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Polarographic Studies on the Effect of Some Ionic & Non-ionic Surfactants on Kinetics of Irreversible Electrode Reactions of *o*-, *m*- & *p*-Nitrotoluenes

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Polarographic reduction of *o*-, *m*- and *p*-nitrotoluenes (in 4% ethanolic solution) has been studied at 25 ± 0.1°C in BR buffer of *p*H 7 in the presence of increasing amounts of some ionic and non-ionic surfactants. The reduction of all the three depolarizers is diffusion-controlled and irreversible. The kinetic parameters (αn_a and $k^\circ_{f,h}$) of the electrode reactions have been calculated by Koutecky's method. The irreversible electrode reactions of *o*-, *m*- and *p*-nitrotoluenes tend to become increasingly more irreversible with increasing concentrations of ionic and non-ionic surfactants. This is borne out by a decrease in kinetic parameters and i_d, and a negative shift in $E_{1/2}$ with increasing concentrations of the surfactants. A tentative mechanism of the polarographic reduction of nitrotoluenes at *p*H 7 has also been proposed. This stipulates the protonation of the depolarizers in the steps preceding as well as succeeding the electrode reaction. The ease of reduction of three isomers at d.m.e. is in the order : *meta*> *ortho* > *para*.

A SURVEY of literature reveals that studies on the effect of surfactants on the kinetics of the irreversible polarographic reduction of depolarizers are sparse. Strassner and Delahay[1] have studied the effect of increasing concentrations of gelatin on the irreversible electrode reaction of *p*-nitroaniline in terms of the values of kinetic parameter, αn_a. It has been found that αn_a decreases with the increase in the concentration of gelatin. Keeping this in view, a polarographic study on the influence of increasing concentrations of some ionic and non ionic surfactants on the kinetics of the electrode reactions of *o*-, *m*- and *p*-nitrotoluenes has been undertaken.

The following surfactants were used :

Cationic —Laurylpyridinium chloride (LPC), cetylpyridinium chloride (CPC), cetylpyridinium bromide (CPB), cetyldimethylbenzylammonium chloride (CDBAC) and cetyltrimethylammonium bromide (CTAB).

Anionic — Dodecylbenzene sulphonate (DBS), sodium lauryl sulphate (SLS), Tergitol-7, Manoxol-OT and Manoxol-IB.

Non-ionic — Triton X-100, gelatin, Decon-90, ethyl digol and 2-ethoxyethanol.

The depolarizers, *o*- (b. p. 220°) and *m*-(b.p., 230) nitrotoluenes were redistilled, and *p*-nitrotoluene (m.p. 54°C) was recrystallised before use. All the three depolarizers were of AR (BDH) grade. The other chemicals used were also of AR (BDH) grade. The polarograms were recorded at 25 ± 0.1° on a manual polarograph (Toshniwal CL 02) in conjunction with a polyflex galvanometer (Toshniwal PL 50). Nitrogen was used for the deaeration of solutions (4% ethanolic) of the depolarizers (1.0×10^{-3} *M*) containing BR buffer of *p*H 7. The buffer also acted as the supporting electrolyte. Aqueous solutions of surfactants of high purity were used. The potentials were measured against a saturated calomel electrode (SCE). The d.m.e. had the following characteristics (in 0.1 *M* KCl, open circuit) : $h_{corr} = 62.4$ cm; $m = 3.0$ mg/sec; $t = 3.0$ sec; $m^{2/3}t^{1/6} = 2.5$ $mg^{2/3}$ $sec^{-1/2}$.

The number of electrons (n) involved in the reduction of *o*-, *m*- and *p*-nitrotoluenes, as determined by millicoulometric method of DeVries and Kroon[2], was found to be 4 in each case. Knowing the value of n, Ilkovic equation was used to calculate the value of D, the diffusion coefficient, of *o*-, *m*- and *p*- nitrotoluenes at various concentrations of the surfactants. The potential-dependent rate constant, $k_{f,h}$ was calculated by Koutecky's method[3,4]. The kinetic parameters, αn_a and $k^\circ_{f,h}$ were calculated[1] from the plots of log $k_{f,h}$ versus $E_{d.e}$. Throughout the measurements, the current at the end of the drop (i.e. the maximum current) was recorded for the reasons given by Meites[5a].

