Effect of Depolarizers on the Desorption Potential of Inhibitor at the Dropping Mercury Electrode in Methanol

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Organic compounds are known to adsorb more or less strongly at the dropping mercury electrode (dme) from aqueous solutions and affect the kinetics of the electrode processes. However, very little data are available for such studies from non-aqueous solutions. We have recently seen that the triphenyl phosphine oxide (TPO) which is known as a strong inhibitor in aqueous solutions[1] is also progressively 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. Only cathodic desorption peak is observed from methanolic solution which is rounded as compared to anodic as well as cathodic desorption peaks of TPO from water which are sharp.

This note, however, gives the effect of depolarizers on the desorption potential of TPO at the dme in methanol.

Experimental

D.C. polarograms were recorded by Polarecord (type E 261) from Metrohm AG, Herisau/Schweiz. The same instrument along with A. C. Modular E 393 was employed for recording tensammetric curves and a.c. polarograms using 50 Hz and 10 mV (r.m.s.). Water free pure methanol was used as the solvent and the other substance used were either chemically pure or were recrystallised/redistilled before use. Ag/AgCl electrode dipped in saturated LiCl solution in methanol and N.C.E. in water were used as reference electrodes.

Results and Discussion

Fig. 1 gives the experimental finding for the influence of various concentrations of azobenzene on the desorption potential of TPO without iR correction ($E_{\text{des.}}$). It can be observed that this desorption potential shifts to more negative value in presence of depolarizer and the negative shift increases with increasing concentration of the depolarizer. Such negative shift is also found with other depolarizers (Table 1) being reduced at potentials $< E_{\text{des.}}$. However, depolarizers with $E_{1/2} > E_{\text{des.}}$ do not produce any shift. Further, $E_{\text{des.}}$ is not shifted by the presence of the reduction product of the investigated depolarizers in the bulk of the solution which leads to the correction of the iR drop in presence of depolarizers.

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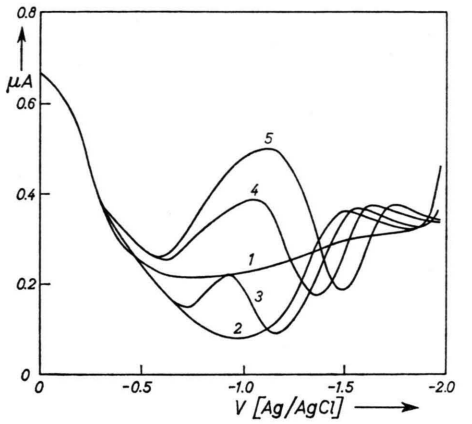

Fig. 1. Effect of the conc. of Azobenzene on E_{des} of TPO. Curve 1: 0.1 M LiCl in methanol. Curve 2: 0.1 M LiCl in methanol + 3.60×10^{-2} M TPO. Curve 3: 0.1 M LiCl in methanol + 3.60×10^{-2} M TPO + 2×10^{-4} M Azobenzene. Curve 4: 0.1 M LiCl in methanol + 3.60×10^{-2} M TPO + 1×10^{-3} M Azobenzene. Curve 5: 0.1 M LiCl in methanol + 3.60×10^{-2} M TPO + 2×10^{-3} M Azobenzene.

Tables 1 and 2 give the iR corrected and uncorrected values of the desorption potential of TPO in presence of the same concentration of various depolarizers and in presence of the same depolarizer with increasing concentration respectively. It can be seen that the desorption potential of TPO becomes more positive in presence of various depolarizers and the positive shift increases with increasing concentration of the same depolarizer when the desorption potentials are corrected for the corresponding iR drops. This result is very significant and shows an opposite behaviour if the desorption potentials are not corrected for the iR drop in presence of the depolarizers.

