extend their coordination number from two to three and finally to four giving an yellow coloured unstable intermediate in the reaction of mercury(I) succinate and iodine in 1:2 molar ratio. Since this intermediate is very unstable and is immediately converted into the final product, it could not be isolated and identified.

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Effect of Some Ionic & Non-ionic Surfactants on Kinetics of Irreversible Electrode Reactions of o-, m- & p-Nitrochlorobenzenes

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Polarographic reduction of o-, m- and p-nitrochlorobenzenes has been studied in aquo-alcoholic medium at $25 \pm 0.1°C$ in borax-boric acid buffer of pH 7.09 in the presence of increasing amounts of some ionic and non-ionic surfactants, viz. laurylpyridinium chloride (LPC), cetylpyridinium chloride (CPC) : dodecylbenzene sulphonate (DBS), sodium lauryl sulphate (SLS), Triton X-100 and gelatin. The reduction of all the three depolarizers has been found to be diffusion-controlled and irreversible. The kinetic parameters (αn_a and $k°_{f,h}$) of the electrode reactions have been calculated by Koutecky's method. A decrease in the value of kinetic parameters shows that the irreversible electrode reactions of o-, m- and p-nitrochlorobenzenes tend to become increasingly more irreversible with the increasing concentrations of ionic and non-ionic surfactants. This is borne out by a decrease in i_d and a negative shift in $E_{1/2}$ values with increasing concentration of the surfactants.

STRASSNER and Delahay[1] have studied the effect of increasing concentration of gelatin on the irreversible electrode reaction of p-nitroaniline in terms of the value of kinetic parameter, αn_a. It has been found that αn_a decreases with increasing concentration of gelatin. In view of this and in continuation of our earlier work[2] on the effect of surfactants on the polarographic reduction of nitrotoluenes, we report here the effect of increasing concentration of some ionic and non-ionic surfactants on the kinetics of the irreversible electrode reactions of o-, m- and p-nitrochlorobenzenes.

o-, m- and p-Nitrochlorobenzenes were of AR grade. These were recrystallised from ethanol before use. The other chemicals used were of AR (BDH) grade. The concentraion of each depolarizer (in aquo-ethanolic solution) was maintained at $1.0 \times 10^{-3} M$. Desired concentrations of various constituents of borax-boric acid buffer of pH 7.09 were added to the solution to be polarographed. Sodium nitrate (0.1 M) was used as a supporting electrolyte. Instrumentation details have been. reported earlier[2].

The number of electrons (n) involved in the reduction of o-, m- and p-nitrochlorobenzeness a determined by millicoulometric method of DeVries and Kroon[3] was found to be 4 for each depolarizer at pH 7.09. Knowing the value of n, Ilkovic equation was used to calculate the value of D, at various concentrations of the surfactants. The potential-dependent rate constant $k_{f,h}$ was calculated by Koutecky's method[4,5]. The kinetic parameters, αn_a and k_f^{c1} were calculated from the plots of $\log k_{f,h}$ versus E_{de}^1. Throughout the measurements the current at the end of the drop (i.e., the maximum current) was recorded for the reasons given by Meites[6(a)]. The d.m.e. had the following characteristics : for o-nitrochlorobenzene, $m = 2.77$ mg/sec; $t = 2.92$ sec; $m^{2/3} t^{1/6} = 2.385$ mg$^{2/3}$ sec$^{-1/2}$ (in 0.1M NaNO$_3$, open circuit) ; $h_{corr} = 56.2$ cm; and $m = 1.498$ mg/sec ; $t = 2.75$ sec, $m^{2/3} t^{1/6} = 1.759$ mg$^{2/3}$ sec$^{-1/2}$ (in 0.1 M NaNO$_3$, open circuit) ; $h_{corr} = 57.1$ cm for m- and p-nitrochlorobenzenes.

The following surfactants were used :
Cationic — Laurylpyridinium chloride (LPC) and cetylpyridinium chloride (CPC).
Anionic — Dodecylbenzene sulphonate (DBS) and sodium lauryl sulphate (SLS).
Non-ionic — Triton X-100 and gelatin.

In the absence of surfactants, o-, m- and p-nitrochlorobenzenes yield sharp polarographic negative maxima at pH 7.09 (borax-boric acid buffer). After the suppression of these maxima by the requisite amounts 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.

The slope values of log plots in the polarographic reduction of o-, m- and p-nitrochlorobenzenes in the presence of increasing [surfactants] are larger than the theoretical value expected for a 4-electron reduction process indicating the irreversible[6(b)] nature of reduction. Further it was found that the current was independent of h_{corr} at the foot of the wave whereas it was proportional to $h_{corr}^{1/2}$ at the plateau of the wave corroborating[7,8] their reversible nature of reduction.

