
DETERMINATION OF THE ADSORPTION FILM CHARACTERISTICS OF ALKYLTRIPHENYLPHOSPHONIUM CATIONS FROM TIME DEPENDENT CAPACITANCE MEASUREMENTS

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The determination of the adsorbed film characteristics at the interface between methanolic solutions of quaternary phosphonium salts and the Hg electrode is carried out by means of time dependent capacitance measurements. The maximum surface concentration, the area *per* adsorbed particle and the orientation of methyltriphenyl-, cyclopropyltriphenyl-, and n-butyltriphenylphosphonium cations are derived by two methods, the first of which is free of isotherm assumptions and the second involves an adsorption isotherm obeyed by the system under examination.

Most of the papers presented in the literature up to now, concerning the study of the adsorption of phenyl substituted quaternary phosphonium cations, have focussed their attention primarily to the qualitative description of the characteristics of the adsorption film development.

Peculiarities were detected during the film formation in aqueous solutions, which were reflected in the shape of the capacitance–potential and capacitance current–time curves in the form of two regions of saturation capacitance and capacitance humps, respectively, denoting the existence of interfacial rearrangements, *viz.* reorientation or surface condensation^{1–3}. In parallel, though to a secondary level, these studies also report quantitative information about the structural characteristics of the adsorbed film, *viz.* the maximum surface concentration, the orientation, and the area *per* adsorbed particle.

When the adsorption of phosphonium cations takes place from nonaqueous⁴ or mixed water–alcoholic systems^{4,5}, the peculiarities in the film formation vanish and the interest is shifted to the determination of the adsorbed film structural characteristics. Such a study is enabled by the moderate adsorption kinetics of phosphonium cations due to the diffusion control over the establishment of adsorption equilibrium of these substances.

Among the structural characteristics of the adsorption film, the maximum surface concentration of the adsorbate is of principal interest. This parameter can be determined from capacitance measurements by appropriate equations expressing the

time dependence of the differential capacitance and which are either free of isotherm assumptions⁶ or involve the certain adsorption isotherm⁷ obeyed by the system.

In the present work we attempt to apply both types of equations and check the reliability of the results obtained against theoretical predictions for the possible orientations and the area occupied by adsorbed methyltriphenyl-, cyclopropyltriphenyl-, and n-butyltriphenylphosphonium cation in methanolic solutions.

Since the application of more elaborate adsorption isotherms for organic cations⁸⁻¹⁰ has not led to definite results, the parameters required for the application of the latter method, though they would be subject to criticism, are estimated by means of Langmuir (MePh₃PBr) and Frumkin (cPrPh₃PBr and nBuPh₃PBr) isotherms which are in fair agreement with our experimental data.

EXPERIMENTAL

The experimental method is described in a previous publication¹¹. Briefly, phase selective recording of the capacitance against time, at constant electrode potentials, was carried out with a long drop time DME ($t \approx 20$ s, flow rate 0.35 mg/s) and a HMDE (drop radius $4.27 \cdot 10^{-2}$ cm). The HMDE and the electrochemical cells were kept at $25 \pm 0.05^\circ\text{C}$.

Methanol (Merck, *pro analysi*), CsCl (Merck, *pro analysi*), methyltriphenylphosphonium bromide, MePh₃PBr, (Fluka, *purum*), cyclopropyltriphenylphosphonium bromide, cPrPh₃PBr, (Fluka, *purum*), and n-butyltriphenylphosphonium bromide, nBuPh₃PBr, (Fluka, *purum*) were used without further purification, while the Hg used was doubly distilled.

The amplitude and frequency of the AC signal used were 10 mV and 75 c/s, respectively.

The reference electrode was a calomel electrode saturated with NaCl.

RESULTS AND DISCUSSION

The works of Koryta⁶ and Jehring¹², for the diffusion controlled adsorption of species at the DME -- solution interface predict a linear dependence of the differential capacitance on the square root of time, of the form:

$$C_t = C_0 - 7.36 \cdot 10^{-4} D^{1/2} (C_0 - C_{lim}) c \Gamma_{max}^{-1} t^{1/2}. \quad (1)$$

In Eq. (1) C_0 and C_{lim} are the differential capacitances at zero and maximum coverage, C_t is the time dependent capacitance at intermediate coverage, D the diffusion coefficient, c the adsorbate concentration in mol l^{-1} , and Γ_{max} the maximum surface concentration of the adsorbate.

