Notes

Role of Ionic & Non-ionic Surfactants in the Suppression of Polarographic Maxima of Ni(II)

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The role of some ionic and non-ionic surfactants in the suppression of polarographic maximum of Ni(II) has been studied. It has been observed that both anionic and cationic surfactants as well as non-ionic surfactants suppress negative maxima of Ni(II), the cationic being the most effective. The characteristic properties, viz. maximum suppression points (m.s.p.), specific suppression coefficients (s.s.c.) and critical micelle concentrations (c.m.c.) of these surfactants have been determined.

EMELIANOVA and Heyrovsky[1] compared the relative efficacies of different valent cations in suppressing the Ni(II) polarographic maxima. In the presence of $NaNO_2$ the maxima of Ni(II) was shown by Burlacu and coworkers[2] to be suppressed in large amounts of gelatin. The effect of various ionic and non-ionic surfactants on the polarographic maxima of Ni(II) has also been investigated[3-6]. The effect of some more ionic and non-ionic surfactants on the polarographic maxima of Ni(II) has now been studied and the results are reported in this note.

$NiCl_2{\cdot}6H_2O$ and KCl were of BDH Analar grade. All the surfactants used were recrystallized from acetone. The surfactants used were: Manoxol-IB, Manoxol-OT, Tergitol-7, sodium lauryl sulphate (SLS), dodecyl benzene sulphonate (DBS), XL-anionic, methyl red, lauryl pyridinium bromide (LPB), lauryl pyridinium chloride (LPC), tetradecyl pyridinium bromide (TDPB), cetyl pyridinium bromide (CPB), cetyl pyridinium chloride (CPC), cetyl dimethyl benzyl ammonium chloride (CDBAC), cetyl trimethyl ammonium bromide (CTAB), 2-ethoxy ethanol, ethyl diagol, Decon-90, Amido black and Triton X-100. All the solutions were prepared in doubly distilled water. A manual polarograph (Worsley Lane's) in conjunction with a Pye galvanometer was used for recording the potential and current respectively. Deoxygenation of the samples was done elaborately by a continuous flow of purified hydrogen[7]. Polarographic half cell was connected to SCE through an ammonium nitrate bridge. The d.m.e. had the following characteristics: $h_{\text{corr}} = 61{\cdot}20$ cm, $m = 1{\cdot}92$ mg/sec, $t = 3{\cdot}80$ sec (in $0{\cdot}1M$ KCl, open circuit); $m^{2/3}.t^{1/6} = 1{\cdot}932$ mg$^{2/3}$ sec$^{-1/2}$. Polarograms of the solutions (conc. of depolarizer, $2\times10^{-3}M$; conc. of supporting electrolyte (KCl, $0{\cdot}1M$) were taken at $25° \pm 0{\cdot}1°$ in the presence of varying amounts of surfactants until the maximum was completely suppressed.

The polarographic properties of the surfactants, viz. maximum suppression point[8] (m.s.p.), specific suppression coefficient[9] (s.s.c.) and critical micelle concentration[8] (c.m.c.), were computed as reported in our earlier publication[10]. The computed values for cationic, anionic and non-ionic surfactants are given in Table 1.

The maxima of Ni(II) which falls in the category of the 'first kind' under the present experimental conditions, appears at $-1{\cdot}13$ V (vs SCE).

Antweiler[11] has unambiguously proved that the polarographic maxima of the first kind are due to tangential streaming of the solution with respect to the drop. The success of a maxima suppressor depends on its capability of curbing this streaming. Since the maxima in the present study lie on the negative side of the electrocapillary curve, the cationic suppressors will move right up to the mercury surface and the anionic ones are likely to move at a distance somewhere in the double layer. A cationic suppressor will prevent streaming more effectively as compared to the anionic one with identical hydrocarbon chain. This is supported by the data in Table 1. The cationic surfactants are effective at low concentrations. Polar head size and the number of charges on the surfactants should also be taken into account for a precise comparison. This explains why lauryl pyridinium chloride is more effective than sodium lauryl sulphate and, in general, the cationic are far more effective than the anionic surfactants.