The polarographic characteristics, viz. i_d, $E_{1/2}$ and D of o-, m- and p-nitrochlorobenzenes have been determined in the presence of increasing concentrations of ionic and non-ionic surfactants. A decrease in i_d of each depolarizer takes place as the concentration of the surfactants is gradually increased

TABLE 1 — KINETIC PARAMETERS (αn_a and $k^\circ_{f,h}$) FOR THE ELECTRODE REACTIONS OF o-, m- AND p-NITROCHLOROBENZENES

[Surfactant] (M)	αn_a	$k^\circ_{f,h}$ (cm/sec)
o-Nitrochlorobenzene (in 4% ethanolic solution).		
Cationic		
LPC		
*1.2 × 10⁻⁴	0.642	6.57 × 10⁻⁷
1.2 × 10⁻³	0.528	4.32 × 10⁻⁷
CPC		
*1.8 × 10⁻⁶	0.591	2.05 × 10⁻⁶
8.0 × 10⁻⁵	0.547	1.27 × 10⁻⁶
Anionic		
SLS		
*5.0 × 10⁻⁵	0.616	5.01 × 10⁻⁷
2.5 × 10⁻³	0.547	1.32 × 10⁻⁷
DBS		
*8.0 × 10⁻⁵	0.721	4.71 × 10⁻⁷
4.0 × 10⁻³	0.492	2.18 × 10⁻⁷
Non-ionic		
†Triton X-100		
*8.0 × 10⁻⁴	0.642	1.03 × 10⁻⁷
1.6 × 10⁻²	0.462	3.60 × 10⁻⁸
†Gelatin		
*4.0 × 10⁻²	0.642	3.60 × 10⁻⁶
6.0 × 10⁻²	0.509	2.45 × 10⁻⁶
m-nitrochlorobenzene (in 4% ethanolic solution)		
Cationic		
LPC		
*2.6 × 10⁻⁵	0.778	1.03 × 10⁻⁶
2.6 × 10⁻³	0.672	6.79 × 10⁻⁷
CPC		
*3.2 × 10⁻⁵	0.985	1.22 × 10⁻⁶
1.0 × 10⁻³	0.869	8.50 × 10⁻⁹
Anionic		
SLS		
*8.0 × 10⁻⁵	0.616	3.94 × 10⁻⁶
2.0 × 10⁻³	0.508	2.65 × 10⁻⁶
DBS		
*7.8 × 10⁻⁵	0.821	7.39 × 10⁻⁷
2.0 × 10⁻³	0.476	3.48 × 10⁻⁷
Non-ionic		
†Triton X-100		
*4.4 × 10⁻⁴	0.616	8.50 × 10⁻⁶
8.0 × 10⁻³	0.493	3.63 × 10⁻⁶
†Gelatin		
*5.0 × 10⁻³	1.056	8.21 × 10⁻⁸
3.0 × 10⁻³	0.778	5.66 × 10⁻⁸
p-Nitrochlorobenzene (in 25% ethanolic solution)		
Cationic		
LPC		
*1.6 × 10⁻⁶	0.672	4.02 × 10⁻⁷
1.8 × 10⁻³	0.616	2.22 × 10⁻⁷
CPC		
*1.8 × 10⁻⁶	0.778	2.02 × 10⁻⁸
8.5 × 10⁻⁴	0.739	9.77 × 10⁻⁹
Anionic		
SLS		
*1.0 × 10⁻⁴	0.642	5.94 × 10⁻⁷
1.0 × 10⁻³	0.568	3.11 × 10⁻⁷
DBS		
*1.2 × 10⁻⁴	0.778	3.09 × 10⁻⁶
6.0 × 10⁻³	0.642	1.32 × 10⁻⁸
Non-ionic		
†Triton X-100		
*4.0 × 10⁻⁴	0.616	9.35 × 10⁻⁷
8.0 × 10⁻³	0.492	4.45 × 10⁻⁷
†Gelatin		
*5.0 × 10⁻³	0.821	6.64 × 10⁻⁸
1.0 × 10⁻¹	0.704	5.35 × 10⁻⁸

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

beyond the concentration at which the maxima get just suppressed. $E_{1/2}$ values shift towards more negative potentials as the concentration of the surfactants is gradually increased. A decrease in i_d and a negative shift in $E_{1/2}$ indicate the inhibition[9] of the electrode reactions of o-, m- and p-nitrochlorobenzenes. This may be due to the coverage of the electrode surface by the molecules of the surfactants.