According to its derivation, Eq. (1) is free of any isotherm constraints and it can be used as a means for the calculation of the maximum surface concentration of the adsorbing species, regardless of the isotherm obeyed.

We also know from Levich⁷ and Sathyanarayana¹³ that under diffusion control at the potential range where $d\theta/dE \approx 0$ and particularly at the potential of maximum adsorption, the differential capacitance C_t can be related to time, for a system

obeying an arbitrary isotherm, $f(\theta)$, by an equation of the form:

$$C_t = C_e + \frac{(C_0 - C_{lim}) \Gamma_{max} \theta_e f(\theta_e)}{2c f'(\theta_e)} \left(\frac{\pi}{Dt} \right)^{1/2}, \quad (2)$$

where C_e is the equilibrium value of C_t at $t \rightarrow \infty$, $\theta_e = (C_0 - C_e)/(C_0 - C_{lim})$ and all the other symbols have their usual meaning.

Therefore if the system follows the Frumkin isotherm then

$$f(\theta_e) = \theta_e(1 - \theta_e)^{-1} \exp(-2a\theta_e) \quad (3)$$

and

$$\left[\frac{dC_t}{d(t^{-1/2})} \right]_{E=E_{max}} = \frac{(C_0 - C_{lim}) \Gamma_{max} \theta_e^2 (1 - \theta_e)}{2c [1 - 2a\theta_e(1 - \theta_e)]} \left(\frac{\pi}{D} \right)^{1/2}. \quad (4)$$

On the other hand if Langmuir isotherm is obeyed, then $a = 0$ and

$$\left[\frac{dC_t}{d(t^{-1/2})} \right]_{E=E_{max}} = \frac{1}{2c} (C_0 - C_{lim}) \Gamma_{max} \theta_e^2 (1 - \theta_e) \left(\frac{\pi}{D} \right)^{1/2}. \quad (5)$$

From Eqs (4) and (5), the maximum surface concentration can be derived from the slopes of the $C-t^{-1/2}$ experimental plots, provided that we know D , θ_e , C_0 , C_{lim} and for Eq. (4) the interaction parameter, a .

Eqs (1), (4), and (5) are applied for low concentrations of the phosphonium cations ($c < 5 \cdot 10^{-5} \text{ mol l}^{-1}$), to assure the complete dissociation of the phosphonium salts in methanol and also the diffusion control on the adsorption process. The derivation of the necessary parameters was enabled by a parallel isotherm analysis of the data obtained by a conventional DME (drop time 5 s), the results of which are provided in Table I.

The measurements at the DME with long drop times for the $(\text{cPrPh}_3\text{P})^+$ and $(\text{nBuPh}_3\text{P})^+$ cations led to linear $C-t^{1/2}$ plots in agreement with Eq. (1), which are provided in Figs 1 and 2. Deviations from linearity were observed only in the $C-t^{1/2}$ plots of $(\text{MePh}_3\text{P})^+$ cations, where the experimental points are markedly scattered and so they are not provided.

The measurements at the HMDE for all the cations studied have shown that in agreement with Eqs (4) and (5), capacitance is linearly dependent on $t^{-1/2}$, (see Figs 3, 4, and 5).

From the values of Table I, the Figs 1–5 and applying equations (1), (4), and (5), we obtained the values of the maximum surface concentration, which are provided in Table II together with the corresponding values of the area occupied by each

adsorbed cation in nm^2 , obtained from the relation $S = 10^{14} \Gamma_{\text{max}}^{-1} N_{\text{A}}^{-1}$, where N_{A} is Avogadro number.

