EFFECT OF SURFACE ACTIVE CATIONS UNDERGOING INTERFACIAL REARRANGEMENTS ON DEPOSITION TYPE ELECTRODE REACTIONS

Anastos ANASTOPOULOS and Anastasia CHRISTODOULOU

Laboratory of Physical Chemistry, Chemistry Department
University of Thessaloniki, 54006 Thessaloniki, Greece

The influence of the adsorption of methyltriphenyl- and cyclopropyltriphenylphosphonium cations on simple deposition reactions of Cd^{2+} and Zn^{2+} at the dropping mercury electrode, is studied by polarographic techniques. The size parameters of the activated complex, $r^{\ne}$, and adsorbate particles, r_i, are determined and discussed. It is shown that for substances undergoing interfacial rearrangements, i.e. condensation and reorientation, the values of the size ratio $r^{\ne}/r_i$ can hardly be correlated to independently determined values of $r^{\ne}$ and r_i. Electrode coverages are related to formal rate constants and an elucidation of the inhibition mechanism is attempted.

In a series of publications[1–10], concerning the study of the adsorption of phosphonium cations, it was pointed out that these substances present an irregular development of the adsorption layer in aqueous solutions, while in non aqueous ones irregularities fade away. Of course this is not a rule, as far as it was found that the adsorption film of benzyltriphenyl phosphonium cations develops regularly both in aqueous[8] and non aqueous solutions[5].

The same also happens for methyltriphenyl phosphonium cations[7], studied in the present work. The study of the effect of adsorption of these substances, on simple deposition type electrode reactions, has proved[8,9] the validity of the well known equation suggested by Lipkowski, Gallus et al[11,12], for varying values of the ratio $r^{\ne}/r_i$ with respect to the electrode potential, where $r^{\ne}$ and r_i represent the number of solvent molecules replaced at the interface by each activated complex and surfactant particle, respectively. On the other hand, the correlation of the experimental values of r_i and $r^{\ne}$, respectively, determined from adsorption isotherms and from equations relating rate constants to the electrode coverage, is generally difficult and when condensation occurs it seems to be impossible[9], unless the mechanism of the inhibited reaction is properly determined.

The pair of substances studied in the present work offers a good opportunity for the above assertion to be verified, as far as for methyltriphenyl phosphonium bromide $(MePh_3PBr)$ no remarkable irregularities are detected, while for cyclopropyltriphenyl phosphonium bromide $(cPrPh_3PBr)$ condensation of the adsorption film occurs.

In our opinion, the study of the influence of other onium compounds of the elements of the VA group on various types of electrode reactions, viz. simple charge transfer and deposition reactions and the reduction of anions, will enable us to get safer conclusions regarding the applicability of the various kinetic equations and the nature of the inhibition mechanism.

EXPERIMENTAL

The polarographic current with respect to potential and time was recorded using the instrumentation described in earlier publications[5,6,8].

Phase selective capacitance measurements were performed using a 10 mV p.p. measuring signal with a frequency of 75 c s^{-1} and a voltage scan rate of 2 mV s^{-1}. The flow rate of the DME was equal to 2·12 mg s^{-1}, at a reservoir height of 40 cm and an open circuit free drop time of 5 s, controlled to 3 s during i–E and C–E measurements.

All solutions were bubbled by a stream of nitrogen, saturated with vapours of the base solution. Temperature was controlled at $25 \pm 0.05°C$. All potentials were measured against a large area calomel electrode saturated with KCl. Water and mercury were used after double distilation. KNO_3 (Merck, purris p.a.), MePh$_3$PBr (Fluka, purum), and CPrPh$_3$PBr (Fluka, purum) were used without further purification.

RESULTS AND DISCUSSION

Characteristics of the Adsorption Film of $(MePh_3P)^+$ and $(cPrPh_3P)^+$ Cations

The differential capacitance vs potential curves of $(MePh_3P)^+$ and $(cPrPh_3P)^+$ cations, obtained by phase selective a.c. polarographic measurements, are provided in Figs 1a and 1b, respectively. Contrary to the C–E curves of Fig. 1a, the shape of the capacitance against potential curves in the presence of $(cPrPh_3P)^+$ cations reveals the occurence of interfacial rearrangements. The abrupt decrease of the capacitance values, at $E = -0.75$ V (SCE) for $c \geqq 0.125$ m mol l^{-1} may be identified with a condensation of the adsorption layer.

