

Coadsorption of organic molecules on mercury electrode

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Received 6 March 1990; revised 16 July 1990; accepted 3 September 1990

Coadsorption of *o*-hydroxybenzoic acid with *o*-methoxybenzoic acid and/or *o*-aminobenzoic acid at the mercury/0.1 M Na₂SO₄ solution interface has been studied using a capillary electrometer. Thermodynamic parameters, such as surface charge density (q^M), surface excess of the organic molecule adsorbed (Γ_{org}) and coverage (θ) have been evaluated. It is observed from the adsorption data that coadsorption takes place by the partial replacement of already adsorbed organic compound on the metal surface and the adsorption of both the compounds is found to take place over a wide range of potentials.

It is well known that the formation of strong adsorbed layers on metals plays an important role in electroplating and in corrosion inhibition. One way of producing adsorbed surface films, which are stable over a wide range of potentials, is by the coadsorption of organic molecule at the electrode/solution interface. Most of the studies at the electrode/solution interface have involved single organic molecules. Some studies have been carried out on the coadsorption of two organic molecules. It is observed that in the case of coadsorption, the coverage is less than the sum of coverages in individual adsorptions. The effect of concentration of adsorbate as well as the mechanism of adsorption has been studied for different organic adsorbents¹⁻¹¹. The present study aims at the investigation of the adsorption of *o*-hydroxybenzoic acid (OHB), *o*-aminobenzoic acid (OAB) and *o*-methylbenzoic acid (OMB) singly on a mercury electrode and also the coadsorption of OAB or OMB with OHB using a capillary electrometer.

Materials and Methods

Reagents

Mercury used was of AR grade and it was further purified electrolytically and distilled twice in all-glass pyrex Hullet still under reduced pressure¹². AR(BDH) grade sodium sulphate was twice recrystallised from deionised water and dried to the anhydrous state. OHB (pure) was a May and Baker product, while OMB was a Koch-Light (England) product. OAB was obtained from Riedel, Germany. As all the above-mentioned organic compounds were of extrapure quality, they were used without

further purification. Throughout this study, it was assumed that the solute activity can be replaced by its molar concentration since fairly dilute solutions are involved.

Procedure

The evaluation of thermodynamic quantities for the adsorption at the mercury electrode necessitated the measurement of interfacial tension, using a capillary electrometer as described elsewhere¹³. Purified hydrogen was used for deaeration of experimental solutions. The capillary electrometer was calibrated with 1 M KCl, for which the interfacial tension was 424.2 mN/m¹⁴, and rechecked with 1 M KI taking the electrocapillary maximum as 401.4 mN/m at 25°C. For each concentration at least two runs were made and results were found to be reproducible to ± 0.2 mN/m at the electrocapillary maximum and ± 1 mN/m at the extreme of the curve. All the measurements were made in an air thermostat controlled at a temperature of $25 \pm 0.2^\circ\text{C}$.

To understand the mixed adsorption of organic molecules, first a study of adsorption of individual organic compounds is essential. So, interfacial tension measurements were carried out separately, using 0.1 M sodium sulphate as the base electrolyte. The mercury in the capillary electrometer was polarised at various values of potentials ranging from -0.1V to -1.6V applied with reference to Hg/Hg₂SO₄/0.1 M Na₂SO₄ electrode using a precision potentiometer. Two types of observations were made for the mixed adsorption of substances in the same base electrolyte. In one, the concentration of

adsorbate 1 was kept constant and the concentration of the adsorbate 2 was varied. In the second case, the concentration of adsorbate 1 was varied. One of the concentrations taken for the study of the adsorption of the individual organic compound was chosen as the common concentration for mixed adsorption studies.

Results and Discussion

The single adsorption of all the three organic compounds reported in this study has already been studied thoroughly¹⁵ and only salient features are reported here.

The adsorption of OHB, OMB and OAB alone was studied at the mercury/0.1M Na₂SO₄ solution interface. The adsorption of OHB was found to be more pronounced on the positive side of electrocapillary maximum and desorption occurred on the negative side of the electrocapillary maximum. A similar behaviour was observed in the case of OMB also, but the extent of adsorption was comparatively less. But OAB was found to adsorb on both the sides of electrocapillary maximum, though the adsorption was more on the positive side and less on the negative side. Maximum adsorption (maximum surface excess) for all the three compounds occurred at surface charges in the range of +2 to 3.5 $\mu\text{C}\cdot\text{cm}^{-2}$.