TABLE 1 — M.S.P., S.S.C. AND C.M.C. VALUES FOR CATIONIC, ANIONIC AND NON-IONIC SURFACTANTS

Surfactants	m.s.p.	s.s.c.	c.m.c.
CATIONIC			
LPC	$1{\cdot}05\times10^{-5}M$	$8{\cdot}20\times10^{-7}M$	$6{\cdot}76\times10^{-7}M$
LPB	$2{\cdot}00\times10^{-5}M$	$8{\cdot}50\times10^{-7}M$	$7{\cdot}035\times10^{-7}M$
TDPB	$40{\cdot}00\times10^{-7}M$	$5{\cdot}00\times10^{-7}M$	$1{\cdot}90\times10^{-7}M$
CPB	$40{\cdot}00\times10^{-8}M$	$3{\cdot}00\times10^{-8}M$	$2{\cdot}50\times10^{-8}M$
CPC	$5{\cdot}00\times10^{-8}M$	$3{\cdot}82\times10^{-8}M$	$3{\cdot}34\times10^{-8}M$
CDBAC	$8{\cdot}00\times10^{-7}M$	$5{\cdot}00\times10^{-7}M$	$4{\cdot}95\times10^{-7}M$
CTAB	$9{\cdot}52\times10^{-8}M$	$2{\cdot}08\times10^{-8}M$	$0{\cdot}35\times10^{-8}M$
ANIONIC			
Manoxol-IB	$8{\cdot}25\times10^{-3}M$	$3{\cdot}75\times10^{-3}M$	$2{\cdot}00\times10^{-3}M$
Manoxol-OT	$6{\cdot}00\times10^{-5}M$	$2{\cdot}76\times10^{-5}M$	$2{\cdot}00\times10^{-5}M$
Tergitol-7	$12{\cdot}85\times10^{-5}M$	$8{\cdot}00\times10^{-5}M$	$3{\cdot}40\times10^{-5}M$
SLS	$5{\cdot}00\times10^{-4}M$	$1{\cdot}00\times10^{-4}M$	$1{\cdot}15\times10^{-4}M$
DBS	$4{\cdot}00\times10^{-4}M$	$1{\cdot}00\times10^{-4}M$	$0{\cdot}50\times10^{-4}M$
XL-Anionic	$6{\cdot}50\times10^{-4}\%$	$2{\cdot}00\times10^{-4}\%$	$1{\cdot}38\times10^{-4}\%$
Methyl red	$1{\cdot}00\times10^{-4}\%$	$0{\cdot}25\times10^{-4}\%$	$0{\cdot}10\times10^{-4}\%$
NON-IONIC			
2-Ethoxy ethanol	$3{\cdot}0\%$	$1{\cdot}25\%$	$0{\cdot}75\%$
Ethyl diagol	$8{\cdot}00\times10^{-2}\%$	$3{\cdot}50\times10^{-2}\%$	$1{\cdot}50\times10^{-2}\%$
Triton X-100	$12{\cdot}00\times10^{-4}\%$	$2{\cdot}65\times10^{-4}\%$	$1{\cdot}85\times10^{-4}\%$
Decon-90	$18{\cdot}00\times10^{-4}\%$	$3{\cdot}95\times10^{-4}\%$	$2{\cdot}25\times10^{-4}\%$
Amido black	$4{\cdot}50\times10^{-4}M$	$1{\cdot}50\times10^{-4}M$	$0{\cdot}15\times10^{-4}M$

For identical polar heads the effectiveness should solely depend upon the hydrocarbon chain (this can be either a side chain or one having the polar head). Hence the following orders of effectiveness are justified: CPB>TDPB>LPB; CPC>LPC; Manoxol-OT>Manoxol-IB.

Molecules of a suppressor with a smaller polar head will crowd the double layer and its vicinity more and hence will be more effective, as in the case of CTAB and CDBAC.