Another remarkable feature of the curves in Fig. 1b is the inflection observed at -1.10 V (SCE), for cPrPh$_3$PBr concentrations lower than 0·3 mmol l^{-1}, which cannot be attributed to some condensation effect. The irregularities during film development, at the vicinity of -1.10 V (SCE), are also reflected in the form of the polarographic i–t curves of Fig. 2. At potentials out of a $\approx$ 100 mV range, around -1.05 V (SCE), the i–t curves in the presence of cPrPh$_3$PBr return to what is considered as a regular shape. Current–time curves of not unusual shape are also recorded in the presence of MePh$_3$PBr, for the overall potential range examined (Fig. 3).

The irregular features of the curves in Fig. 2, viz. the attainment of the minimum current not in one but in two steps, are similar, although much more pronounced, to those reported earlier[2,4]. It is notable that the observed hump on the i–t curves

of Fig. 2 and the inflection of the $C-E$ curves, at $E = -1\cdot10$ V (SCE), of Fig. 1b are decreasing with increasing surfactant concentration, tending to disappear com-
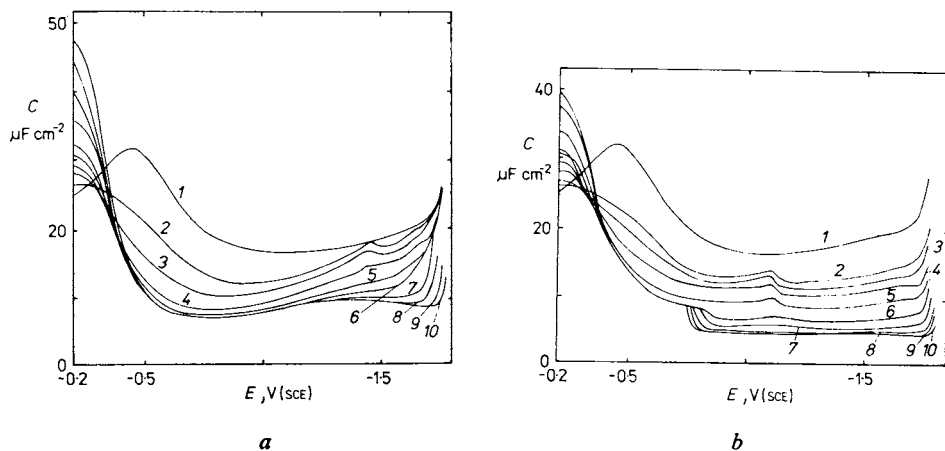

FIG. 1

Dependence of differential capacitance on the electrode potential: a for the following additions of MePh$_3$PBr in mmol l^{-1}: *1* 0·0, *2* 0·05, *3* 0·08, *4* 0·1, *5* 0·125, *6* 0·15, *7* 0·2, *8* 0·3, *9* 0·4, *10* 0·5, aqueous 0·2M-KNO$_3$; b in the presence of cPrPh$_3$PBr additions, otherwise like a
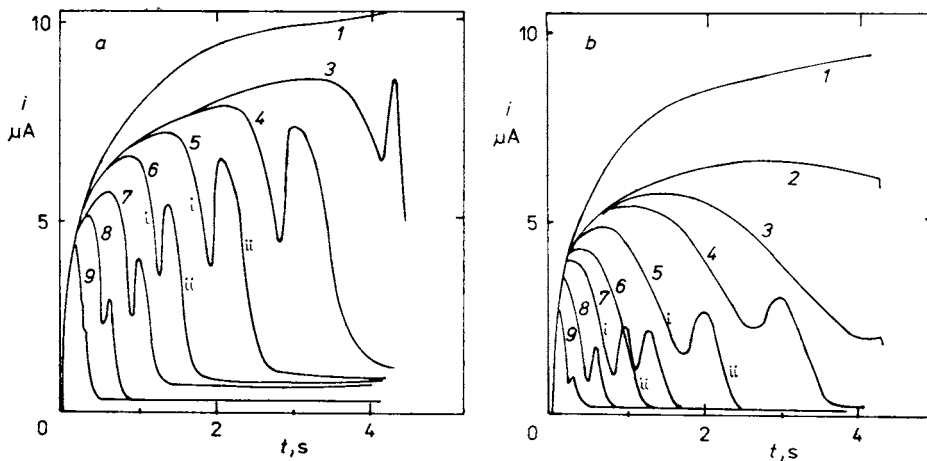