The tetrahedral structure of quaternary phosphonium cations prevents the direct contact of central atom with metal and so we can conclude that there are two permissible orientations of the adsorbed cations:

TABLE I

Adsorption parameters of MePh_3PBr , cPrPh_3PBr , and nBuPh_3PBr at the DME-methanolic solutions interface. Diffusion coefficient obtained from dc polarographic measurements

Substance	E_{max} V(SCE)	C^0 $\mu\text{F}/\text{cm}^2$	C_{lim} $\mu\text{F}/\text{cm}^2$	θ_c	Isotherm	a	D cm^2/s
MePh_3PBr	-1.00	11.5	6.08	0.19 ^a 0.24 ^b	Langmuir	0.00	$5 \cdot 10^{-6}$
cPrPh_3PBr	-1.10	13.5	6.15	0.29 ^c 0.40 ^a	Frumkin	1.00	$5 \cdot 10^{-6}$
nBuPh_3PBr	-1.00	11.5	5.04	0.34 ^c 0.42 ^a	Frumkin	0.70	$5 \cdot 10^{-6}$

^a For 10^5 . $c = 2.5 \text{ mol l}^{-1}$; ^b 3.75; ^c 1.25.

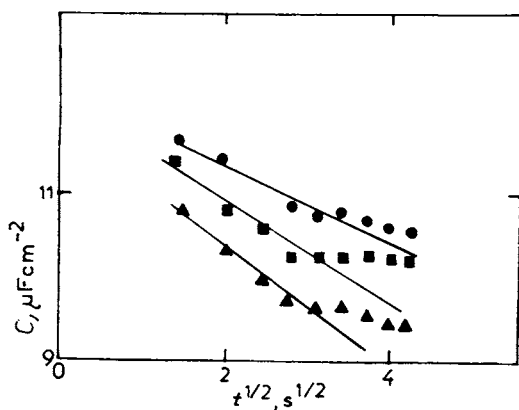


FIG. 1

Variation of the differential capacitance with $t^{1/2}$ at the DME-0.1M CsCl methanol solution interface for the following cPrPh_3PBr concentrations (mol l^{-1}): ● $7.5 \cdot 10^{-6}$, ■ $1.25 \cdot 10^{-5}$, ▲ $2.5 \cdot 10^{-5}$, at the potential of maximum adsorption

a) With the two phenyl and the alkyl group in contact with the electrode. For this case the theoretically predicted areas for the projections of $(\text{MePh}_3\text{P})^+$, $(\text{cPrPh}_3\text{P})^+$, and $(\text{nBuPh}_3\text{P})^+$ cations are respectively equal to about 0.60, 0.70, and 0.76 nm², assuming that the shape of the chain of the n-butyl group is not significantly distorted.

b) With the three phenyl groups in contact with the electrode. Here for all three substances the approximate value of 0.77 nm² is theoretically predicted.

The comparison of the experimental values of Table II with the above theoretical values shows that for $(\text{MePh}_3\text{P})^+$ cations, the experimental value of 0.73 nm² does not agree with the theoretical value of 0.60 nm². Therefore the orientation with the methyl and the two phenyl groups in contact to the electrode must be excluded.

TABLE II
Values of maximum surface concentration, Γ_{max} and area *per* adsorbed cation, S

Substance	Γ_{max} , mol cm ⁻² / S , nm ²		
	Equation (1)	Equation (4)	Equation (5)
MePh ₃ PBr	—	—	2.27 · 10 ⁻¹⁰ /0.73
cPrPh ₃ PBr	2.38 · 10 ⁻¹⁰ /0.70	2.28 · 10 ⁻¹⁰ /0.73	—
nBuPh ₃ PBr	2.15 · 10 ⁻¹⁰ /0.77	2.20 · 10 ⁻¹⁰ /0.76	—