Results and Discussion

In the absence of surfactants, *o*-, *m*- and *p*-nitrotoluenes yield sharp polarographic negative maxima at *p*H 7 (BR buffer). After the suppression of these maxima by requisite amounts (marked by an asterisk, Table 1) of ionic and non-ionic surfactants, each depolarizer gives a single well-defined wave. These are diffusion-controlled as evidenced by the linearity of i_d versus $h_{corr}^{1/2}$ plots and their passing through the origin.

Irreversibility tests — The slope values (Table 1) of log plots in the polarographic reduction of *o*-, *m*- and

p-nitrotoluenes in the presence of increasing[surfactants] are much larger than the theoretical value expected for a 4-electron reduction process. From this it follows that the reduction is irreversible[5b]. Further, dependence of current on h_{corr} at different stages of the wave was studied and the current was found to be independent of the pressure-head of the mercury at the foot of the wave whereas it was proportional to $h_{cor}^{1/2}$ at the plateau of the wave. This corroborates the irreversible nature[6,7] of the polarographic reduction in the present case.

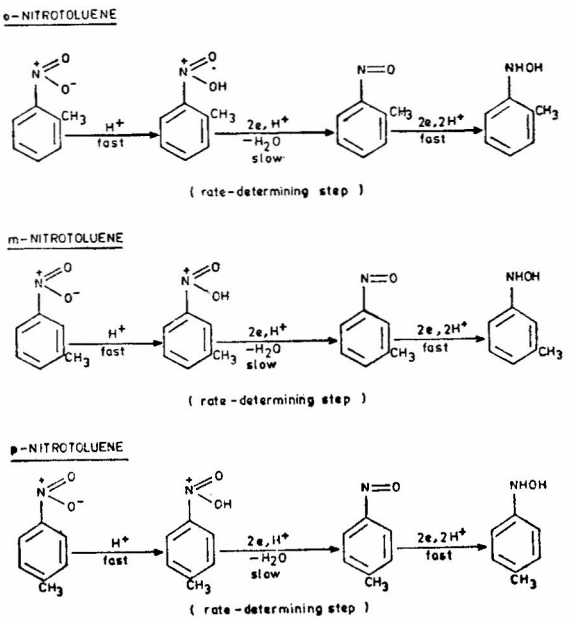
Effect of increasing concentrations of ionic and non-ionic surfactants on polarographic characteristics — The polarographic characteristics, viz., i_d, $E_{1/2}$ and D, of *o*-, *m*- and *p*-nitrotoluenes have been determined in the presence of increasing concentrations of ionic and non-ionic surfactants and the values have been summarized in Table 1. A perusal of this Table shows that a decrease in i_d of each depolarizer takes place as the concentration of the surfactant is gradually increased beyond the concentration at which the maxima get just suppressed (marked by an asterisk in Table 1). A decrease in i_d and a negative shift in $E_{1/2}$ with increasing concentraions of surfactants indicate the inhibition[8] of the electrode reactions of *o*-, *m*- and *p*-nitrotoluenes due to the coverage of the electrode surface by the molecules of the surfactants.

Mechanism of polarographic reduction of o-, m- and p-nitrotoluenes at pH 7 — As already pointed out *o*-, *m*- and *p*-nitrotoluenes are reduced at *p*H 7 in a single step which corresponds to a 4-electron reduction process. Thus the reduction of all the three depolarizers is analogous to the reduction of nitrobenzene. The 4-electron reduction process represents the reduction of nitrotoluenes to the corresponding phenylhydroxylamine derivatives.

Since the plots of log $k_{f,h}$ versus $E_{d.e}$ in the presence of different ionic and non-ionic surfactants are linear, there is only one rate-determining step[9,10] involved in the reduction of each depolarizer. The values of kinetic parameters (αn_a and $k_{f,h}^0$) have been calculated at different concentrations of ionic and non-ionic surfactants (Table 1). An attempt to estimate n_a, the number of electrons involved in the rate-determining step, gave[9,11] a value of 2 because for totally irreversible systems, as the present ones are, α should be less than[12] 0.5. However, according to Meites[5c] only a single electron can be transferred at a time during the course of electrode reaction, a value of n_a exceeding 1 should merely mean that the successive steps are too nearly placed to be distinguished on the time scale implicit in the polarographic measurements.

From a separate study[13] concerning $E_{1/2}$ versus *p*H plots in respect of polarographic reduction of *o*-, *m*- and *p*-nitrotoluenes, it has been concluded that the number of H^+ ions involved in the rate-determining step is 1.