Non-ionic or amphoteric substances suppress maxima on the basis of preferential adsorption on the mercury drop. The efficiency of these suppressors depends upon the potential range of the maxima. Different non-ionic suppressors are adsorbed on the mercury drop to different extents at a given potential. The order of effectiveness amongst the suppressors used is: Triton X-100 > Decon-90> Amido black > ethyl diagol > 2-ethoxy ethanol.

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Kinetics of Reaction Between Substituted Benzoyl Chlorides & Anilines in Benzene

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The resultant effect on the activation energy of two or three substituents in the benzene nucleus is nearly the sum of their individual effects. The reaction is bimolecular and the plot of specific rate constants against the dipole moments of substituted benzoyl chlorides is linear. The Hammett's equation is also applicable in the present case.

THE reaction of some mono substituted benzoyl chlorides and anilines in CCl_4 and hexane was studied by Grant and Hinshelwood[1] and in benzene by Williams and Hinshelwood and coworkers[2-4]. In this note we report the kinetics of reaction between di- and tri-substituted benzoyl chlorides with aniline in benzene. The conclusions drawn from the present study are similar to those reported by Saksena and Bose[5].

Aniline reacts with substituted benzoyl chlorides as shown in Eqs. (i) and (ii).

$$R.C_6H_4COCl+C_6H_5NH_2 \underset{\text{fast}}{\overset{\text{slow}}{=}} R.C_6H_4CONHC_6H_5 + HCl \quad \ldots(i)$$

$$HCl+C_6H_5NH_2 = C_6H_5NH_2.HCl \quad \ldots(ii)$$

Step (i) is the rate determining step. In order to study the reaction kinetics, standard solutions of aniline (0·04*M*) and substituted benzoyl chlorides (0·02*M*) were prepared in benzene. After equilibrating at the desired temperature (30° ± 0·1°) the solution of benzoyl chloride (5 ml) was mixed with the solution of aniline (5 ml) in a reaction vessel containing benzene (10 ml), and the reaction mixture shaken well. The final concentrations of benzoyl chloride and aniline in the reaction mixture were 0·01*M* and 0·005*M* respectively.

The precipitate of aniline hydrochloride formed after definite intervals of time was filtered off through Gooch crucible. The reaction vessel was washed twice with benzene and finally with distilled water. To the washings and the precipitate was added 5 ml of 6*N* nitric acid to dissolve the precipitate completely. The chloride was estimated by Volhard's method.

A slightly modified bimolecular velocity constant equation was used for calculating k values for this reaction. If a is the initial concentration of substituted benzoyl chloride, $2a$ that of aniline and if x is the amount of substituted benzoyl chloride which reacted in time t, then the concentration of aniline that reacted should be $2x$.

Thus $dx/dt = k\,(a-x)(2a-2x)$, whence

$$k = \frac{1}{120t}\left(\frac{1}{100-Z} - \frac{1}{100}\right)\frac{100}{a}$$

where k is the velocity constant in litre mole^{-1} sec^{-1}, t is the time in min and Z is the percentage conversion. The bimolecular rate constants have been found to be constant up to 70% conversion. The energy of activation was calculated by 'least square method' and also from the Arrhenius plot.

It is evident from the data given in Table 1 that there is marked variation of the energy of activation with the substituent. The energy of activation

Table 1 — Energy of Activation and Frequency Factor at 30° in Benzene

Benzoyl chloride	log A litre mole^{-1} sec^{-1}	$\Delta E\ddagger$	$\log_{10}(R_{30}\sqrt{M}\times 10^3)$
—	4·41	—	1·8190
2,4-Dichloro-	4·11	+210	2·6224
3,5-Dinitro-	4·25	−530	2·6870
3-Nitro-4-chloro-	4·19	+60	2·6492
3,4-Dimethoxy-	4·61	+360	1·5699
3,4,5-Trimethoxy-	4·42	+100	1·5650
3-Methoxy-4-ethoxy-	4·48	—	1·3406

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