*Mechanism of polarographic reduction of o-, m- and p-nitrochlorobenzenes* — As already point out, o-, m- and p-nitrochlorobenzenes are reduced at pH 7.09 in a single step which corresponds to a 4-electron reduction process. Thus, the reduction of o-, m- and p-nitrochlorobenzenes at this pH is analogous to the reduction of nitrobenzene. 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[10,11] involved in the reduction of each depolarizer. The values of kinetic parameters (αn_a and $k^\circ_{f,h}$) 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, apparently leads to a conclusion[10,12] that n_a is equal to 2 because for totally irreversible systems, as the present ones are, α should be less than[13] 0.5. However, according to Meites[6(c)] 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 to onearly placed to be distinguished on the time scale implicit in the polarographic measurements.

From a separate study[14] concenring $E_{1/2}$ versus pH plots in respect of polarographic reduction of nitrochlorobenzenes, it has been concluded that the number of H⁺ ions involved in the rate-determining step is 1. Having thus established 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-nitrochlorobenzenes at pH 7.09 (Scheme 1).

The effect of surfactants on electron-transfer process—that is, on the kinetic parameters αn_a and $k^\circ_{f,h}$ for irreversible electrode process—results from

o-CHLORONITROBENZENE

(rate-determining step)

m-CHLORONITROBENZENE

(rate-determining step)

p-CHLORONITROBENZENE

(rate-determining step)
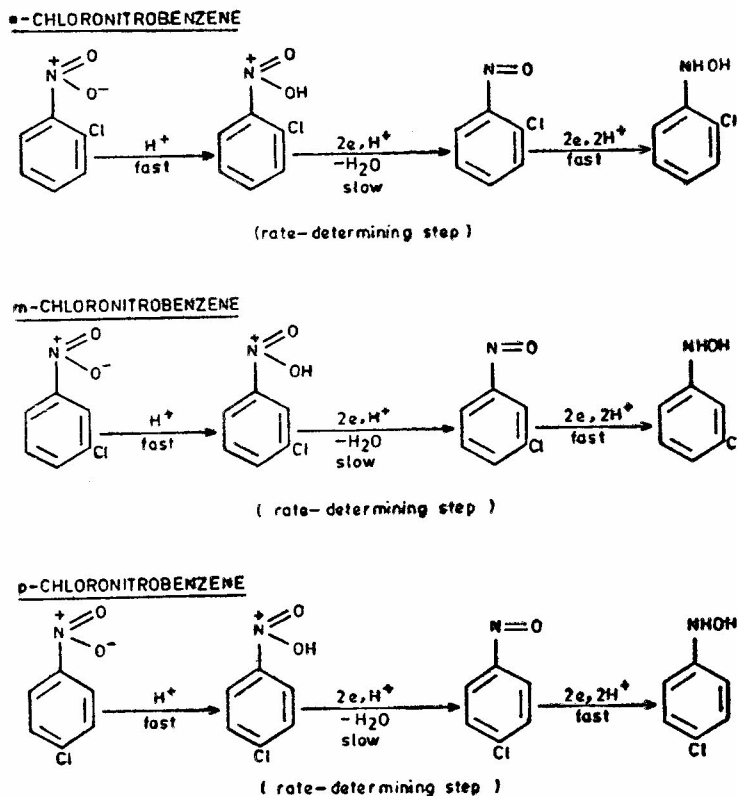
Scheme 1

the changes in the structure of the double layer[2]. Thus, the mechanism of the electron-transfer process may change[6(d)] in the presence of surfactants. A perusal of Table 1 shows that the values of αn_a and $k^o_{f,h}$ decrease as the concentration of the surfactants is gradually increased from the stage at which the maxima get just suppressed. This shows[6(e)] that the irreversible electrode reactions of o-, m- and p-nitrochlorobenzenes 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 $E_{1/2}$ with increasing concentrations of the surfactants lend support to the above conclusion.

From a perusal of Table 1 the following order of $k^o_{f,h}$ values in respect of various surfactants is obtained :

Electrode reaction of o-nitrochlorobenzene — CPC >LPC (cationic); SLS>DBS (anionic) ; gelatin >Triton X-100 (non-ionic).

Thus CPC, SLS and gelatin suppress the maximum of o-nitro chlorobenzene with minimum influence on the kinetics of its electrode reaction.

Electrode reaction of m-nitrochlorobenzene — LPC>CPC (cationic); SLS>DBS (anionic); Triton X-100>gelatin (non-ionic).

Thus LPC, SLS and Triton X-100 suppress the maximum of m-nitrochlorobenzene with minimum influence of the kinetic s of its electrode reaction.

Electrode reaction of p-nitrochlorobenzene—LPC>CPC (cationic); SLS>DBS (anionic); Triton X-100>gelatin (non-ionic)

Thus LPC, SLS and Triton X-100 suppress the maximum of p-nitrochlorobenzene with minimum influence on the kinetics of its electrode reaction.

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