

TIME DEPENDENT INTERFACIAL BEHAVIOUR OF TRIBUTYLPHOSPHINE OXIDE AT THE MERCURY – SOLUTION INTERFACE

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A series of methods are used for the quantitative description of the time dependent interfacial behaviour of tributylphosphine oxide (TBPO). These methods include measurements of the interfacial tension by a capillary electrometer as well as differential capacitance measurements with a dropping mercury electrode (D.M.E.) of short drop times (≤ 5 s), a D.M.E. of large drop times (≈ 20 s) and a hanging mercury drop electrode (H.M.D.E.).

The capacitance measurements with large drop times reveal the existence of peculiarities during the development of the adsorption film. The adsorption equilibrium of TBPO, at the vicinity of the adsorption maximum, is generally established within times shorter than 10 s. At the region of the adsorption pseudocapacity, time intervals ranging from 200 to 400 seconds are required for the equilibrium. The adsorption parameters derived with the large drop time D.M.E., are in reasonable agreement with those obtained by electrocapillary measurements.

The study of the interfacial behaviour of large organic molecules and organic cations with particular emphasis to the time dependence of the adsorption of these substances, is a subject which keeps attracting attention of various investigators. However, except for some noticeable theoretical papers¹⁻³, there are rather few ones⁴⁻⁷ which attempt a straight forward involvement of time dependent measurements of the interfacial tension and the double layer capacitance in the derivation of the adsorption parameters.

As a contribution to this topic in the present paper we attempt the study of the time dependence of the adsorption of tributylphosphine oxide (TBPO) from aqueous electrolyte solutions, making use of systems which allow for long exposition times of the electrode surface and comparing results obtained at different degrees of approach to the equilibrium conditions. These experimental methods include electrocapillary and differential capacity measurements with a D.M.E. of short (≈ 5 s) and large (≈ 20 s) drop times and the H.M.D.E.

Our selection of TBPO was guided by the need to have an adsorbate-solvent pair where the competition between their molecules leads to strong adsorbability, diffusion controlled adsorption and good agreement of the experimental data to one of the

non ionic adsorption isotherms, a fact that gives an internal consistency to the results obtained. Attention is also paid to the discussion which appeared in the literature^{5,6,8-12} related to the characteristics of the film formation and to the experimental findings concerning the adsorption of various phosphine oxides.

EXPERIMENTAL

Capacitance measurements were performed by fundamental harmonic phase sensitive AC polarography, at a phase difference of $(90 \pm 0.2)^\circ$, with a 10 mV pp alternate signal of 75 c/s, applied across the cell using a E-506 METROHM POLARECORD system. The accuracy of our measurements was checked against Grahame's measurements¹³ for KCl. The *C-E* curves were recorded with a voltage scan rate of 2 mV/s followed by a point by point static scan. The capillary electrometer used is described in a previous publication¹⁴. The electrochemical system used was the following:

Hg	xM TBPO 0.1M-LiClO ₄ H ₂ O	0.1M-LiClO ₄ H ₂ O electrolytic contact	0.1M-LiClO ₄ H ₂ O	s.c.e. NaCl H ₂ O
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Mercury was a product of double distillation. The characteristic of the D.M.E. with short drop times were: 2.024 mg/s (flow rate) and a drop time of 5 s controlled to 2 s by a drop timer system. The D.M.E. with large drop times had a flow rate of 0.258 mg/s and a drop time of about 20 s. The H.M.D.E. was carefully controlled to obtain a drop radius of $4.57 \cdot 10^{-2}$ cm during all the measurements. Anhydrous LiClO₄ (Ventron GMBH, 99.5%) and TBPO (Merck, zur Synthese) were used without further purification. The solutions were deaerated by a stream of purified nitrogen previously saturated with vapours of the test solution. All measurements were carried out at $(25 \pm 0.05)^\circ\text{C}$.

RESULTS AND DISCUSSION

Measurements at the D.M.E. with Short Drop Times

Figure 1 shows the differential capacitance *vs* the DC bias voltage curves of aqueous 0.1M-LiClO₄ in the presence of various TBPO concentrations.