Depolarizers [5×10^{-4} M]	i_d. [μA]	iR [V]	$E_{\text{des.}}$* [V]	$E'_{\text{des.}}$** [V]	ΔE [V]
—	0.0	—	— 1.511	— 1.511	—
Azobenzene	5.7	0.154	— 1.560	— 1.406	+ 0.150
Azoxybenzene	9.2	0.248	— 1.583	— 1.335	+ 0.176
Nitrobenzene	10.8	0.292	— 1.583	— 1.291	+ 0.220
Nitroazobenzene	15.5	0.418	— 1.611	— 1.193	+ 0.318
Ferric Chloride	6.3	0.170	— 1.588	— 1.418	+ 0.093

Table 1. Effect of depolarizers on the desorption potential of TPO in methanol. Supporting Electrolyte: 0.1 M LiCl; R = 27 000. Concentration of TPO: 3.60×10^{-2} M. Reference electrode: (Ag/AgCl in methanol). * E_{des} = Desorption potential of TPO. ** E'_{des} = Desorption potential of TPO corrected for iR drop.

It can also be seen from Table 2 that the positive shift of the desorption potential of TPO in presence of the same concentration of depolarizer becomes less if the concentration of the supporting electrolyte is in-

Conc. of Depolarizer [M]	i_d. [μA]	Ref. Electrode : Ag/AgCl in Methanol				Ref. Electrode : N.C.E. in Water			
		iR [V]	$E_{des.}$ [V]	$E'_{des.}$ [V]	ΔE [V]	iR [V]	$E_{des.}$ [V]	$E'_{des.}$ [V]	ΔE [V]
Supporting Electrolyte : 0.1 M LiCl *in Methanol*									
0.00	0.0	—	− 1.511	− 1.511	—	—	− 1.639	− 1.639	—
2×10^{-4}	2.2	0.059	− 1.555	− 1.496	+ 0.015	0.044	− 1.655	− 1.611	+ 0.028
5×10^{-4}	5.7	0.154	− 1.560	− 1.406	+ 0.105	0.114	− 1.655	− 1.541	+ 0.098
1×10^{-3}	11.5	0.310	− 1.600	− 1.290	+ 0.221	0.230	− 1.666	− 1.436	+ 0.203
2×10^{-3}	23.0	0.621	− 1,722	− 1.101	+ 0.410	0.460	− 1.700	− 1.240	+ 0.399
Supporting Electrolyte : 1.0 M LiCl *in Methanol*									
0.00	0.0	—	− 1.433	− 1.433	—	—	− 1.544	− 1.544	—
2×10^{-4}	1.8	0.032	− 1.466	− 1.434	0.00	0.016	− 1.560	− 1.544	0.00
5×10^{-4}	4.6	0.081	− 1.477	− 1.396	+ 0.037	0.040	− 1.560	− 1.520	+ 0.024
1×10^{-3}	9.4	0.169	− 1.544	− 1.375	+ 0.058	0.084	− 1.577	− 1.493	+ 0.051
2×10^{-4}	19.0	0.342	− 1.644	− 1.302	+ 0.131	0.171	− 1.605	− 1.434	+ 0.110

Table 2. Effect of the concentration of Azobenzene on the desorption potential of TPO. Conc. of TPO: 3.60×10^{-2} M.

creased. The results obtained with different reference electrodes are in good agreement (Table 2).

The adsorption activity of TPO in methanol is very much decreased and it shows that the adsorptive forces are weak. The positive shift of the desorption potential of TPO in presence of depolarizers is due to the decrease in the activity of the inhibitor molecules at the surface of the dme as a result of displacement of some of the molecules of the inhibitor by the adsorbable molecules of the depolarizer. The greater the concentration of the depolarizer, the larger is the positive shift of the desorption potential. The difference in the positive shift of the desorption potential of TPO in presence of depolarizers having same concentration may be due to the variation in the surface activity of the depolarizer molecules. Further, the increase in the positive shift of the desorption potential of TPO with tenfold decrease in the concentration of the supporting electrolyte may be due to the increased ratio of the depolarizer molecules at the surface to the cations of the supporting electrolyte.

The effect of the concentration and the nature of the supporting electrolyte as well as the addition of water in methanol on the adsorption of TPO and its desorption potential in presence and in the absence of depolarizer has been studied and will be reported in a separate communication.

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[1] L. HOLLECK, B. KASTENING, and R. D. WILLIAMS, Z. Elektrochem. **66**, 396 [1962] and other subsequent papers. B. KASTENING and L. HOLLECK, J. electroanalyt. Chem. [Amsterdam] **27**, 355 [1970].