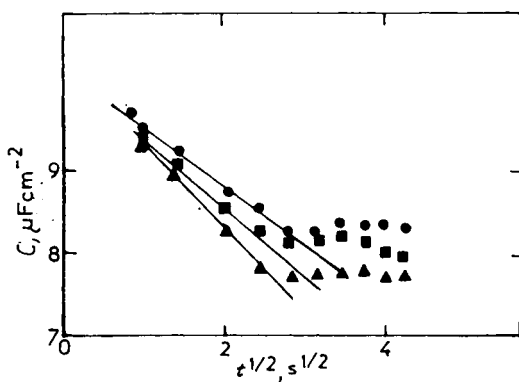


FIG. 2

See Fig. 1, nBuPh₃PBr concentrations (mol l⁻¹): ● 1.25 · 10⁻⁵, ■ 2.5 · 10⁻⁵, ▲ 3.75 · 10⁻⁵

The same can be assumed for $(n\text{BuPh}_3\text{P})^+$ cations because the theoretical projection of the n-butyl group is almost equal to 0.25 nm^2 , but under the strong interfacial fields and the close packing of the adsorption layer at high coverages, the shape of the n-butyl group must be strongly distorted, thus occupying a considerably smaller area.

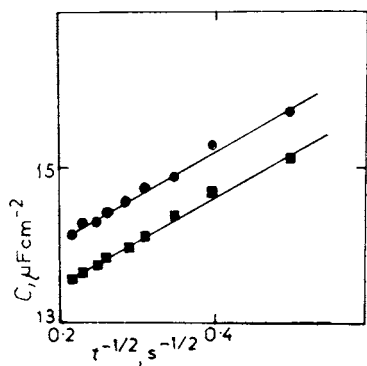


FIG. 3

Variation of the differential capacitance with $t^{-1/2}$ at the HMDE-0.1M CsCl methanol solution interface for the following MePh_3PBr concentrations (mol l^{-1}): ● $2.5 \cdot 10^{-5}$, ■ $3.75 \cdot 10^{-5}$, ▲ at the potential of maximum adsorption

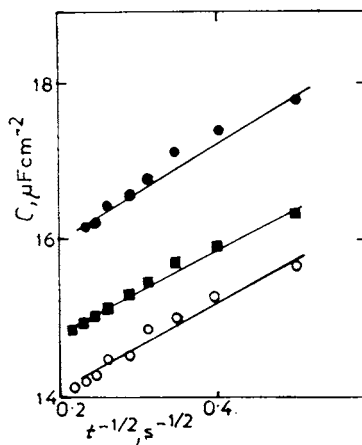


FIG. 4

See Fig. 3. $c\text{PrPh}_3\text{PBr}$ concentrations (mol l^{-1}): ● $7.5 \cdot 10^{-6}$, ■ $1.25 \cdot 10^{-5}$, ▲ $2.5 \cdot 10^{-5}$

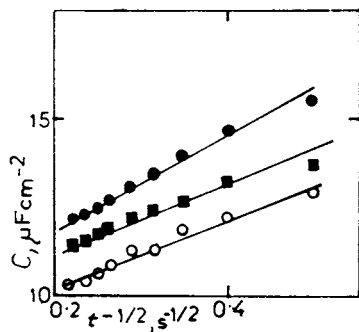


FIG. 5

See Fig. 3. $n\text{BuPh}_3\text{PBr}$ concentrations (mol l^{-1}): ● $1.25 \cdot 10^{-5}$, ■ $2.5 \cdot 10^{-5}$, ▲ $3.75 \cdot 10^{-5}$

Therefore, for $(\text{MePh}_3\text{P})^+$ and $(\text{nBuPh}_3\text{P})^+$ cations it can be assumed that the most probable orientation is that with the three phenyl groups in contact to the electrode surface.

