Influence of Anions on the Adsorption of Thiophenol at the Mercury/ Aqueous Solution Interface

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Electrocapillary curves for 1 M NaCl, $NaNO_3$ and Na_2SO_4 in the presence of different concentrations of thiophenol show that the compound is adsorbed more on the positively charged metal surface. The extent of adsorption from these base electrolytes follows the order: Na_2SO_4 > $NaNO_3$ > NaCl. Thermodynamic parameters like charge on the metal surface, surface excess of organic molecules adsorbed, surface coverage and free energy of adsorption have been evaluated. The adsorption of thiophenol at the mercury/solution interface obeys the Langmuir adsorption isotherm in all cases irrespective of the base electrolyte used.

Thiophenols have a low solubility in water and are characterised by their abnoxious odour. Probably because of these, study of their adsorption on metal/ solution interface and also corrosion inhibition is limited. Riggs and Every [1] have studied its influence as an inhibitor for the corrosion of iron in acidic solutions. Generally the adsorption of organic molecules at the metal / solution interface is primarily a competition for sites on the metal surface between organic molecules and other constituents in the electrolyte. Ions present in aqueous solutions have been found to possess significant influence on the extent of adsorption of organic compounds on the metal electrode. Such influence of ions on the mercury electrode has been studied by many workers [2-7]. In the present study, the adsorption behaviour of thiophenol on mercury from three different electrolytes are reported.

EXPERIMENTAL

The design of the capillary electrometer and the experimental cell used for the interfacial tension measurements are the same as described earlier [8]. All chemicals were of AR (BDH) quality. Purified hydrogen was used for the deaeration of the experimental solution. Mercury (AR) was purified electrolytically and distilled in an all glass pyrex still under reduced pressure. All the measurements were carried out in an air thermostat at 25±0.2°C. Reference electrodes used were Hg/Hg_2Cl_2/1 M NaCl or $Hg/HgNO_3$/1M $NaNO_3$ or Hg/Hg_2SO_4/1M Na_2SO_4.

A lead acid battery (6.0 V) and a precision potentiometer were used to apply potential (0.1 to 1.6 V) to the mercury in the capillary electrometer. All the potentials were measured using a digital multimeter (HTL 2120).

RESULTS

Electrocapillary Curves

Electrocapillary curves are obtained for 1 M NaCl, 1 M $NaNO_3$ and 1 M Na_2SO_4 in the presence of

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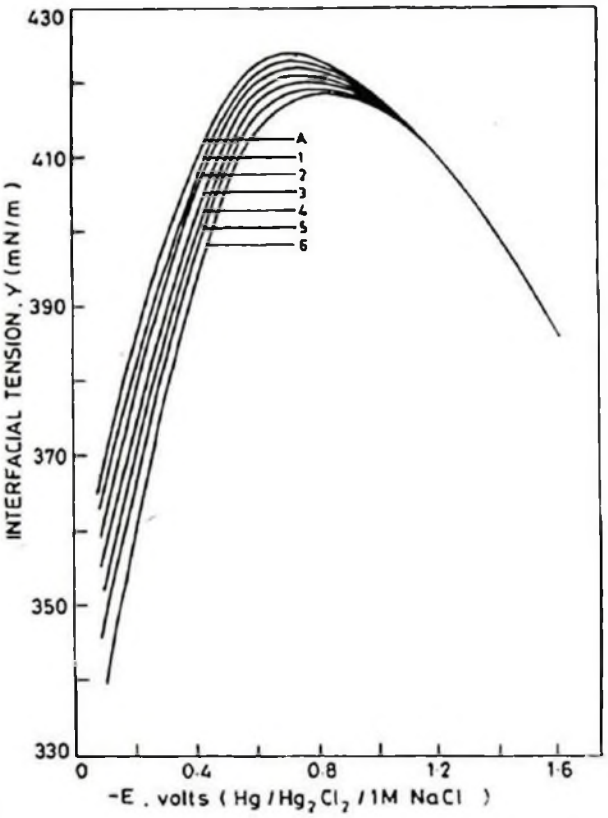


Fig 1. Electrocapillary Curves for 1 M NaCl with Different Concentrations of Thiophenol
A. 0 1. 1 x 10^{-5} M 2. 5 x 10^{-5} M
3. 1 x 10^{-4} M 4. 2.5 x 10^{-4} M
5. 5 x 10^{-4} M 6. 1 x 10^{-3} M

thiophenol concentrations ranging from 1 x 10^{-5} M to 1 x 10^{-3} M. All the runs were duplicated and the results are reproducible to 0.2 mN.m^{-1} at ecm and 0.8 mN.m^{-1} (in other words dynes) at the extremes of curves. Electrocapillary curves of different base electrolytes exhibit similar features showing variations only in the extent of adsorption. Fig 1 shows electrocapillary curves for thiophenol in 1 M NaCl; the variations in the extent of adsorption observed for different electrolytes are shown in Table 1.