Based on the above observations, adsorption studies were carried out using OHB as one of the two adsorbates, keeping its concentration constant in one case and varying its concentrations in the other cases. The present study aims at examining the effect of addition of a second adsorbate (OMB or OAB) on the extent of adsorption of OHB. The order of adsorption in the single adsorbate system is OMB > OHB > OAB. This observed order is in accordance with the polarisabilities of these adsorbates. The electrode/solution system under study can be represented as Hg/Na₂SO₄ (0.1M)_{x,y}/Hg₂SO₄(S)/Hg where x,y represent the two organic compounds.

Simultaneous adsorption of OHB with OMB and OAB

(i) Electrocapillary curves

Electrocapillary curves obtained in the presence of fixed concentrations of OHB and varying concentrations of OMB, or vice versa are shown in Figs 1 and 2. It is seen from these figures that curves are more separated for the systems with fixed concentration of OMB and variable concentrations of OHB than those for the system containing fixed concentration of OHB and varying concentrations of OMB. Moreover, the separation of the curve is greater near the electrocapillary maximum, than

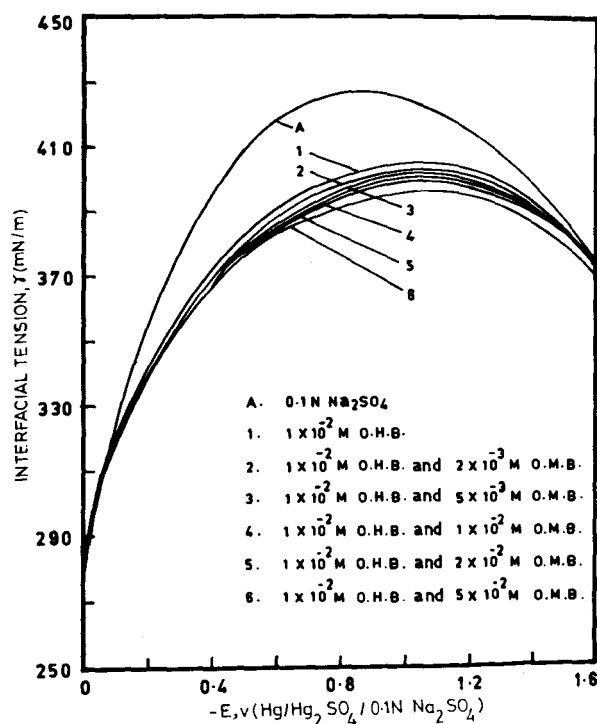


Fig. 1 – Electrocapillary curves for *o*-hydroxybenzoic acid and *o*-methylbenzoic acid

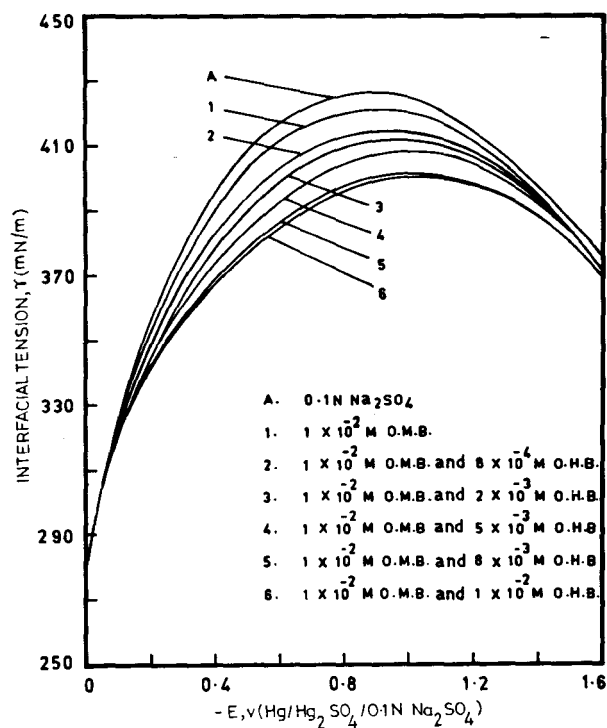


Fig. 2 – Electrocapillary curves for *o*-methylbenzoic acid and *o*-hydroxybenzoic acid

that at the extremes. It is also observed that both the compounds get desorbed at the extremes of potentials and that there is a shift in the electrocapillary maximum to more negative potentials on the addition of second adsorbate. These observations may be explained in terms of the adsorption of second compound occurring at the expense of the first, the substitution not being in the 1:1 ratio (which may be due to different polarisabilities of the two organic compounds). These observations further indicate that there is simultaneous adsorption of both the adsorbates. A similar behaviour was observed for the simultaneous adsorption of OHB and OAB. In both the systems it was observed that the lowering of interfacial tension was greater for the system where the varying concentration constituent was OAB or OMB and the fixed concentration constituent was OHB.