After establishing the stoichiometry of the rate-determining step, i.e., $n_a = 2$ and $H^+ = 1$, the following mechanism can be suggested for the polarographic reduction of *o*-, *m*- and *p*-nitrotoluenes at *p*H 7 (Scheme 1) :



Scheme 1

Effect of increasing concentrations of ionic and non-ionic surfactants on the electrode reactions of o-, m- and p-nitrotoluenes — The effect of surfactants on electron-transfer processes — i.e. on the kinetic parameters αn_a and $k_{f,h}^0$—results from changes produced in the structure of the double layer. The adsorbed molecules displace ions from the Helmholtz layer thereby altering the charge distribution in the double layer. They may also move the reaction surface away from the electrode. Both of these effects alter the potential at the reaction surface. In addition, a bridge that may serve to effect electron-transfer from the electrode to an ion or molecule at the reaction surface when the surfactant is absent, may become impossible to construct in the presence of surfactant. Thus, the entire mechanism of the electron transfer process may change[5d]. A perusal of Table 1 shows that the values of αn_a and $k_{f,h}^0$ decrease as the concentration of the surfactants is gradually increased from the stage at which the maxima get just suppressed. Thiss hows[5e] that the irreversible electrode reactions of *o*-, *m*- and *p*- nitrotoluenes tend to become increasingly more irreversible with increasing concentrations of ionic and non-ionic surfactants. A decrease in i_d and a negative shift in $E_1/_2$ (Table 1) with increasing concentrations of surfactants lend support to the above conclusion.

The order of $k_{f,h}^0$ values in respect of the electrode reactions of *o*-, *m*- and *p*-nitrotoluenes in the presence of ionic and non-ionic surfactants at the concentration at which the maxima of these depolarizers get just suppressed is as follows : *m*-nitrotoluene > *o*-nitrotoluene > *p*-nitrotoluene. Thus *m*-nitrotoluene is easiest to reduce at d.m.e. followed by *o*-nitrotoluene and *p*-nitrotoluene.

A comparison of $k_{f,h}^0$ values at the stage where maxima of *o*-, *m*- and *p*- nitrotoluenes get just suppre-

TABLE 1 — POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS (αn_a AND $k^\circ_{f,h}$) FOR THE ELECTRODE REACTIONS OF *o*-, *m*-AND *p*-NITROTOLUENES IN THE PRESENCE OF INCREASING AMOUNTS OF IONIC AND NON-IONIC SURFACTANTS