FIG. 2

Polarographic current–time curves: a for mM-Cd^{2+} reduction in the presence of the following cPrPh$_3$PBr additions in mmol l^{-1}: *1* 0·0, *2* 0·05, *3* 0·065, *4* 0·08, *5* 0·1, *6* 0·125, *7* 0·15, *8* 0·2, *9* 0·3, aqueous 0·2M-KNO$_3$, i and ii denote the two descending branches of the $i-t$ curves, potential (vs SCE) $-1\cdot00$ V; b for mM-Zn^{2+} reduction, potential (vs SCE) $-1\cdot10$ V, otherwise like a

pletely. Presumably the irregularities observed in Fig. 2 and the inflection on the
C–E curves of 1b, at $E = -1.10$ V (SCE), are due to the same structural change
in the adsorption layer. Since the condensation, already occuring at $E \cong -0.75$ V
(SCE), cannot be related to the irregularities observed at the vicinity of -1.05 V (SCE),
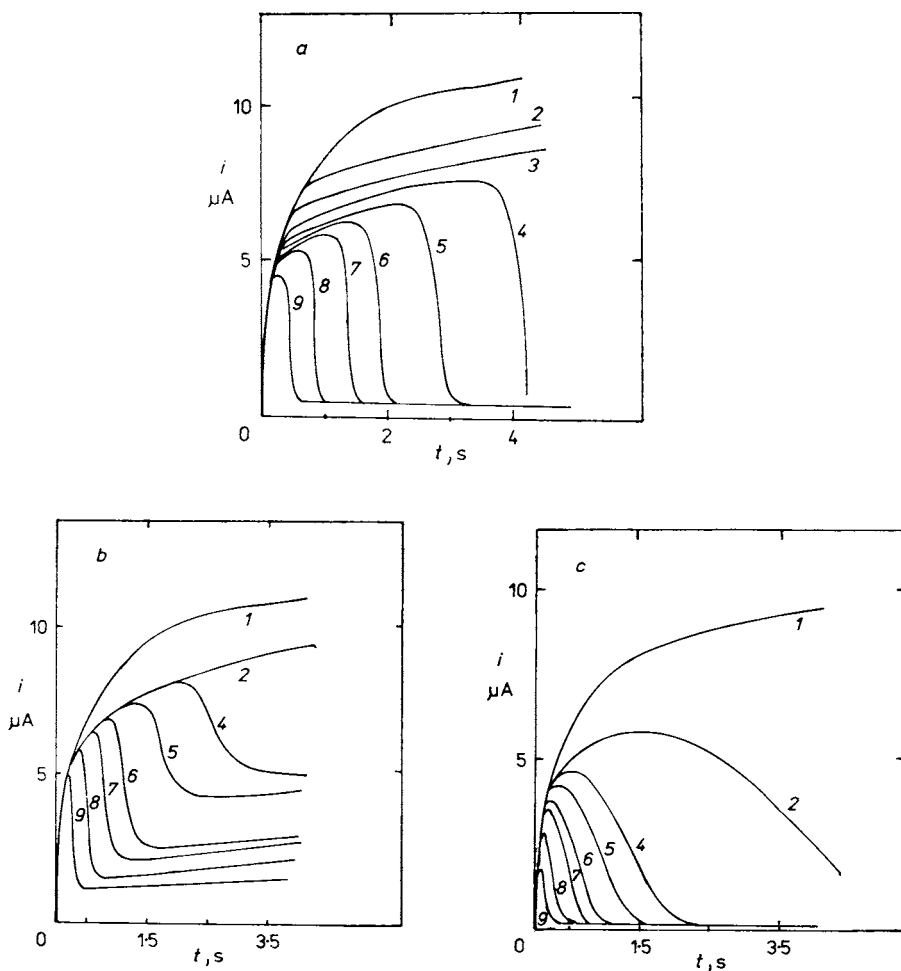only reorientation remains to be taken into account. This assumption is justified