The electrocapillary equation for the above systems can be written as

$$-d\gamma = q^M dE^- + 1/2 \Gamma_{Na^+} + d\mu_{Na_2SO_4} + \Gamma_{OHB} d\mu_{OHB} + \Gamma_{OMB} d\mu_{OMB} \quad \dots (1)$$

The above equation enables the evaluation of the charge density (q^M) and surface excess (Γ_{org}) for the individual organic compounds in the mixture at different potentials. This equation can be reduced to

$$\left(\frac{\partial \gamma}{\partial E^-} \right)_{\mu_{Na_2SO_4}, \mu_{OHB}, \mu_{OMB}} = -q^M \quad \dots (2)$$

$$\left(\frac{\partial \gamma}{\partial \mu_{OHB}} \right)_{E^-, \mu_{Na_2SO_4}, \mu_{OMB}} = \Gamma_{OHB} \quad \dots (3)$$

$$\left(\frac{\partial \gamma}{\partial \mu_{OMB}} \right)_{E^-, \mu_{Na_2SO_4}, \mu_{OHB}} = \Gamma_{OMB} \quad \dots (4)$$

Similar equations can be obtained for the simultaneous adsorption of OHB and OAB on the mercury electrode.

(ii) Surface excess versus charge density curves

For a better understanding of the preferential adsorption of one adsorbate out of the chosen two, a study of the variation of relative surface excess with charge on the metal surface is essential. The surface excess of the adsorbate with varying concentration was obtained by the graphical differentiation of the γ vs $RT \ln C$ curve using Eqs (3) and (4) where C is the concentration of the altered adsorbate. As the ionic strength is not altered significantly, the activity of the varying adsorbate is equated to its concentration. Surface charge density values were obtained (using Eq. 2) for different potentials by the graphical differentiation of electrocapillary curves. Surface excess versus charge density curves obtained for the OHB-OMB system are shown in Figs 3 and 4. Similar curves were obtained for the OHB-OAB system. It is observed from these figures that surface excess obtained for the mixed system is always greater (for all concentrations) than that for systems with single

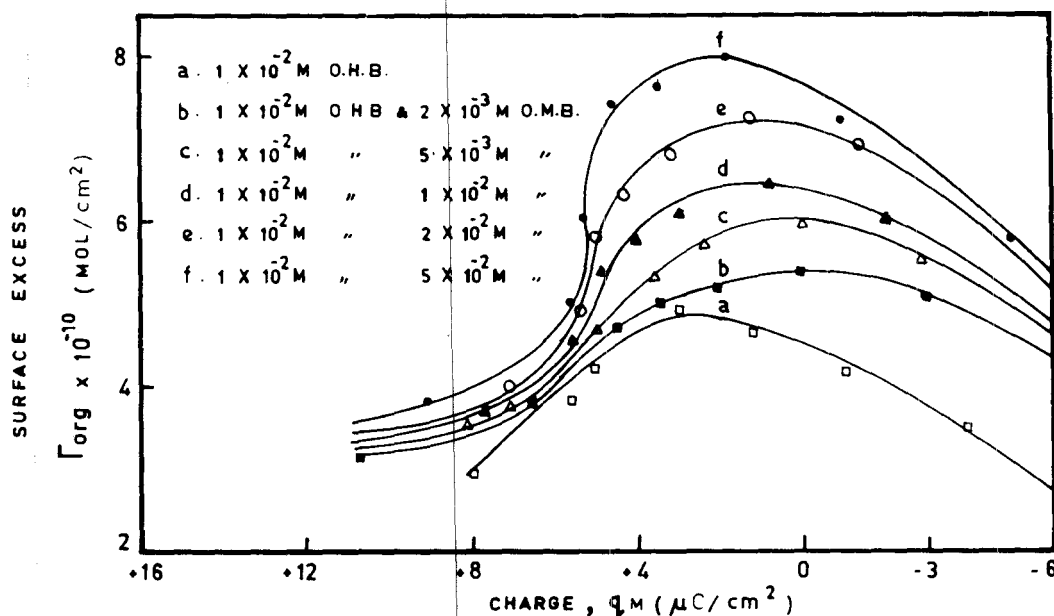


Fig. 3 – Variation of Γ_{org} with q^M for the adsorption of fixed concentration of *o*-hydroxybenzoic acid with variable concentrations of *o*-methylbenzoic acid on mercury

