



The depolarizers, *m*-, and *p*-nitrobenzoic acids (BDH) were recrystallised from ethanol before use. The other chemicals used were of AR (BDH) grade. The concentration of each of the depolarizers in the solution was  $1.0 \times 10^{-3}$  M (in 4% ethanol). BR buffer of pH 5.02 acted as a supporting electrolyte.

A manual polarograph (Toshniwal CLO<sub>2</sub>) in conjunction with a polyflex galvanometer (Toshniwal PL 50) was used. All the measurements were made at  $25 \pm 0.1^\circ\text{C}$ . Purified nitrogen was used for deaeration. The potentials were measured against SCE. The d.m.e. had the following characteristics (in 0.1 M KCl, open circuit) :  $h_{\text{corr}} = 62.4$  cm;  $m = 3.0$  mg/sec;  $t = 3.02$  sec;  $m^{2/3} t^{1/6} = 2.504$  mg<sup>-2/3</sup> sec<sup>-1/6</sup>. The number of electrons (*n*) involved in the reduction process was determined by millicoulometric method of DeVries and Kroon<sup>3</sup>. This gave the value of *n* equal to 4 for each depolarizer at pH 5.02.

The surfactants used were : Laurylpyridinium chloride (LPC), Cetylpyridinium chloride (CPC), Cetylpyridinium bromide (CPB), Cetyldimethylbenzylammonium chloride (CDBAC) and Cetyltrimethylammonium bromide (CTAB) (all cationic); dodecyl-benzene sulphonate (DBS), sodium lauryl sulphate (SLS), Tergitol-7, Manoxol-OT and Manoxol-IB (all anionic); and Triton X-100, gelatin, Decon-90, ethyldigol and 2-ethoxyethanol (all non-ionic).

The maxima of *m*- and *p*-nitrobenzoic acids ( $-0.57\text{V}$  and  $-0.56\text{V}$  respectively) lie on the negative side of the electro-capillary zero ( $-0.3\text{V}$ ) and hence these are of negative polarity<sup>4</sup>. The relative heights of the maxima under identical conditions follow the order : *m*-nitrobenzoic acid > *p*-nitrobenzoic acid.

Both the maxima get shifted to less negative potentials (positive shift) as the concentration of cationic, anionic and non-ionic surfactants is increased (Table 1).

The  $i_{\text{max}}$  values also decrease with increase in surfactant concentration. The order of decrease in the values of  $i_{\text{max}}$  is : *m*-nitrobenzoic acid > *p*-nitrobenzoic acid.

The maximum suppression point (MSP), specific suppression coefficient (SSC) and critical micelle concentration (CMC) values of the cationic surfactants are much less than those for anionic ones (Table 2). This indicates that the amount of ionic surfactants required to suppress maxima of similar sign is greater than that for those possessing dissimilar charges<sup>5</sup>. Since the maxima in the present study show negative polarity, the cationic surfactants will move right up to the mercury surface and the anionic ones are likely to remain at a greater distance somewhere in the double layer. A cationic surfactant will prevent streaming<sup>5</sup> more effectively as compared to the anionic one having identical hydrocarbon chain. This is supported by the fact that LPC is more effective than SLS, though both the surfactants have the same carbon chain length.

On the basis of MSP values, the order of relative efficacies of cationic, anionic and non-ionic surfactants in suppressing the negative maxima of *m*- and *p*-nitrobenzoic acids has been established as follows : (i) for cationic surfactants : CTAB > CDBAC > CPC > LPC > CPB, (ii) for anionic surfactants : Manoxol-OT > SLS > DBS > Tergitol-7 > Manoxol-IB, and (iii) for non-ionic surfactants : Triton X-100 > Gelatin > Decon-90 > Ethyldigol > 2-Ethoxyethanol. It is evident that in the case of cationic and anionic surfactants, the surfactants with the same

TABLE 2 — MAXIMUM SUPPRESSION POINT, SPECIFIC SUPPRESSION COEFFICIENT AND CRITICAL MICELLE CONCENTRATION VALUES FOR IONIC AND NON-IONIC SURFACTANTS FOR THE MAXIMA OF *m*- AND *p*-NITROBENZOIC ACIDS