Table 1

Adsorption of Thiophenol from Different Base Electrolytes

Reduction in $\Delta\gamma$ around ecm (mN.m^{-1})
Base Electrolyte = 1 M; Thiophenol = 2.5 x 10^{-4} M

NaCl	$NaNO_3$	Na_2SO_4
8	12	14

Charge Density on the Metal Surface (q^M)

q^M has been evaluated by the graphical differentiation of electrocapillary curves at 50 mV intervals. The plots of q^M *vs* E for NaCl are presented in Fig 2. The error limits for the charge density are 0.25 μC.cm^{-2} around ecm and 0.5 μC.cm^{-2} at the extremes of the curves. q^M *vs* E

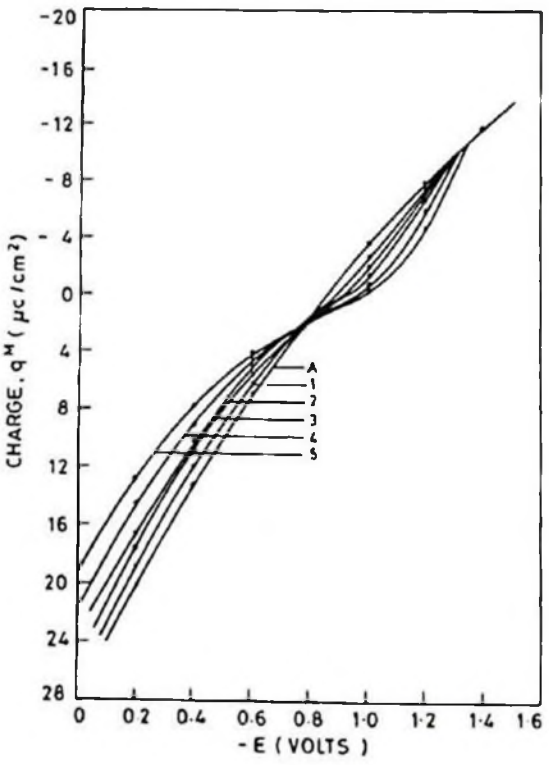


Fig 2. Charge *vs* E Curves for 1 M NaCl with Different Concentrations of Thiophenol
A. 0 1. 1 x 10^{-5} M 2. 5 x 10^{-5} M
3. 1 x 10^{-4} M 4. 5 x 10^{-4} M 5. 1 x 10^{-3} M

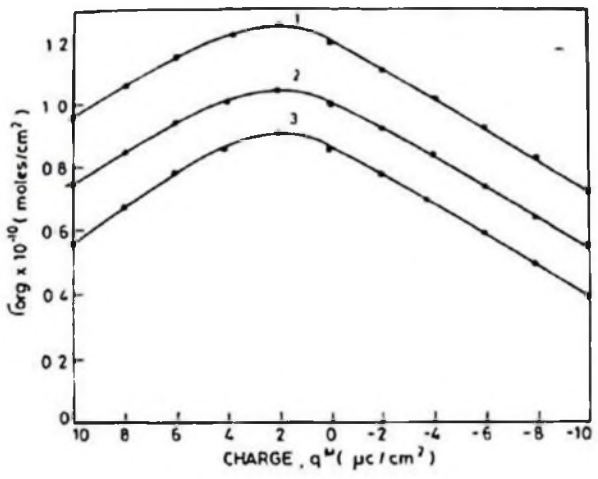


Fig 3 Surface Excess (Γ_{org}) *vs* charge (q^M) Curves for Different Base Solutions

Thiophenol Conc 2.5 x 10^{-4}
1 1 M NaCl, 2 1 M $NaNO_3$; 3 1 M Na_2SO_4

curves obtained in the presence of solutions of the other two salts follow similar pattern as in Fig 2.

Surface Excess of Organic Molecule adsorbed (Γ_{org})

Surface excess of neutral organic molecule adsorbed is calculated by the graphical differentiation of the interfacial tension *vs* concentration curve at constant potential. Values of Γ_{org} were obtained for different concentrations of thiophenol as a function of q^M. For the sake of comparison, surface excess *vs* charge curves obtained in the three base electrolytes at a concentration of 2 x 10^{-4} M thiophenol are shown in Fig 3.

DISCUSSION

It can be seen from Fig 1 that thiophenol is adsorbed more on the positively charged mercury surface and it gets desorbed on the negatively charged surface. Interaction of delocalised π-electrons of the aromatic ring [9] and also the lone pair of electrons of the sulphur atom present in the thiophenol with the positively charged mercury surface [10] results in adsorption on the positively charged metal. Since the interacting groups are electron - rich, they are desorbed from the negatively charged metal surface.

