic sides. This may be due to the fact that π -electron polarisability may apply only at low field strengths and may be much smaller at high anodic and cathodic fields.

Orientation of adsorbed naphthalene — Area of the molecule evaluated from the experimental values, i.e. 33.7 \AA^2 corresponds almost to the area of the molecule obtained from catalin model, when it is adsorbed in the flat position, i.e. 42 \AA^2 . π -Electron interaction of naphthalene with positively charged metal surface is maximum when it is adsorbed in the flat position. This interaction is responsible for the strong adsorption of naphthalene on the anodic side. As the number of π -electrons in naphthalene is more than that in benzene, the extent of adsorp-

TABLE 1 — VALUES OF CONSTANTS USED IN THE EVALUATION OF ELECTROSTATIC FREE ENERGIES OF ADSORPTION

Molecular area (from catalin models)	..	42.0 \AA^2
Molecular area (from experimental)	..	33.63 \AA^2
Dipole moments	..	0
Dielectric constant	..	2.540
Number of water molecules replaced	..	7

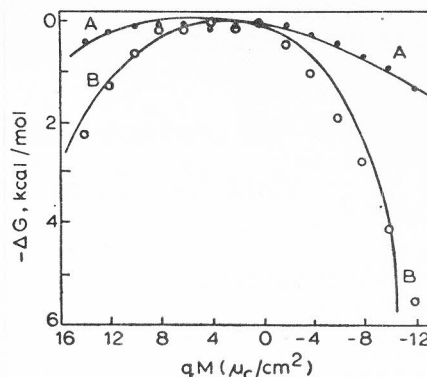


Fig. 8 — Variation of electrostatic free energy of adsorption ($-\Delta G_E$) with q_M for the adsorption of naphthalene. [A, experimental; and B, theoretically calculated curves]

tion is more. There is desorption of naphthalene molecule on the cathodic side due to the lack of interaction between the π -electrons and the negatively charged metal surface and strong attraction of water molecules to the metal surface.

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