Adsorption of Triphenyl Phosphine Oxide at the Dropping Mercury Electrode in Methanolic Solutions

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(Z. Naturforsch. 27 b, 631—636 [1972] ; received January 22, 1972)

Triphenyl Phosphine Oxide (TPO) which is known as a strong inhibitor of electrode processes in aqueous solutions is progressively adsorbed at the dme from methanol in the potential range —0.5 to —1.3 volts as compared with water, —0.15 to —1.6 volts (Ag/AgCl), for the concentrations studied. Adsorption activity as well as the sharpness of the desorption peak of TPO decrease in the order: water > 50% methanol > methanol and the adsorption region contracts as the solvent is changed from water to methanol. Adsorption isotherms in methanol and 50% methanol follow Langmuir’s equation with adsorption coefficients equal to 1.58 x 10^2 l/mole and 1.62 x 10^4 l/mole respectively.

Triphenyl phosphine oxide (TPO) is known to be a strong inhibitor in aqueous solutions. However, the behaviour of this substance in non-aqueous solvents has until now remained unstudied. The study of this problem is of definite interest as much as non-aqueous solutions are widely used in electrochemistry, particularly in polarography, where adsorption effects play a large role.

The present investigation, therefore, gives the results obtained in the study of adsorption of TPO in methanolic solutions and the comparison of its surface activity in aqueous solutions.

Experimental

Tensammetric curves were recorded by Polarecord (type E 261) from Metrohm AG, Herisau/Schweiz, along with A.C. Modulator E 393 using 50 Hz and 10 mv (r.m.s.). Water free pure methanol was used as the solvent and the other substances used were either chemically pure or were recrystallised/redistilled before use. The dissolved atmospheric oxygen was removed from the solution with a stream of purified nitrogen which was preliminary saturated with vapours of the test solution. Ag/AgCl electrode dipped in
saturated LiCl solution in methanol was used as a reference electrode. The outer jacket of the reference electrode was filled with 1 M LiCl solution in methanol and this solution was changed from time to time to avoid any contamination of the electrode with surfactant and the change of the alternating current due to change in the resistance of the system. The capillary used for the dropping mercury electrode (dme) gave \( m = 2.36 \text{ mg/s} \) and \( t = 3.50 \text{ s/drop} \) in 0.1 M LiCl in methanol (open circuit) at \( h = 40 \text{ cm} \) (uncorrected for back pressure). The mercury used was first purified chemically and subsequently distilled under reduced pressure.

The tensammetric curves in presence of TPO in various solvents represent the equilibrium curves as determined by the variation of the drop-time.

**Results and Discussion**

Figs. 1, 2, and 3 give the adsorption of TPO at various concentrations in pure methanol, 50% methanol and pure water respectively. As can be seen, TPO gets adsorbed at the dme from methanol in the potential range \(-0.5\) to \(-1.3\) volts (Ag/AgCl) although its adsorption activity decreases markedly and the adsorption region contracts considerably as compared with that from water and 50% methanol. Only cathodic desorption peak is observed from methanolic and 50% methanolic solutions as compared to cathodic and anodic desorption peaks of TPO in water. The adsorption activity and the sharpness of the cathodic peak of TPO decrease in the order water > 50% methanol > methanol. Further, the potential corresponding to the maximum adsorption of TPO varies with concentration of TPO in methanolic and 50% methanolic solutions at lower concentrations.

The fact that on passing from water to methanol the adsorption activity of TPO decreases markedly and its adsorption region contracts considerably
can be explained firstly by the effect of the adsorption of solvent molecules and secondly by the adsorption of cations of the supporting electrolyte and the increase in the solvation of TPO in methanol which leads to a decrease in the surface activity of TPO in methanol.

Fig. 4 gives the dependence of the desorption potential ($E_{\text{des.}}$) on log concentration of the surfactant in methanol, 50% methanol and water respectively. The relations are linear as expected from F r u m - k i n - D a m a s k i n theory.

HANSEN et al. showed that at the potential corresponding to maximum adsorption, the fraction of the surface covered, $\theta$, is related to the differential double layer capacity per unit area $C$, by the equation:

$$\theta = \frac{(C_0 - C)}{(C_0 - C')}$$

where $C_0$ is the value of $C$ at the same potential in the absence of surface active agent and $C'$ is the value corresponding to a saturated monolayer. The value of $C'$ is given by extrapolating the dependence of the reciprocal of the capacitance at the minimum of the $C$ vs. $V$ curve from the reciprocal of the concentration to $1/c = 0$.

If the tensammetric currents are taken proportional to the differential capacity of the double layer, Fig. 5 gives the adsorption isotherms of TPO in methanol and 50% methanol at potentials corresponding to their maximum adsorption. It can be seen that the adsorption isotherms follow L a n g - m u i r's equation in the concentration ranges $0.011 \text{ m}$ to $0.072 \text{ m}$ and $0.028 \times 10^{-2}$ to $0.288 \times 10^{-2} \text{ m}$ of TPO with adsorption coefficients equal to $1.58 \times 10^2/\text{mole}$ and $1.62 \times 10^4/\text{mole}$ in methanol and 50% methanol respectively (vide Fig. 6).

Fig. 5. Adsorption isotherms of TPO; curves 1 and 2 — in methanol and 50% methanol respectively.

Fig. 6. Plot of $1/\theta$ vs. $1/c$; curves 1 and 2 — in methanol and 50% methanol respectively.

One of the authors (S. L. G.) is indebted to the Alexander von Humboldt Foundation, BRD, for the award of a senior fellowship and to the B.I.T.S., Pilani (India) for sanctioning leave of absence.

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