FIG. 3
Polarographic current–time curves: a for the reduction of Cd^{2+} in the presence of the following
cPrPh$_3$PBr additions in mmol l^{-1}: *1* 0·0, *2* 0·05, *3* 0·065, *4* 0·08, *5* 0·1, *6* 0·125, *7* 0·15, *8* 0·2,
9 0·3, aqueous 0·2M-KNO$_3$, $E = -1.20$ V; b for the reduction of Cd^{2+} in the presence of
MePh$_3$PBr, $E = -1.20$ V, other data like a; c for the reduction of Zn^{2+} in the presence of
MePh$_3$PBr, $E = -1.10$ V, other data like a

by the strong attractive metal–adsorbate interactions between the phenyl groups and the conduction band of the positively charged Hg electrode. With increasing negative electrode charge the above interactions are drastically weakened. Therefore, as phosphonium cations remain adsorbed up to approximately -1.6 V (SCE), their orientation is changed in order to minimize the interactions of the phenyl groups with the electrode surface.

However, the depression of the hump observed on the i–t curves of Fig. 2 with increasing cPrPh$_3$PBr concentration, may reflect a "competition" between the simultaneously progressing condensation and reorientation processes. It seems that as the adsorbed film becomes less mobile (i.e. the more it is condensed) the rate of reorientation drops gradually. Application of the relation[13]:

$$t_s = 1.82 \cdot 10^6 \Gamma_s^2 / Dc^2 \qquad (1)$$

to both the descending branches of the i–t curves of Fig. 2 has revealed an excellent linearity (Fig. 4), (t_s is the time at which saturation coverage is attained, Γ_s is the saturation surface concentration, and $D = 5 \cdot 10^{-6}$ cm^2 s^{-1} is the diffusion coefficient of both the $(MePh_3P)^+$ and $(cPrPh_3P)^+$ cations, estimated from the polarographic limiting diffusion currents).

The values of Γ_s determined via Eq. (1) for the two branches (i and ii) of the i–t curves of Fig. 2 are found respectively equal to $(2.40 \pm 0.01) \cdot 10^{-10}$ and $(2.55 \pm 0.07) \cdot 10^{-10}$ mol cm^{-2} at $E = -1.00$ V (SCE) and $(2.40 \pm 0.08) \cdot 10^{-10}$ and $(2.48 \pm 0.02) \cdot 10^{-10}$ mol cm^{-2} at $E = -1.10$ V (SCE). It can be presumed that the structural change corresponding to these values is rather a reorientation and not

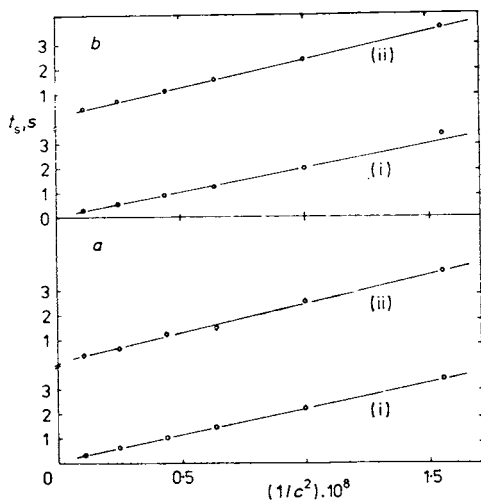

FIG. 4

Dependence of the time required for saturation coverage on the inverse square of cPrPh$_3$PBr concentration for Cd^{2+} (a) and Zn^{2+} (b) reduction, aqueous 0.2M-KNO$_3$; a $E = -1.00$ V, b $E = -1.10$ V

the condensation of the adsorption film which would produce a more pronounced increase of the Γ_s values.

The adsorbed $(cPrPh_3P)^+$ cations can be oriented with either the three phenyl groups or the two phenyl groups and the alkyl residue in contact with the electrode surface. These orientations according to space filling models correspond to 0·77 and 0·70 nm^2, respectively.