It can be seen that the potential region of the "true" differential capacity ranges from -0.15 to -1.40 V/s.c.e. The *C-E* curves of TBPO present well formed cathodic and anodic maxima. At potentials out of the adsorption region the capacitance curve of the base electrolyte coincides with the curves in the presence of TBPO because at these polarizations it is desorbed from the interface.

At the minimum of the *C-E* curves, the capacitance goes down to a limiting value equal to $4.07 \mu\text{F}/\text{cm}^2$. However for the saturation capacitance, C_s , we used in our calculations the value $4.03 \mu\text{F}/\text{cm}^2$, obtained from capacitance *versus* time measurements at the H.M.D.E. at potentials -0.60 , -0.65 and -0.70 V/s.c.e. and at times greater than 60 s.

From the $C-E$ curves of Fig. 1 the experimental adsorption isotherms of TBPO are obtained and they are given in reduced coordinates in Fig. 2.

The coincidence of the experimental points corresponding to various potentials from -0.50 to -1.20 V/s.c.e. at a single curve suggests that the experimental isotherms are congruent with respect to the electrode potential.

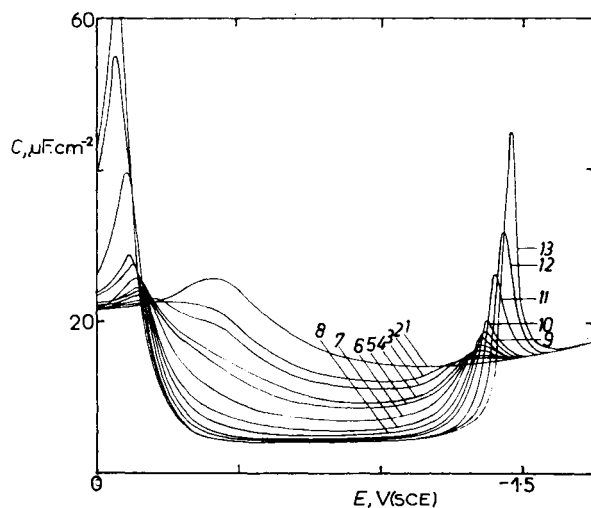


FIG. 1

Differential capacitance curves of aqueous 0.1M-LiClO_4 in the presence of the following TBPO concentrations in mmol/l : 1 0.00; 2 0.025; 3 0.035; 4 0.05; 5 0.06; 6 0.075; 7 0.10; 8 0.125; 9 0.15; 10 0.20; 11 0.40; 12 0.80; 13 1.00

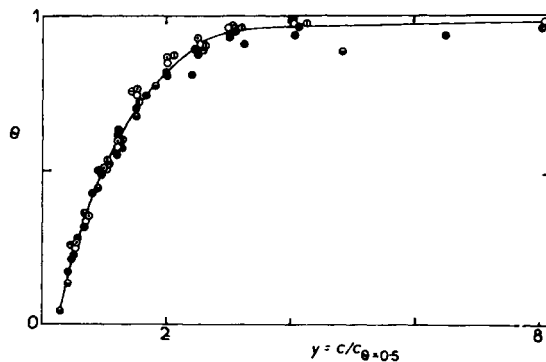


FIG. 2

Adsorption isotherms in reduced coordinates of TBPO from aqueous 0.1M-LiClO_4 solutions at constant potentials: ○ -0.5 ; ⊙ -0.6 ; ⊖ -0.7 ; ⊕ -0.8 ; ⊗ -0.9 ; ⊘ -1.00 ; ● -1.10 ; ⊙ -1.20 V/s.c.e.

In order to obtain further information about TBPO, the experimental adsorption isotherms were tested against the theoretical adsorption isotherm of Frumkin¹⁵ set in linear form:

$$\ln \frac{\theta}{(1-\theta)c} = \ln B + 2a\theta. \quad (1)$$

The results of this test are shown in Fig. 3.

It can be seen that the experimental data for the adsorption of TBPO are in fair agreement with the Frumkin isotherm.