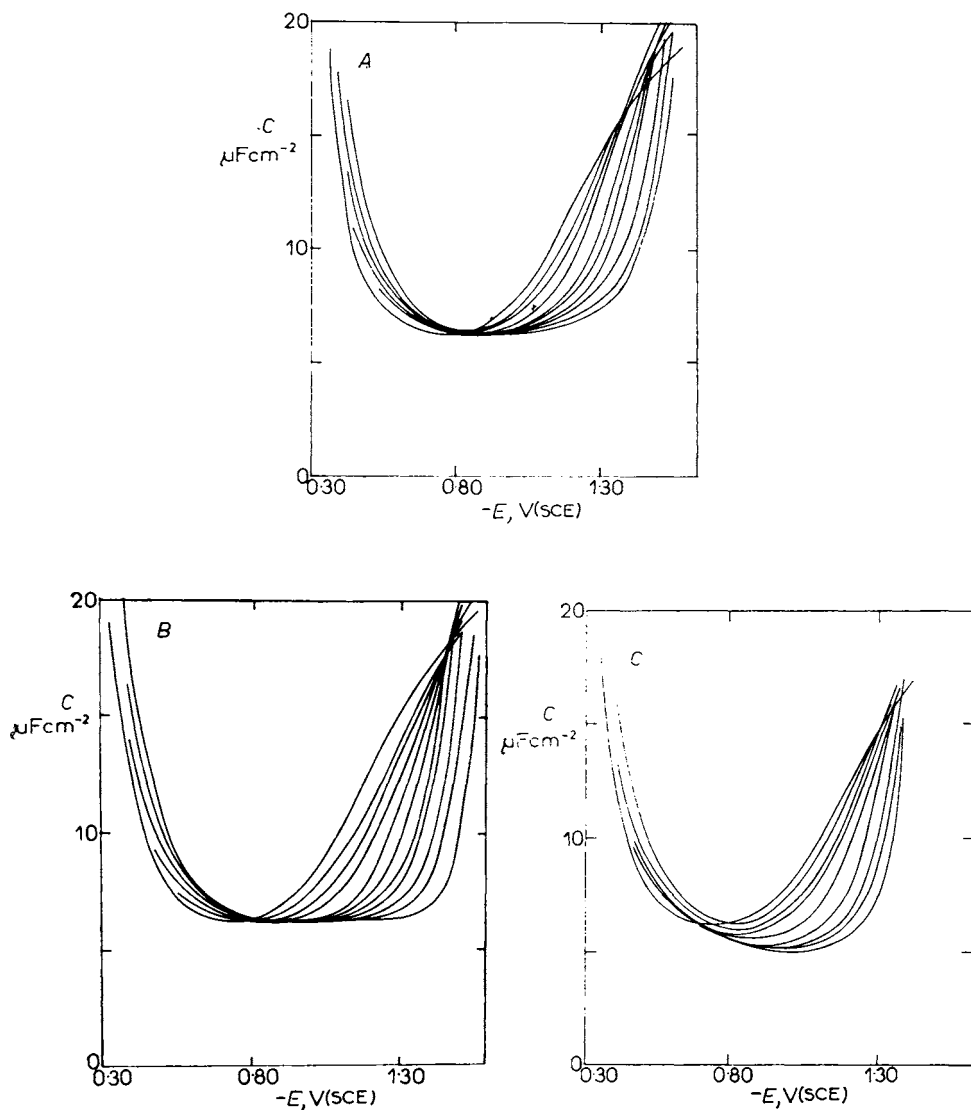


FIG. 6

Capacitance vs potential curves of 0.1M CsCl methanol solutions at the DME, with additions of A MePh_3PBr ; B cPrPh_3PBr , and C nBuPh_3PBr ; from 0.0 to $2.0 \cdot 10^{-3} \text{ mol l}^{-1}$

This orientation is supported by the strong metal – adsorbate interactions between the phenyl groups and the conduction band of Hg at positive and small negative polarizations. Since the $C-E$ curves (Fig. 6) and the time variation of the differential capacitance do not offer any indication for the occurrence of some interfacial rearrangement, such as a reorientation process, at higher negative potentials, it is concluded that $(\text{MePh}_3\text{P})^+$ and $(\text{nBuPh}_3\text{P})^+$ cations maintain the above orientation till their discharge potential, which precedes their desorption as evidenced from the $C-E$ curves of Fig. 6. For the $(\text{cPrPh}_3\text{P})^+$ cations, the agreement of the results of Eqs (1) and (4) with both the predicted orientations makes hard to decide between them. However, in our opinion, as far as at potentials positive to E_{max} the second orientation is favoured, it is also maintained up to the discharge potential of the $(\text{cPrPh}_3\text{P})^+$ cations.

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