[Surfactant] (*M*)	i_d (μ A)	$-E_{1/2}$ V (S.C.E.)	Slope (mV)	$D\times10^6$ (cm²/sec)	αn_a	$k^\circ_{f,h}\times10^3$ (cm/sec)
			o-NITROTOLUENE			
Cationic						
LPC						
*2.0×10^{-5}	16.72	0.570	60	5.617	0.870	5. 6
2.0×10^{-4}	15.20	0.575	70	4.463	0.778	4.78
1.0×10^{-3}	14.06	0.582	75	3.972	0.739	4.37
CPC						
*2.5×10^{-5}	17.48	0.580	60	6.140	0.896	6.86
1.0×10^{-4}	16.34	0.582	70	5.365	0.778	3.09
5.0×10^{-4}	15.58	0.585	75	4.877	0.672	1.34
CPB						
*2.0×10^{-5}	16.72	0.580	60	5.617	0.924	5.87
1.0×10^{-4}	14.58	0.585	70	4.877	0.821	1.73
5.0×10^{-4}	1.482	0.590	80	4.413	0.739	1.27
CDBAC						
*2.0×10^{-5}	16.72	0.580	58	5.617	0.924	4.91
1.0×10^{-4}	15.58	0.605	67	4.877	0.870	3.99
1.0×10^{-3}	14.82	0.612	70	4.413	0.821	2.64
CTAB						
*1.0×10^{-5}	17.10	0.560	58	5.876	0.954	8.31
1.0×10^{-4}	16.34	0.565	62	5.365	0.870	7.74
5.0×10^{-4}	14.82	0.578	68	4.413	0.739	3.18
Anionic						
DBS						
*1.2×10^{-4}	16.72	0.592	58	5.617	0.954	0.87
5.0×10^{-4}	15.58	0.640	65	4.877	0.886	0.64
1.0×10^{-3}	14.06	0.700	90	3.972	0.591	0.11
SLS						
*9.0×10^{-5}	16.72	0.590	59	5.617	0.942	1.16
1.0×10^{-3}	15.96	0.635	63	5.118	0.870	0.89
3.0×10^{-3}	14.44	0.660	68	4.190	0.778	0.56
Tergitol-7						
*1.0×10^{-4}	17.86	0.600	57	6.409	0.983	1.38
5.0×10^{-4}	16.72	0.642	65	5.617	0.886	0.66
1.0×10^{-3}	15.58	0.695	70	4.877	0.778	0.31
Manoxol-OT						
*2.0×10^{-4}	17.10	0.595	58	5.876	0.954	1.86
5.0×10^{-4}	15.96	0.635	72	5.118	0.757	0.60
1.0×10^{-3}	14.06	0.690	90	3.972	0.591	0.60
Manoxol-IB						
*5.0×10^{-3}	16.72	0.560	57	5.617	0.983	6.20
8.0×10^{-3}	15.20	0.562	62	4.643	0.908	2.20
1.0×10^{-2}	14.44	0.570	66	4.190	0.874	0.71
Non-ionic						
†*Triton X*-100						
*5.0×10^{-4}	16.72	0.575	58	5.617	0.954	0.63
1.0×10^{-3}	15.96	0.590	65	5.118	0.886	0.20
5.0×10^{-3}	13.68	0.685	110	3.760	0.493	0.13
†*Gelatin*						
*4.5×10^{-4}	16.72	0.570	58	5.617	0.954	3.57
1.0×10^{-3}	15.20	0.580	75	4.643	0.739	1.53
5.0×10^{-3}	14.06	0.625	85	3.972	0.621	0.58
†*Decon-90*						
*4.0×10^{-2}	16.72	0.585	56	5.617	1.002	0.21
1.0×10^{-1}	15.96	0.610	60	5.118	0.896	0.08
2.0×10^{-1}	14.82	0.615	80	4.413	0.730	0.04
Ethyl digol						
*9.0×10^{-3}	17.48	0.585	55	6.140	1.013	0.64
1.0×10^{-1}	16.34	0.590	65	5.365	0.886	0.41
3.0×10^{-1}	15.20	0.600	80	4.643	0.730	0.30
2-Ethoxyethanol						
*10.0×10^{-1}	17.10	0.300	150	5.876	0.328	622.00
15.0×10^{-1}	16.34	0.302	180	5.369	0.307	448.90
20.0×10^{-1}	15.58	0.305	215	4.877	0.295	376.70
			m-NITROTOLUENE			
Cationic						
LPC						
*2.5×10^{-5}	18.12	0.550	85	6.598	0.637	8.65
1.0×10^{-4}	17.05	0.560	89	5.841	0.609	7.32
1.0×10^{-3}	16.52	0.575	91	5.484	0.595	6.54
CPC						
*2.8×10^{-5}	17.59	0.553	87	6.217	0.622	9.79
1.0×10^{-4}	17.05	0.558	91	5.841	0.595	9.34
5.0×10^{-4}	15.99	0.570	93	5.138	0.582	7.62
CPB						
*2.6×10^{-5}	18.12	0.559	80	6.598	0.677	11.34
1.0×10^{-4}	17.05	0.570	82	5.841	0.661	5.94
5.0×10^{-4}	15.99	0.577	94	5.138	0.576	3.21
CDBAC						
*2.0×10^{-5}	18.12	0.550	83	6.598	0.653	7.34
1.0×10^{-4}	17.59	0.558	86	6.217	0.630	6.98
1.0×10^{-3}	15.99	0.566	90	5.138	0.602	6.21
CTAB						
*1.2×10^{-5}	18.65	0.556	92	6.989	0.589	17.80
1.0×10^{-4}	17.59	0.574	97	6.217	0.587	16.63
5.0×10^{-4}	16.52	0.582	99	5.484	0.547	15.32
Anionic						
DBS						
*1.2×10^{-4}	18.12	0.560	67	6.598	0.809	3.17
5.0×10^{-4}	17.05	0.570	73	5.841	0.742	1.08
1.0×10^{-3}	15.99	0.575	75	5.138	0.722	0.44
SLS						
*1.0×10^{-4}	18.65	0.560	82	6.989	0.661	9.83
1.0×10^{-3}	17.59	0.565	88	6.217	0.616	7.78
3.0×10^{-3}	17.05	0.575	91	5.841	0.595	5.33
Tergitol-7						
*1.4×10^{-4}	18.65	0.554	76	6.989	0.713	9.75
6.0×10^{-4}	18.12	0.565	79	6.598	0.686	2.48
1.0×10^{-3}	17.05	0.570	93	5.841	0.582	1.37
Manoxol-OT						
*2.0×10^{-4}	18.65	0.558	71	6.989	0.763	11.13
5.0×10^{-4}	17.59	0.560	84	6.217	0.645	5.89
1.0×10^{-3}	15.99	0.566	93	5.138	0.583	1.11