The interaction parameter, a , of Eq. (1), derived from Fig. 3, is found equal to 1.10, within the accuracy of our measurements, over the whole potential range from -0.60 to -1.20 V/s.c.E. The interaction parameter was also calculated at the potentials of the anodic and cathodic capacitance maxima by means of the non thermo-

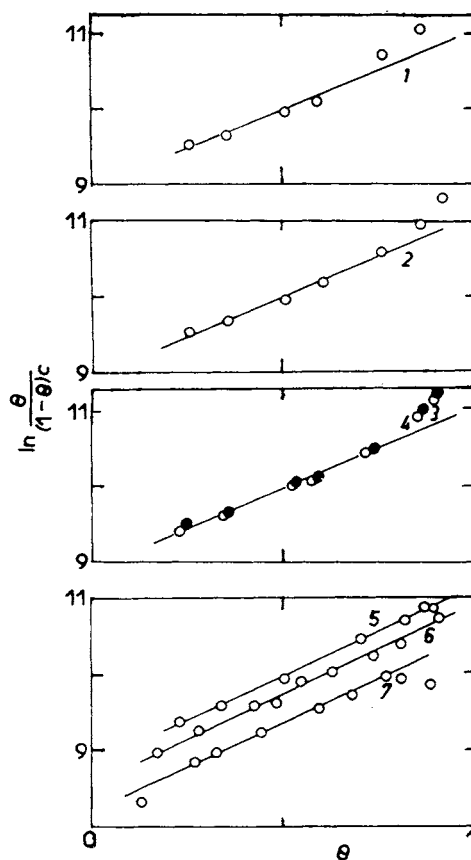


FIG. 3

Test of Frumkin isotherms at constant potentials: 1 -0.6 ; 2 -0.7 ; 3 -0.8 ; 4 -0.9 ; 5 -1.0 ; 6 -1.1 ; 7 -1.2 V/s.c.E. for the adsorption of TBPO from aqueous $0.1M$ - $LiClO_4$ solutions

dynamic method proposed by Damaskin¹⁵, by using the width of the maxima at the three quarters of their height. The eventual non equilibrium character of the the $C-E$ curves was taken into account and a value of $a = 1.46$ was obtained at the cathodic peaks while a value of $a = 0.31$ was obtained at the anodic ones. These values are only in qualitative agreement with the findings of¹².

The above values of the interaction parameter of TBPO are systematically lower than the values suggested in the literature^{5,10-12} for similar or analogous substances. These differences can be understood if we examine the two types of interactions, *i.e.* the adsorbate-solvent (A-S) and adsorbate-adsorbate (A-A) – which mainly determine the value of the interaction parameter.

For TBPO in contrast to other phosphine oxides – especially those which are phenyl substituted – the A-S interactions do not have an hydrophobic character due to its high solubility in water, and therefore they act oppositely to the A-A attraction, thus producing lower values (< 1.50) of the interaction parameter.

From Fig 3. and Eq. (1) we also obtained the variation of the adsorption equilibrium constant, B , against the potential which is presented in Fig. 4.

The maximum of the curve in Fig. 4 is located between -0.60 and -0.70 V/s.c.e. Evidently the potential of maximum adsorption of TBPO is located within these limits. The value of B corresponding to the maximum of Fig. 4 is equal to $7.6 \cdot 10^3 \text{ l mol}^{-1}$. This rather low value is presumably due to the low contribution of the metal-adsorbate (M-A) interactions which mainly determine the values of the ad-

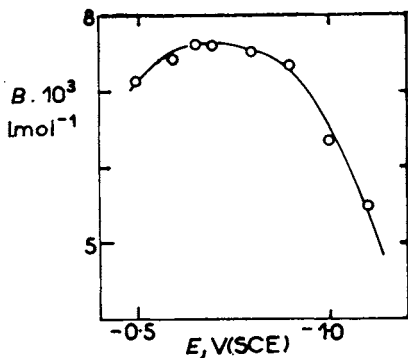


FIG. 4

Potential dependence of the adsorption equilibrium constant of TBPO from aqueous 0.1M-LiClO_4 solutions