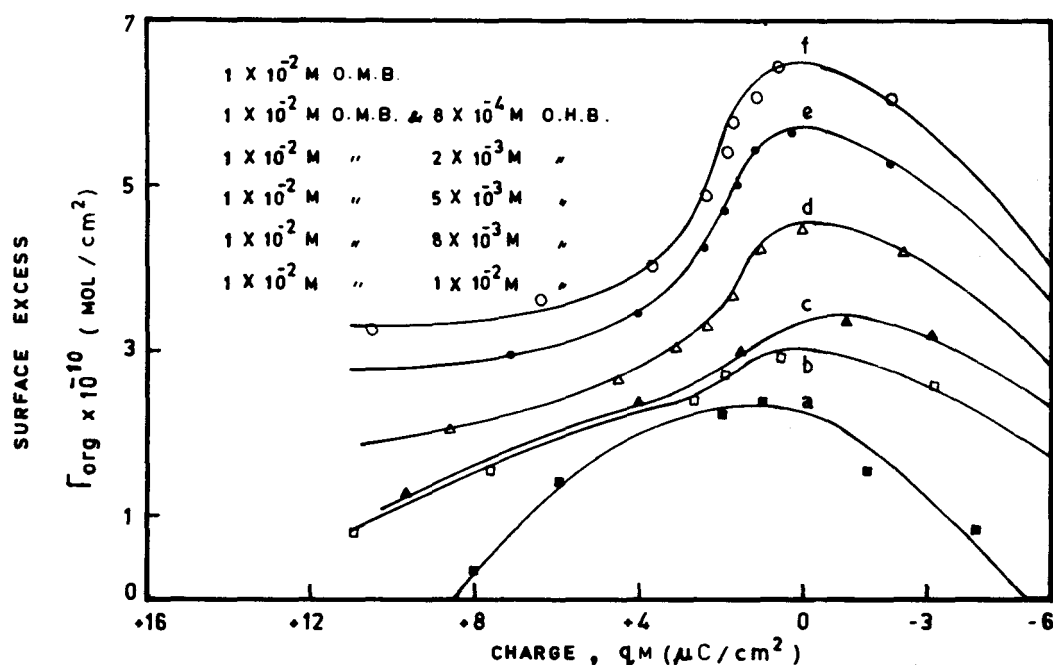


Fig. 4 – Variation of Γ_{org} with q^M for the adsorption of fixed concentration of *o*-methylbenzoic acid with variable concentrations of *o*-hydroxybenzoic acid on mercury

organic adsorbate. Another notable feature seen from these curves is that for all concentrations the surface excess of the mixed system is always less than the sum of surface excesses of individual components. It is also found that for both the mixed systems maximum surface excess is noticed at charge value ranging from +3 to +4 $\mu\text{C}\cdot\text{cm}^{-2}$. But for individual systems, maximum surface excess is obtained at less positive charges. This difference may probably be due to the simultaneous adsorption of two adsorbates on the mercury surface.

Table 1 – Variation of surface coverage for different surface charges at the mercury/solution interface

q^M ($\mu\text{C}\cdot\text{cm}^{-2}$)	θ_1	θ_2	θ_3	θ_4	$\theta_3 + \theta_4$
8	0.5011	0.0568	0.3655	0.1742	0.5397
7	0.5919	0.1640	0.3765	0.2023	0.5730
6	0.6709	0.2494	0.4073	0.2308	0.6381
5	0.7340	0.3019	0.4460	0.2550	0.7010
4	0.7735	0.3194	0.4857	0.2620	0.7477
3	0.8089	0.3718	0.5057	0.2925	0.7982
2	0.8129	0.3938	0.5164	0.3068	0.8232
1	0.7893	0.4068	0.5206	0.3502	0.8708

θ_1 : θ due to $1 \times 10^{-2} \text{ M OHB} + 0.1 \text{ M Na}_2\text{SO}_4$

θ_2 : θ due to $1 \times 10^{-2} \text{ M OMB} + 0.1 \text{ M Na}_2\text{SO}_4$

θ_3 : θ due to $1 \times 10^{-2} \text{ M OHB} + 2 \times 10^{-3} \text{ M OMB} + 0.1 \text{ M Na}_2\text{SO}_4$