On the other hand the experimental values of Γ_s reported above correspond to $S_i = 0.69$ nm^2 and $S_{ii} = 0.65$ nm^2 at $E = -1.00$ V (SCE) and $S_i = 0.69$ nm^2 and $S_{ii} = 0.67$ nm^2 at -1.10 V (SCE). The agreement between experimental and estimated values can be considered as satisfactory within experimental error. The differences between estimated and the S_{ii} values can be attributed to the fact that reorientation occurs in an already condensed adsorption layer which implies a reduction of the area per adsorbate particle.

Figure 3b reveals that the i–t curves of Cd^{2+} reduction in the presence of $(MePh_3P)^+$ cations cannot be considered as absolutely regular ones. Curves of this type are known[13] to represent surface coverages controlled by adsorption rate. According to ref.[13], this may be due to a "reduced rate of transfer from the dissolved into the adsorbed state or to slow condensation reaction of the adsorbed particles". Although the physical interpretation of the shape of the curves in Fig. 3b is difficult, we may point out that condensation is not evidenced by the C–E curves of Fig. 1a.

The application of Eq. (1), to all the systems examined, reveals the diffusion control over the tranfer of $(MePh_3P)^+$ and $(cPrPh_3P)^+$ cations from the bulk to the adsorption layer (Table I).

The experimental adsorption isotherms of $(MePh_3P)^+$ and $(cPrPh_3P)^+$ cations, determined by means of the known[14] equation:

$$\Theta_{app} = (C_o - C)/(C_o - C_s), \qquad (2)$$

where C_o, C_s, and C are the differential capacities at $\Theta_{app} = 0$, $\Theta_{app} = 1$, and at intermediate coverage values, respectively, were found in fair agreement with the Frumkin isotherm (see Table II). The results of the isotherm analysis are reported only for the potential range from -1.00 to -1.40 V (SCE) i.e. at the vicinity of $E = -1.20$ V (SCE). This potential may be approximately related to the potential of maximum adsorption, marked by the maximum value of ΔG^0_{ads} (Table II). On the other hand the agreement with Flory–Huggins isotherm, accounting or not for interfacial interactions, was very poor for $(MePh_3P)^+$ cations.

Inhibitory Action of $(MePh_3P)^+$ and $(cPrPh_3P)^+$ Cations

The electrochemical formal rate constants of Cd^{2+} and Zn^{2+} discharge, in the presence of MePh$_3$PBr and cPrPh$_3$PBr additions, were determined by the standard

Koutecký procedure, from polarographic current vs potential curves in the potential range from -0.80 to -1.40 V (SCE) for Cd^{2+} and -1.10 to -1.40 V (SCE) for Zn^{2+} (not accounting for double layer effects). The values of the diffusion coefficients of Cd^{2+} and Zn^{2+} were found equal to $6.87 \cdot 10^{-6}$ and $6.32 \cdot 10^{-6}$ cm^2 s^{-1}, respectively. The determination of the size ratio, r^*/r_i, of the activated complex, with respect to the adsorbate particles, was made via the known equation[11]:

$$\ln k_F = -(r^*/r_i) \ln c_i + \text{const} \qquad (3)$$

at adsorbate concentrations $c_i \geqq 0.15$ mmol l^{-1}, in order to asure high coverage values $(\Theta_{app} > 0.8)$.

TABLE I

Values of the saturation surface concentration of $(MePh_3P)^+$ and $(cPrPh_3P)^+$ cations

E V (SCE)	$\Gamma_s \cdot 10^{10}$, $(MePh_3P)^+$ mol cm^{-2}	$\Gamma_s \cdot 10^{10}$, $(cPrPh_3P)^+$ mol cm^{-2}
-0.80	$2.43 + 0.08$	$2.29 + 0.02$
-1.00	$2.41 + 0.06$	(i) $2.40 + 0.01$
		(ii) $2.55 + 0.07$
-1.10	$2.40 + 0.08$	(i) $2.40 + 0.08$
		(ii) $2.48 + 0.02$
-1.20	$2.67 + 0.10$	$2.75 + 0.01$
-1.40	$3.75 + 0.27$	$2.54 + 0.03$

TABLE II

Values of the free energy adsorption, ΔG^0_{ads} (kJ mol^{-1}), the interaction parameter, a, the number of solvent molecules displaced by each adsorbate particle, r_i, and the correlation coefficient resulting from the test of the Frumkin and Flory–Huggins isotherms