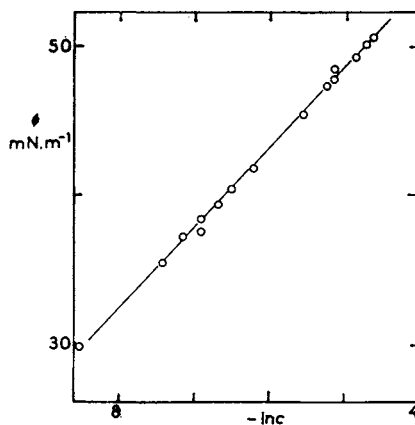


FIG. 5

Surface pressure due to the adsorption of TBPO on Hg from 0.1M-LiClO_4 aqueous solutions, plotted as a function of $\ln c$

sorption equilibrium constant. For TBPO the M–A interactions must be considerably weaker than those for the phenyl substituted phosphinoxides, where the π -electrons of the phenyl groups strongly interact with the conduction band of Hg thus leading to markedly higher values for B and ΔG_{ads}^0 (refs⁵⁻¹⁰). The value of the standard free energy of adsorption at the potential of maximum adsorption was calculated by means of Eq. (2):

$$\Delta G_{\text{max}}^0 = -RT \ln 55.5 B_{\text{max}} \quad (2)$$

and it was found equal to -32.1 kJ/mol which is in reasonable agreement to the values given in ref.¹².

Electrocapillary Measurements

The electrocapillary measurements of TBPO have revealed the existence of moderate adsorption kinetics especially at low TBPO concentrations. To overcome the difficulties imposed by the kinetic effects, we used the same method as in⁸. The procedure was as follows: Electrocapillary curves were first recorded at high TBPO concentrations ($\geq 8 \cdot 10^{-3}$ mol/l) at the potential range from -0.10 to -1.00 V/s.c.e., such as to minimize the kinetic effects. In turn we calculated the electrode charge and potential of maximum adsorption from charge *vs* potential curves¹⁶. The coordinates of the point of maximum adsorption of TBPO are $\sigma_{\text{max}}^M = -4.20$ $\mu\text{C}/\text{cm}^2$ and $E_{\text{max}} = -0.65$ V/s.c.e. Finally systematic measurements of the interfacial tension were made at the potential of maximum adsorption of TBPO. The results of these measurements are given in Fig. 5 in the form of surface pressure *vs* $\ln c$ curves.

The linearity of the Φ *vs* $\ln c$ curves does not enable the determination of the form of the adsorption isotherm. However, from Fig. 5 we can obtain the value of the saturation surface excess $\Gamma_s = 2.19 \cdot 10^{-10}$ mol/cm². This value leads to the corresponding value of the area, S_{org} , per adsorbed TBPO molecule which is equal to 0.76 nm².

Measurements at the H.M.D.E.

Measurements of the differential capacitance against time at the H.M.D.E. in the presence of low TBPO concentrations ($< 10^{-4}$ mol/l) were made at potentials -0.1 , -0.2 , -0.5 , -0.6 , -0.65 , -0.7 , -1.4 , and -1.5 V/s.c.e. In Fig. 6a we provide indicatively the C - t curves at the potentials: -0.2 V/s.c.e. (anodic maxima) and -1.4 V/s.c.e. (cathodic maxima). In Fig. 6b the C - t variation at the potential of maximum adsorption, $E_{\text{max}} = -0.65$ V/s.c.e., is provided.

It can be seen that the major variation of C against time for not too low concentration takes place in all cases within the first 10 s, in agreement with⁵. Beyond this point we have a slower decrease toward the equilibrium value. At intermediate polarizations

and for $c_{\text{TBPO}} \geq 2.5 \cdot 10^{-5}$ mol/l, the equilibrium is established after about 10 s at the value of $C_s = 4.03 \mu\text{F}/\text{cm}^2$ which is assumed as the equilibrium saturation capacitance. At the cathodic capacitance maxima we have a much slower establishment of equilibrium at $t_{\text{eq}} > 200$ s, while at the anodic peaks the equilibrium capacitance is always reached within 100 s.

Measurements at the D.M.E. with Long Drop Times

The capacitance current *versus* time measurements at the D.M.E. with drop time up to ≈ 20 s, have revealed the existence of i_c - t AC polarographic curves (Fig. 7) of unusual form, similar to that observed in ref.⁵.