θ_4 : θ due to $1 \times 10^{-2} \text{ M OMB} + 2 \times 10^{-3} \text{ M OHB} + 0.1 \text{ M Na}_2\text{SO}_4$

(iii) Coverage (θ) of the metal surface by adsorbed organic compounds

Coverage (θ) was obtained using the relation $\theta = \Gamma/\Gamma_m$, where Γ_m is the maximum value of the surface excess. Values of Γ_m were evaluated from the slopes of C/Γ vs C curves for $q^M = 0$. It was found to be $8.0 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ for OMB, $12.75 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ for OHB and $14.64 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ for OAB. Values of coverage have been obtained for both the systems for different charge densities and are shown in Tables 1 and 2. From these data for coverage at different charge densities, the following general observations can be made:

Table 2 – Variation of surface coverage for different surface charges at the mercury/solution interface

q^M ($\mu\text{C}\cdot\text{cm}^{-2}$)	θ_1	θ_2	θ_3	θ_4	$\theta_3 + \theta_4$
+8	0.5011	0.4193	0.2288	0.2189	0.4477
+6	0.6709	0.4574	0.2902	0.2653	0.5555
+4	0.7735	0.5869	0.3483	0.3493	0.6978
+2	0.8129	0.6937	0.3381	0.4684	0.8063
0	0.7577	0.6403	0.3278	0.4211	0.7489
-2	0.6551	0.5412	0.2902	0.2947	0.5849

θ_1 : θ due to $1 \times 10^{-2} \text{ M OHB} + 0.1 \text{ M Na}_2\text{SO}_4$

θ_2 : θ due to $1 \times 10^{-2} \text{ M OAB} + 0.1 \text{ M Na}_2\text{SO}_4$

θ_3 : θ due to $1 \times 10^{-2} \text{ M OHB} + 8 \times 10^{-4} \text{ M OAB} + 0.1 \text{ M Na}_2\text{SO}_4$

θ_4 : θ due to $1 \times 10^{-2} \text{ M OAB} + 8 \times 10^{-4} \text{ M OHB} + 0.1 \text{ M Na}_2\text{SO}_4$

(a) Simultaneous adsorption of both the components takes place.

(b) At very low concentrations, the extent of adsorption of the fixed concentration constituent from the mixed solution is found to be less than that of the same constituent studied individually. This fact clearly shows that the adsorption of one constituent of a mixture takes place by bringing down the adsorption of the other. So the adsorption of one constituent is found to take place by partial replacement of the already adsorbed organic compound and the adsorption of both is observed over the whole range of potential.

(c) At lower concentrations of the adsorbate with varying concentration, an important behaviour is noticed. The sum of the surface coverages of mixed adsorbates (θ_3 and θ_4) is almost equal to the coverage of the component which is adsorbed more as an individual adsorbate. It is seen from Table 1 that at a charge of $+4 \mu\text{C}\cdot\text{cm}^{-2}$ the coverage values of the individual adsorbate (of concentration $1 \times 10^{-2} \text{ M}$) are found to be 0.7733 and 0.3194 respectively. But coverages from mixed solutions, θ_3 and θ_4 , are 0.4857 and 0.2620 respectively and the sum total is 0.7477. This is equal to the coverage (θ_1) of the adsorbate with more adsorption. A similar behaviour is observed from Table 2 also. This behaviour is shown almost at all electrode charges, especially at low concentrations of the varying constituent. These observations are in keeping with observations by previous workers¹⁻⁴.

(d) Though there is a general agreement and correlation among the chosen systems at very low concentrations, there is a considerable disagreement for more concentrated solutions. This may be due to an error in the value of θ obtained by graphical differentiation. Moreover, the calculation of coverage is based on assumptions that adsorbates are adsorbed in one orientation. But this may not be

so in reality because π -electron interaction may involve a flat or mixed orientation. Calculation of θ , ignoring lateral interactions between like and unlike molecules, will introduce an error in the value of θ . The true value will vary depending on whether the interaction is attractive or repulsive and this depends on the orientation of the molecule at the metal/solution interface.

Acknowledgement

The authors are thankful to the Director, Central Electrochemical Research Institute, Karaikudi 623 006 for his interest in the work and for providing facilities.

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