—Contiinued

TABLE 1 — *Contd.*

[Surfactant] (M)	i_d (μ A)	$-E_{1/2}$ V (S.C.E.)	Slope (mV)	$D\times10^6$ (cm²/sec)	αn_a	$k°_{f,h}\times10^8$ (cm/sec)
Manooxl-IB						
*1.0×10^{-3}	18.12	0.554	68	6.598	0.797	13.32
5.0×10^{-3}	17.05	0.556	78	5.841	0.694	2.72
8.0×10^{-3}	16.52	0.558	94	5.484	0.576	0.60
Non-ionic						
†*Triton X*-100						
*5.0×10^{-4}	18.65	0.554	75	6.989	0.722	3.47
1.0×10^{-3}	18.12	0.558	78	6.598	0.695	3.23
3.0×10^{-3}	17.05	0.565	82	5.841	0.661	3.01
†*Gelatin*						
*4.8×10^{-4}	18.65	0.550	73	6.989	0.742	5.73
1.0×10^{-3}	17.59	0.552	75	6.217	0.722	2.39
5.0×10^{-3}	16.52	0.560	85	5.484	0.637	0.71
†*Decon*-90						
*4.5×10^{-2}	18.65	0.546	75	6.989	0.722	8.26
1.0×10^{-1}	17.59	0.548	79	6.217	0.686	4.52
2.0×10^{-1}	10.52	0.555	86	5.484	0.630	2.76
Ethyl digol						
*1.0×10^{-2}	18.65	0.550	75	6.989	0.722	12.31
7.0×10^{-2}	18.12	0.557	91	6.598	0.595	7.37
1.0×10^{-1}	17.59	0.562	94	6.217	0.576	2.35
*2-*Ethoxyethanol*						
15.0×10^{-1}	18.12	0.535	73	6.598	0.742	12.54
20.0×10^{-1}	17.59	0.544	80	6.217	0.677	3.87
25.0×10^{-1}	17.05	0.558	91	5.841	0.595	2.03
		p-NITROTOLUENE				
Cationic						
LPC						
*3.0×10^{-5}	20.52	0.560	55	8.461	0.924	1.39
1.0×10^{-4}	19.38	0.595	62	7.547	0.896	0.60
1.0×10^{-3}	18.62	0.660	70	6.967	0.870	0.11
CPC						
*3.0×10^{-5}	19.76	0.560	55	7.846	0.870	2.30
1.0×10^{-4}	18.62	0.572	70	6.967	0.845	1.88
5.0×10^{-4}	17.48	0.580	72	6.140	0.821	1.73
CPB						
*3.0×10^{-5}	20.14	0.565	54	8.151	0.895	1.86
1.0×10^{-4}	19.38	0.575	65	7.547	0.870	1.46
5.0×10^{-4}	17.86	0.580	70	6.409	0.821	1.34
CDBAC						
*2.0×10^{-5}	20.14	0.570	55	8.151	0.926	1.01
1.0×10^{-4}	19.00	0.595	65	7.254	0.845	0.91
1.0×10^{-3}	18.24	0.620	70	6.685	0.821	0.62
CTAB						
*1.0×10^{-5}	19.38	0.560	55	7.547	0.870	2.51
1.0×10^{-4}	18.24	0.565	60	6.685	0.865	1.65
5.0×10^{-4}	17.10	0.575	70	5.876	0.821	0.68
Anionic						
DBS						
*1.2×10^{-4}	19.76	0.580	45	7.846	1.056	0.17
5.0×10^{-4}	17.10	0.630	55	5.876	0.924	0.13
1.0×10^{-3}	15.20	0.670	60	4.643	0.780	0.05
SLS						
*1.3×10^{-4}	19.38	0.580	45	7.547	1.054	0.19
1.0×10^{-3}	18.24	0.610	50	6.685	1.005	0.09
3.0×10^{-3}	17.10	0.625	52	5.876	0.960	0.09
Tergitol-7						
*2.0×10^{-4}	19.00	0.580	44	7.254	1.056	0.13
6.0×10^{-4}	17.48	0.620	55	6.140	0.954	0.07
1.0×10^{-3}	15.20	0.670	65	4.643	0.896	0.05
Manoxol-OT						
*2.0×10^{-4}	19.76	0.580	46	7.846	1.048	0.21
5.0×10^{-4}	18.24	0.600	49	6.685	0.990	0.16
8.0×10^{-4}	16.34	0.615	53	5.365	0.954	0.12
Manoxol-IB						
*1.0×10^{-1}	19.76	0.510	55	7.846	0.986	5.49
1.2×10^{-1}	18.24	0.512	57	6.685	0.952	4.76
1.5×10^{-1}	16.72	0.514	60	5.617	0.923	0.05
Non-ionic						
†*Triton X*-100						
*5.0×10^{-4}	19.00	0.570	50	7.254	1.005	0.22
2.0×10^{-3}	15.96	0.590	55	5.118	0.986	0.13
5.0×10^{-3}	13.68	0.660	75	3.760	0.821	0.12
†*Gelatin*						
*5.0×10^{-4}	20.14	0.550	55..	8.151	0.924	2.14
2.0×10^{-3}	17.86	0.590	73	6.409	0.739	1.37
5.0×10^{-3}	16.34	0.605	78	5.365	0.672	0.79
**Decon*-90						
*5.0×10^{-2}	20.14	0.575	48	8.151	1.056	0.16
1.0×10^{-1}	19.00	0.600	50	7.254	1.020	0.07
2.0×10^{-1}	16.72	0.625	60	5.617	0.954	0.06
Ethyl digol						
*2.0×10^{-2}	20.14	0.563	50	8.151	1.005	0.40
4.0×10^{-2}	19.00	0.564	53	7.254	0.986	0.32
1.0×10^{-1}	18.24	0.570	60	6.685	0.923	0.29
2-Ethoxyethanol						
*22.0×10^{-1}	18.24	0.370	45	6.685	1.054	553.70
26.0×10^{-1}	17.10	0.380	50	5.876	1.020	475.20
30.0×10^{-1}	15.96	0.390	67	5.118	0.873	138.00