The form of the curves of Fig. 7 shows that, for certain concentrations irregularities in the form of broad humps occur during the development of the adsorption film of TBPO and they can be reasonably identified with abrupt changes of the electrode surface coverage. These broad humps are observed only within the intermediate potential region (from -0.4 to -1.3 V/s.c.E.) and they gradually shift to the beginning of the drop life increasing TBPO concentration. In ref.⁵ the irregularities

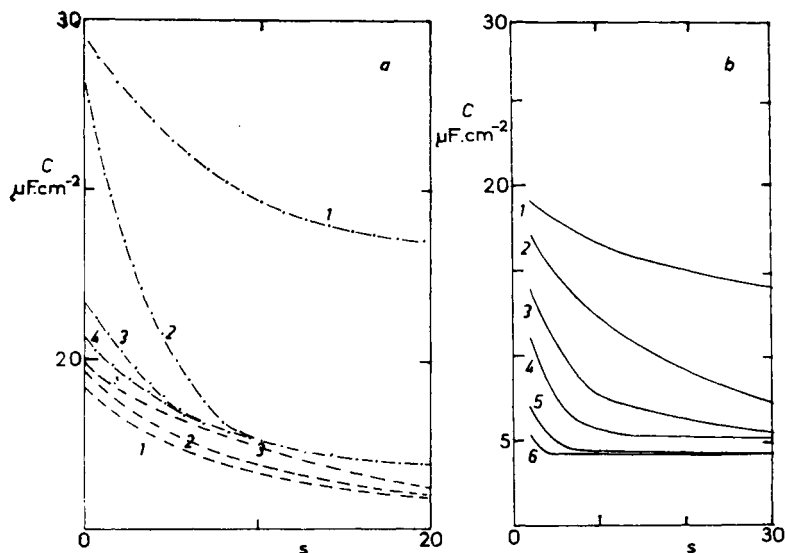


FIG. 6

Time dependence of the capacitance of the H.M.D.E. in aqueous 0.1M-LiClO_4 solutions containing the following TBPO concentrations in mmol/l: a: 1 0.025; 2 0.05; 3 0.075; 4 0.1; b: 1 0.001; 2 0.005; 3 0.0075; 4 0.01; 5 0.025; 6 0.05. Potentials in V/s.c.E. indicated by: (----) -0.2 ; (-.-.-) -1.4 ; (—) -0.65

observed during the film formation of triphenylphosphine oxide and triphenylphosphonium propyl bromide were interpreted in terms of strong intermolecular attraction ($a > 1.5$) and large surface activity ($B \approx 10^6$ l/mol) of these substances. Our views for the values of B are presented in the first part of the discussion section of this work. For the interaction parameter as far as it is of a so called "sum up" character it is helpful to recourse to the particular types of interactions which finally determine its values. As mentioned above, these interactions are the A-A, A-S, and S-S interactions which for the pair TBPO-H₂O can be assumed as attractive ones. As far as the possibility of the reorientation of the adsorbed TBPO molecules at a certain time instant and at E_{\max} can be excluded for the interpretation of the irregular i_c-t curves, the most reasonable possibility that can be examined is that of a sudden desorption of the adsorbed water molecules. It can be assumed that these water molecules were hold at the interface by some sort of "hysteresis" effect produced in the interfacial region by the strong A-S interactions. The above reasoning can be understood in terms of the competition between the attractive A-A and A-S interactions. In this sense at the beginning of the drop life and for low TBPO concentrations the A-S attraction prevails thus causing some hysteresis in the structure of the adsorption layer. With increasing time the surface concentration of TBPO increases and at some instant the A-A attraction overcomes the effect of the A-S attraction

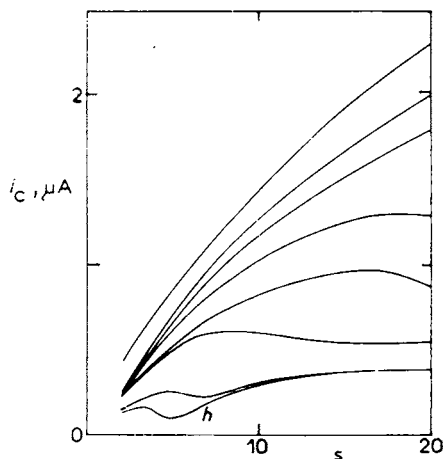


FIG. 7

AC polarographic i_c-t curves of 0.1M-LiClO₄ in the presence of the following TBPO concentrations mmol/l, from top to bottom: 1 0.0; 2 0.001; 3 0.005; 4 0.0075; 5 0.01; 6 0.025; 7 0.05; 8 0.075