E V (SCE)	Frumkin isotherm, $r_i = 1$						Flory–Huggins isotherm			
	MePh$_3$PBr			cPrPh$_3$PBr			cPrPh$_3$PBr			
	ΔG^0_{ads}	a	R^2	ΔG^0_{ads}	a	R^2	ΔG^0_{ads}	r_i	a	R^2
-1.00	29.88	1.67	0.941	29.14	1.77	0.953	29.91	0.44	2.03	0.995
-1.10	30.55	1.28	0.960	29.48	1.48	0.976	29.73	0.40	2.17	0.984
-1.20	30.59	1.07	0.965	29.78	1.57	0.953	30.63	0.46	2.01	0.934
-1.30	29.91	1.09	0.980	29.56	1.69	0.934	30.31	0.42	1.98	0.963
-1.40	28.56	1.48	0.982	28.99	1.80	0.975	30.98	0.39	1.50	0.962

The determination of the parameter r^+, which represents the number of adsorption sites occupied by the activated complex, was performed by means of equation[11]:

$$\log k_F = \log k_0 + r^+ \log (1 - \Theta) \tag{4}$$

at $0 < \Theta_{app} < 1$, where k_0 is the rate constant at zero coverage. The dependence of the logarithm of the formal rate constant of Cd^{2+} and Zn^{2+} discharge, in the presence of $(MePh_3P)^+$ and $(cPrPh_3P)^+$ cations, on the logarithm of $(1 - \Theta)$, according to Eq. (4) is shown in Fig. 5.

The results of both the calculation of r^+/r_i and r^+ are presented in Table III. An inspection of the results provided in Table III reveals that accounting for the validity of Frumkin isotherm which implies that $r_i = 1$, a reasonable correlation between the corresponding values of r^+/r_i and r^+ can be made only for solutions containing $MePh_3PBr$. From the values of r^+/r_i of Table III it is also seen that at high $(MePh_3P)^+$ and $(cPrPh_3P)^+$ coverages, the cross sectional area of the activated complex is usually 1·5 to 2·5 times greater than that of the adsorbate. In the presence of a condensed adsorption film of $(cPrPh_3P)^+$ cations, the agreement of the values of r^+/r_i and r^+, given that $r_i = 1$, seems to be limited, if it is not accidental, only to the case of Cd^{2+} reduction and at potentials positive to $-1·00$ V (SCE).

It is also interesting to report the results obtained by means of the equation[11,15]:

$$\log k_F = \log k_0 + r^+ \log (1 - \Theta) - \frac{A_{+,i}}{2·3} \Theta, \tag{5}$$
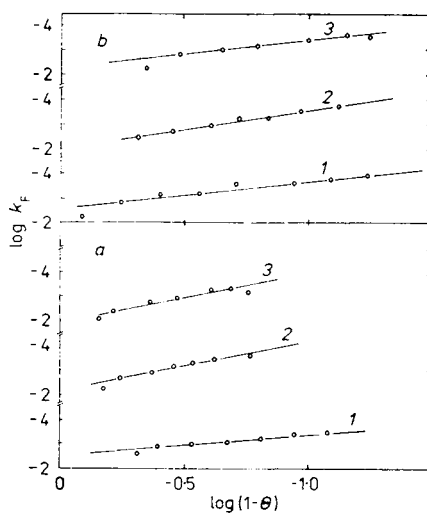

FIG. 5

Dependence of the logarithm of the formal rate constants of the reduction of Cd^{2+} on the logarithm of $(1 - \Theta)$ in the presence of a $MePh_3PBr$ and b $cPrPh_3PBr$; aqueous $0·2M-KNO_3$; E, V: 1 $-1·00$, 2 $-1·20$, 3 $-1·40$

where $A_{\ddagger,i}$ is a parameter which accounts for the specific interactions between the adsorbate and the activated complex.