It can be seen from the Table 1 that the extent of adsorption of thiophenol decreases in the order Na_2SO_4 > $NaNO_3$ > NaCl. Since chloride has a greater tendency for adsorption on the mercury surface, it competes with the organic molecule for adsorption sites. The order of adsorption in the remaining two electrolytes also follow the adsorption tendency of the respective ions.

Surface Excess (Γ_{org}) *vs* Charge (q^M) Curves

It can be seen from the Fig 3 that maximum adsorption of thiophenol occurs around a charge of +2 μC.cm^{-2} irrespective of the nature of the base electrolyte. Further, it can be seen that the values of surface excess for 2 x 10^{-4} M thiophenol from 1 M Na_2SO_4 is found to be definitely more than those in the other two base electrolytes. This observation clearly brings out the effect of anions in the base electrolyte on the adsorption of thiophenol on the mercury electrode. Further this Figure shows that there is more adsorption of thiophenol on the positively charged mercury surface and the compound is completely desorbed on the negatively charged mercury.

Coverage (Θ) *vs* Charge (q^M) Curves

Coverage (Θ) was evaluated using the relation $\Theta = \Gamma/\Gamma_m$, where Γ is the value of the surface excess and Γ_m is the surface excess maximum. Coverage *vs* charge curves are identical to surface excess *vs* charge curves. These curves for different electrolytes have almost similar features, except the fact that the coverage is more from Na_2SO_4 solution

followed by $NaNO_3$ and NaCl in the decreasing order as seen from Table 2.

Table 2

Values of Coverage (Θ) for different Values of Charge for the Adsorption of Thiophenol from Different Base Electrolytes

Base Electrolyte Concentration 1 M

	Value of Θ in		
Charge	NaCl	$NaNO_3$	Na_2SO_4
+10	0.48	0.52	0.58
+ 6	0.44	0.50	0.54
+ 2	0.40	0.46	0.52
0	0.40	0.44	0.50
- 6	0.28	0.32	0.34
-10	0.20	0.26	0.28

Application of Adsorption Isotherms

The adsorption data obtained have been analysed graphically to choose a proper isotherm which can explain the adsorption characteristics of thiophenol on mercury from different base electrolytes. It is found that a plot of C/Θ *vs* C for various values of charge density gave a family of parallel straight lines with a slope of unity. This observation shows that the adsorption of thiophenol from mercury from different base electrolytes obey Langmuir's adsorption isotherm. Intercepts have been noted for each value of q^M for different isotherm plots from which free energy of adsorption is evaluated.

Free Energy *vs* q^M Curves

The variation of free energy of adsorption with charge on the metal surface from different base electrolytes Figure 4 clearly brings out the fact that

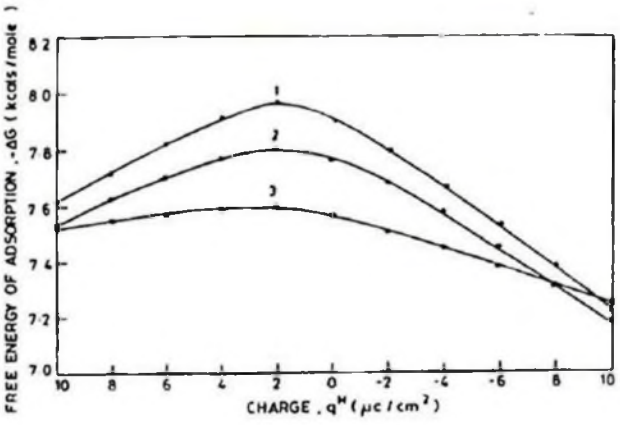


Fig 4 Free Energy (-ΔG°) *vs* Charge (q^M) Curves for the adsorption of Thiophenol on Mercury from Different Base Solutions

1 1 M NaCl; 2 1 M $NaNO_3$; 3 1 M Na_2SO_4

$-\Delta G^\circ$ values for a charge at which maximum adsorption occurs ($+2\mu C.cm^{-2}$) follows the order:

1 M Na_2SO_4 > 1 M $NaNO_3$ > 1 M NaCl
(7.9 kcals/mole) (7.7 kcals/mole) (7.55 kcals/mole)

CONCLUSION

A systematic study of the adsorption of thiophenol from 1 M Na_2SO_4, 1 M $NaNO_3$ and 1 M NaCl brings out the following salient features:

1. Thiophenol is adsorbed more on the positively charged mercury surface. It is desorbed on the negatively charged surface.

2. The nature of the anions in the base electrolyte only alters the extent of adsorption and not the general adsorption characteristics of the compound. Langmuir's adsorption isotherm is obeyed in all cases.

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