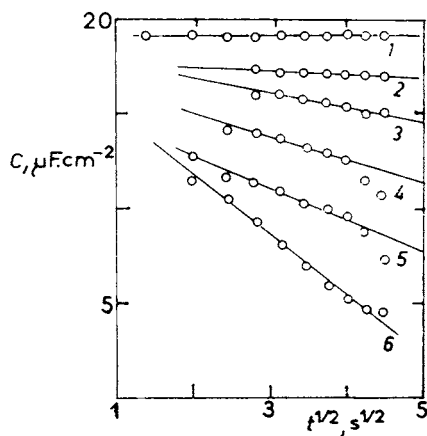


FIG. 8

Plots of C versus $t^{1/2}$ for aqueous 0.1M-LiClO₄ containing 1 0.0; 2 0.001; 3 0.005; 4 0.0075; 5 0.01; 6 0.025 mmol/l TBPO

thus leading to the desorption of water molecules and their subsequent replacement by more TBPO molecules. In any way the complexity of the interfacial conditions makes such qualitative interpretations to be open to dispute. Further investigations for the existence of irregular i_c-t curves in non aqueous or mixed solvent media would probably offer additional evidence for the role of the A-S interactions.

From the i_c-t AC polarographic curves, the plots of C vs $t^{1/2}$ were derived for TBPO concentrations $\leq 2.5 \cdot 10^{-5}$ mol/l and they are presented in Fig. 8.

The linearity of the plots of Fig. 8 is considered as satisfactory and this is in agreement to Eq. (3) which is derived on the basis of the assumption of purely diffusion controlled adsorption¹⁻².

$$C_t = C_{ot} - 7.36 \cdot 10^{-4} D^{1/2} (C_{ot} - C_s) c_{org} \Gamma_s^{-1} t^{1/2}. \quad (3)$$

The application of Eq. (3) also accounts for the fact that no condensation effects¹ can be detected in the adsorption layer of TBPO as it is evident from the form of the C-E curves of Fig. 1. In Eq. (3) C_{ot} and C_t are the instantaneous values of capacitance in the absence and in the presence of TBPO, C_s is the saturation capacitance, c_{org} is the surfactant concentration in mol/l, Γ_s is the saturation surface excess concentration and D is the diffusion coefficient of TBPO which is taken equal to the value of $6.3 \cdot 10^{-6}$ cm²/s, provided in¹⁰ for a series of phosphine oxides. For $c_{TBPO} > 2.5 \cdot 10^{-5}$ mol/l the almost immediate attainment of the equilibrium capacitance leads to C- $t^{1/2}$ curves with zero slope, which does not allow for the application of Eq. (3) for the calculation of Γ_s . The fit of the experimental curves of Fig. 8 to Eq. (3) yields Γ_s values ranging from 2.00 to $2.23 \cdot 10^{-10}$ mol/cm² increasing with TBPO concentration. Although this variation lacks physical meaning, the values obtained are in reasonable agreement to that of $\Gamma_s = 2.19 \cdot 10^{-10}$ mol/cm² obtained by electrocapillary measurements. As it results from Eq. (3), for Γ_s to be concentration independent the slope of the C vs $t^{1/2}$ plots should counterbalance the increase in c_{org} . This was not achieved, possibly because of the scatter of our experimental points, which is mainly produced by the unusual form of the i_c-t curves. In addition if we account for the positive shift of the pzc ($E_N \cong 0.4$ volts), which implies that the TBPO dipole is adsorbed with its positive end towards the electrode surface, we can coestimate the experimental value of $S_{TBPO} = 0.76$ nm².

Although it was not possible to achieve an accurate calculation of the theoretical value of S_{TBPO} , an approximate calculation for the three butyl groups oriented towards the electrode gives a value ranging from 0.7 to 0.8 nm² which does not contradict our experimental findings.

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