TABLE III

Experimental values of $r^{\ddagger}/r_i$ and $r^{\ddagger}$ calculated via Eqs (3) and (4), respectively

E	MePh$_3$PBr		cPrPh$_3$PBr	
V (SCE)	$r^{\ddagger}/r_i$	$r^{\ddagger}$	$r^{\ddagger}/r_i$	$r^{\ddagger}$
	$Cd^{2+} + 2\,e \rightarrow Cd(Hg)$			
−0·80	1·42 ± 0·23	—	1·49 ± 0·14	1·52 ± 0·19
−1·00	1·40 ± 0·14	1·12 ± 0·28	1·77 ± 0·17	1·66 ± 0·40
−1·20	1·88 ± 0·13	1·93 ± 0·16	2·04 ± 0·21	1·70 ± 0·15
−1·40	2·22 ± 0·09	2·09 ± 0·23	2·10 ± 0·14	1·62 ± 0·26
	$Zn^{2+} + 2\,e \rightarrow Zn(Hg)$			
−1·10	1·28 ± 0·17	1·33 ± 0·40	2·56 ± 0·09	1·00 ± 0·10
−1·20	1·67 ± 0·22	1·57 ± 0·15	2·70 ± 0·18	1·35 ± 0·17
−1·30	2·23 ± 0·12	2·31 ± 0·07	2·38 ± 0·05	1·10 ± 0·14
−1·40	2·26 ± 0·24	2·46 ± 0·28	2·41 ± 0·18	1·22 ± 0·09

TABLE IV

Experimental values of $r^{\ddagger}$ and $A_{\ddagger,i}$ calculated via Eq. (5)

E	MePh$_3$PBr		cPrPh$_3$PBr	
V (SCE)	$r^{\ddagger}$	$A_{\ddagger,i}$	$r^{\ddagger}$	$A_{\ddagger,i}$
	$Cd^{2+} + 2\,e \rightarrow Cd(Hg)$			
−1·00	1·54	3·12	1·04	4·59
−1·20	1·68	0·67	0·77	−3·74
−1·40	3·57	2·35	1·74	3·10
	$Zn^{2+} + 2\,e \rightarrow Zn(Hg)$			
−1·10	2·55	5·68	1·16	−0·97
−1·20	1·99	1·10	1·18	−0·75
−1·30	2·52	0·49	1·01	0·89
−1·40	3·12	0·92	1·71	2·92

From Table IV we see that the values of r^+ are generally in poor agreement with corresponding values of r^+/r_i and r^+ determined via Eqs (3) and (4). In addition the interaction parameter, $A_{+,i}$, is seen to vary unreasonably and in some cases assumes negative values which cannot be justified for a pair of depolarizer and adsorbate particles of the same charge type.

These findings show that although the agreement of experimental data with Eq. (5) is generally satisfactory, $R^2 > 0.93$, this equation does not offer a realistic relation between the experimental values of k_F and Θ.

Concluding, the characteristics of the adsorption and inhibition behaviour of $(MePh_3P)^+$ cations are the following: (i) Regular development of the adsorption film within the potential region $-0.50 \leq E \leq -1.40$ V (SCE). (ii) Fair agreement with Frumkin isotherm in the above potential region. No agreement with Flory--Huggins isotherm. (iii) Satisfactory compatibility of the values of r^+/r_i and r^+, provided that Frumkin isotherm is obeyed, i.e. $r_i \approx 1$. (iv) Higher corresponding values of k_F compared to $(cPrPh_3P)^+$ cations, i.e. weaker inhibitory action.

The corresponding characteristics of $(cPrPh_3P)^+$ cations are the following: (i) Irregular development of the adsorbed film. Condensation takes place at concentration higher than 0.1 mmol l^{-1} and at potentials negative to -0.75 V (SCE). In addition, at $E = -1.10$ V (SCE) another interfacial rearrangement is taking place which can be probably identified with a reorientation of the adsorbate particles. In the above potential range the reduction of Cd^{2+} and Zn^{2+} may take place through holes[16] in the adsorbed film, at rates decreasing with increasing $cPrPh_3PBr$ concentrations. (ii) Satisfactory agreement with Frumkin and Flory–Huggins isotherm. (iii) No agreement between the values of r^+/r_i and r^+, provided that $r_i \approx 1$, at potentials where condensation occurs. (iv) Markedly lower corresponding values of k_F, i.e. stronger inhibitory action, probably due to the simultaneous action of the electrostatic repulsion between the reactant and adsorbate particles and the enhanced blocking effect from a condensed layer.

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