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N. B. The numbering of the references has been altered in the translation to make it consistent with the text. This is still subject to doubt however (Ed. of Translation).

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NATURE OF THE ELECTRICAL EFFECT AT THE SOLUTION-AIR INTERFACE ACCOMPANYING THE FORMATION OF MULTIMOLECULAR FILMS OF CONDENSED AROMATIC HYDROCARBONS

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In previous papers^{1,2} on the electrical properties of films of condensed aromatic hydrocarbons (phenanthrene, anthracene, chrysene, etc.) on the surface of solutions of inorganic salts and pure water it has been shown that, under conditions such that these hydrocarbons spread with formation of thin multimolecular layers, a positive potential arises at the solution-air interface. The relationship found between the magnitude of the surface potential of the multimolecular layer and the concentration and valency of the solute cation suggested that the effects of spreading and production of a positive charge are associated with adsorption of the cations of the salt and the hydrogen ions of the water and the polarisation of the molecules of the non-polar compound. It may also be supposed that, as a result of interaction in the surface layer between the cations of the salt and the molecules of the aromatic hydrocarbon, the surface energy at the phase boundary is diminished, favouring the spreading of the aromatic molecules at this boundary. This explanation was confirmed in an investigation of the behaviour of aromatic carbons at a mercury-solution interface by recording electrocapillary curves^{3,4}.

This investigation showed that the preferential adsorption of aromatic hydrocarbons observed on the positively charged mercury surface is due to interaction between the π electrons of the aromatic ring and the positive charges on the metal surface. The occurrence of interaction in the bulk of the solution between aromatic hydrocarbons and silver ions, which leads to the formation of molecular complexes of the type AgAr^+ ,⁵ is a similar phenomenon.

If the behaviour of condensed aromatic compounds at the solution-air interface is considered from this viewpoint, it may be supposed that the electrical effect accompanying their spreading is of the same nature as the electrical and adsorption effect at the mercury-solution interface, i.e. that it is due to interaction between the π electrons of the aromatic hydrocarbons and the cations of the salt solution or the hydrogen ions of the water molecules.

It was therefore of interest to investigate the behaviour of condensed aromatic hydrocarbons on the surface of solutions containing silver ions. It might be expected that, on passing from pure water to such solutions, the addition of aromatic hydrocarbons would cause a considerable increase

in the magnitude of the positive potential. The present work was undertaken with the object of confirming this hypothesis.

EXPERIMENTAL

Measurements were made of the surface potential of solutions of silver nitrate of different concentrations, and of several other salts, when anthracene and chrysene dissolved in benzene were applied to their surface. For comparison, measurements were also made of the electrical effects occurring when an aliphatic hydrocarbon, triacontane $\text{C}_{30}\text{H}_{62}$, was added to these solutions.

Surface potential was measured by the radioactive-probe method suggested by Guyot⁶ and Frumkin⁷. The method of measurement and the apparatus have been described in a previous paper². Both the aromatic hydrocarbons and the inorganic salts were first carefully purified. The triacontane was prepared by electrolysis of an alcoholic solution of potassium palmitate (Kolbe synthesis), and purified by subsequent recrystallisation and distillation in vacuo. Its melting point was 65.5° .

The results of the measurements are set out in Table 1.

The surface-potential values in the Table represent the limiting changes in potential difference occurring at the solution-air interface on adding the film-forming substance to the surface of the solution until it is saturated.

TABLE 1. Surface potentials of films of anthracene and chrysene on solutions containing ions of silver and mercury.

Supporting solution	Concentration, <i>N</i>	Anthracene		Chrysene	
		Increase in potential, mV	film thickness, Å	Increase in potential, mV	film thickness, Å
Water	—	85	260	114	220
KNO_3	0.1	90	260	120	210
AgNO_3	0.01	—	—	155	180
AgNO_3	0.05	183	240	—	—
AgNO_3	0.1	240	240	170	180
AgNO_3	1.0	340	220	—	—
$\text{Hg}_2(\text{ClO}_4)_2$	$2 \cdot 10^{-4}$	100	—	—	—
$\text{Hg}_2(\text{ClO}_4)_2$	0.01	150	—	—	—
HClO_4	5.0	145	220	—	—
HClO_4	10.0	260	190	—	—

The data in the Table show that on passing from pure water to dilute solutions of silver nitrate there is a marked rise in the potential of the anthracene film, which increases with increase in the concentration of silver ions in the solution, reaching a constant value (340 mV) at a silver nitrate concentration of about 1.0 *N*. Films of chrysene show a qualitatively similar relationship between the potential and the silver ion concentration, but the magnitude of the increase in potential is considerably less. Relatively large increases in surface potential are obtained also on adding films of anthracene to dilute solutions of mercury perchlorate.