*Concentration at which maximum gets just suppressed.
†Concentration terms are expressed in percentage.

ssed by ionic and non-ionic surfactants may give a quantitative estimation of the influence of surfactants on the kinetics of the electrode reactions of these depolarizers. From a perusal of Table 1, the following orders of $k^0_{f,h}$ values in respect of various surfactants are obtained.

Electrode reaction of o-nitrotoluene — CTAB > CPC > CPB > LPC > CDBAC (cationic); Manoxol-IB > Manoxol-OT > Tergitol-7 > SLS > DBS (anionic); 2-ethoxyethanol > gelatin > ethyl digol > Triton X-100 > Decon-90 (non-ionic).

Thus CTAB, Manoxol-IB and 2-ethoxyethanol

suppress the maximum of *o*-nitrotoluene with minimum influence on the kinetics of its electrode reaction.

Electrode reaction of m-nitrotoluene — CTAB > CPB > CPC > LPC > CDBAC (cationic); Manoxol-IB > Manoxol-OT > SLS > Tergitol-7 > DBS (anionic); 2-ethoxyethanol > ethyl digol > Decon-90 > gelatin > Triton X-100 (non-ionic).

Thus CTAB, Manoxol-IB and 2-ethoxyethanol suppress the maximum of *m*-nitrotoluene with minimum influence on the kinetics of its electrode reaction.

Electrode reaction of p-nitrotoluene — CTAB > CPC > CPB > LPC > CDBAC (cationic); Manoxol-IB > Manoxol-OT > SLS > Tergitol-7 > DBS (anionic); 2-ethoxyethanol > gelatin > ethyl digol > Triton X-100 > Decon-90 (non-ionic).

Thus, CTAB, Manoxol-IB and 2-ethoxyethanol suppress the maximum of *p*-nitrotoluene with minimum influence on the kinetics of its electrode reaction.

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