Comparison of the values for the increase in surface potential ΔE (Table 2) on adding anthracene to solutions of various salts, relative to the potential of pure water taken as zero, shows that ions of silver and mercury produce abnormally high electrical effects. A considerable rise in

TABLE 2. Comparison of values of ΔE for solutions of various salts (anthracene film).

Supporting solution	Concentration, <i>N</i>	ΔE , mV
Water	—	0
Hg ₂ (ClO ₄) ₂	0.01	65
AgNO ₃	0.1	155
KNO ₃	0.1	5
CuSO ₄	0.1	22

TABLE 3. Surface potential of triacontane film on solutions of silver nitrate.

Supporting solution	Concentration, <i>N</i>	Surface potential, mV
Water	—	2
AgNO ₃	0.1	12
AgNO ₃	1.0	25

positive potential was observed also on application of anthracene to concentrated solutions of acids, and, as the data in Table 1 show, the surface potential on 10 *N* perchloric acid reaches 260 mV. It must be remembered, however, that this effect may be due in part to a reduction, accompanying the formation of the film of aromatic hydrocarbon, of the high negative value of the potential of this solution at the air interface which is caused by adsorption of the anion.

To confirm that the observed rise in surface potential of anthracene films on passing from pure water to silver nitrate solution is caused solely by the silver ions, the reversibility of this effect with respect to the concentration of these ions was investigated. This was done with the apparatus described previously⁸, as follows. A film of anthracene was formed on pure water, and a definite concentration of silver ions was produced beneath it by introducing a concentrated solution of silver nitrate, the change in surface potential thus produced being measured. The solution under the film was diluted by gradual withdrawal of solution and introduction of the same amount of water, and the change in potential again determined. The results show that introduction of silver ions beneath the anthracene film produces a sharp increase in surface potential, and the subsequent dilution of the silver nitrate solution produces a fall to values roughly corresponding to the new silver nitrate concentration. Further introduction of silver ions below the film again produces an increase in surface potential. The difference in value between the potential measured in these experiments and on direct addition of anthracene to solutions containing the same concentration of silver ions, which reaches 10–15%, is obviously due to the drop in potential resulting from partial breakdown of the multimolecular film when the solution beneath it is disturbed.

Thus comparison of the present results with those on the bulk reaction between silver ions and aromatic hydrocarbons⁶, as well as the adsorption behaviour of the latter at a solution-mercury interface⁴, suggests that the effect produced by the spreading of condensed aromatic hydrocarbons on aqueous salt solutions is due mainly to interaction between π electrons of the benzene nuclei and the positive charges of the ions in solution. In agreement with the conclusions of other workers⁶, we envisage that such interaction may be accompanied by partial transfer of the charge of the cation to the aromatic nucleus.

The data in Table 3 confirm the correctness of this hypothesis, showing that application of the aliphatic hydrocarbon triacontane, which does not possess π electrons, to the surface of a solution containing silver ions causes no appreciable increase in the surface potential. The slight effect observed is probably due to a considerable extent to a decrease in the negative potential (due to adsorption of the NO₃⁻ ion) of the original solution caused by the formation of the film.

The reversibility of the electrical effect with respect to the concentration of silver ions in the solution, described above, also supports this hypothesis.

In conclusion we offer our grateful thanks to Academician A. N. Frumkin for discussion of the results of the present work.

SUMMARY

1. Measurements have been made of the surface potentials of multimolecular films of the condensed aromatic hydrocarbons anthracene and chrysene on the surfaces of aqueous solutions of silver nitrate and some other inorganic salts and acids.
2. Abnormally high values of the surface potential of these films arise on solutions containing ions of silver and univalent mercury.
3. From an analysis of the results it is suggested that the adsorption and electrical effects arising on adding aromatic hydrocarbons to the surfaces of these solutions are caused by interaction between the π electrons of the aromatic hydrocarbons and the positive charges of the cations.

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THE EFFECT OF ADDED POTASSIUM SULPHATE ON THE LABILITY OF THE OXYGEN IN VANADIUM PENT-OXIDE

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The activity of oxide catalysts may be to some extent assessed by the lability of their oxygen atoms, which can be estimated by the rate at which they exchange with isotopes of oxygen in the gaseous phase. Catalysts based on