Surfactant	<i>m</i> -nitrobenzoic acid			<i>p</i> -nitrobenzoic acid		
	M.S.P. (M)	S.S.C. (M)	C.M.C. (M)	M.S.P. (M)	S.S.C. (M)	C.M.C. (M)
<b>Cationic</b>						
LPC	$1.32 \times 10^{-5}$	$2.71 \times 10^{-5}$	$2.00 \times 10^{-5}$	$1.91 \times 10^{-5}$	$7.41 \times 10^{-5}$	$5.00 \times 10^{-5}$
CPC	$1.17 \times 10^{-5}$	$3.39 \times 10^{-5}$	$3.00 \times 10^{-5}$	$1.76 \times 10^{-5}$	$3.39 \times 10^{-5}$	$2.51 \times 10^{-5}$
CPB	$1.38 \times 10^{-5}$	$2.81 \times 10^{-5}$	$4.00 \times 10^{-5}$	$2.00 \times 10^{-5}$	$2.24 \times 10^{-5}$	$4.00 \times 10^{-5}$
CDBAC	$1.60 \times 10^{-5}$	$1.09 \times 10^{-5}$	$2.00 \times 10^{-5}$	$1.72 \times 10^{-5}$	$5.37 \times 10^{-5}$	$6.00 \times 10^{-5}$
CTAB	$0.86 \times 10^{-5}$	$2.63 \times 10^{-5}$	$5.00 \times 10^{-5}$	$1.51 \times 10^{-5}$	$3.46 \times 10^{-5}$	$7.00 \times 10^{-5}$
<b>Anionic</b>						
DBS	$5.62 \times 10^{-5}$	$1.09 \times 10^{-5}$	$1.29 \times 10^{-5}$	$8.00 \times 10^{-5}$	$1.74 \times 10^{-5}$	$2.00 \times 10^{-5}$
SLS	$4.41 \times 10^{-5}$	$2.23 \times 10^{-5}$	$2.82 \times 10^{-5}$	$4.67 \times 10^{-5}$	$1.41 \times 10^{-5}$	$2.45 \times 10^{-5}$
Tergitol-7	$6.57 \times 10^{-5}$	$1.44 \times 10^{-5}$	$1.82 \times 10^{-5}$	$8.50 \times 10^{-5}$	$3.23 \times 10^{-5}$	$5.37 \times 10^{-5}$
Manoxol-OT	$1.66 \times 10^{-5}$	$3.23 \times 10^{-5}$	$7.00 \times 10^{-5}$	$3.39 \times 10^{-5}$	$9.33 \times 10^{-5}$	$6.00 \times 10^{-5}$
Manoxol-IB	$2.63 \times 10^{-5}$	$3.80 \times 10^{-5}$	$1.00 \times 10^{-5}$	$7.58 \times 10^{-5}$	$1.46 \times 10^{-5}$	$4.00 \times 10^{-5}$
<b>Non-ionic</b>						
Triton X-100*	$2.88 \times 10^{-4}$	$4.57 \times 10^{-5}$	$7.76 \times 10^{-5}$	$6.45 \times 10^{-4}$	$1.71 \times 10^{-4}$	$1.31 \times 10^{-4}$
Gelatin*	$1.29 \times 10^{-3}$	$3.80 \times 10^{-4}$	$8.00 \times 10^{-4}$	$5.12 \times 10^{-3}$	$1.19 \times 10^{-3}$	$1.31 \times 10^{-3}$
Decon-90*	$3.73 \times 10^{-3}$	$7.58 \times 10^{-3}$	$6.92 \times 10^{-3}$	$5.82 \times 10^{-3}$	$1.90 \times 10^{-3}$	$2.00 \times 10^{-3}$
Ethyldigol	$6.16 \times 10^{-3}$	$5.89 \times 10^{-3}$	$1.32 \times 10^{-2}$	$9.55 \times 10^{-3}$	$5.27 \times 10^{-3}$	$5.25 \times 10^{-3}$
2-Ethoxy ethanol	$6.45 \times 10^{-1}$	$7.24 \times 10^{-3}$	$8.00 \times 10^{-3}$	—	—	—

\*M.S.P., S.S.C. and C.M.C. values are expressed in percentage

polar heads but having higher carbon chain lengths are more effective.

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### Solid State Reaction between Mercury(I) Dicarboxylates & Halogens: Part II—Reaction between Mercury(I) Succinate & Iodine

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Reaction of iodine with solid mercury (I) succinate has been studied. An unstable yellow coloured reaction intermediate is formed first which subsequently gives a red final product. The final product has been identified to be a mixture of succinic anhydride and  $HgI_2$ . The kinetics of the bulk diffusion of iodine into the solid mercury(I) succinate has been studied. The mechanism of the propagation of reaction has also been established.

RECENTLY we have reported the study of an exchange reaction of the type  $A(s) + B(g) \rightarrow C(s) + D(g)$  involving mercury(I) oxalate (solid) and iodine (vapour)<sup>1</sup>. The present note deals with a solid-gas exchange reaction between mercury(I) succinate and iodine.

Mercury (I) succinate was prepared by adding succinic acid (S. Merck, GR) solution to mercury(I) nitrate (S. Merck, GR) solution. The precipitate was washed with doubly distilled water and dried *in vacuo* over fused calcium chloride. It was analysed for mercury [Found :  $76.90 \pm 0.3$ . Calc. for  $Hg_2C_4H_4O_4$  : 77.57 %].

The stoichiometry of the reaction between mercury(I) succinate and iodine (S. Merck, GR) was established by a method reported earlier<sup>1,2</sup> using

TABLE 1 — STOICHIOMETRIC DATA FOR THE REACTION BETWEEN MERCURY(I) SUCCINATE AND IODINE

Temp. (°C)	Mercury(I) succinate taken (g)	Increase in mass (g)	
		Obs.	(Calc.)*
$45 \pm 1$	0.3958	0.3732	(0.3765)
	0.4900	0.4625	(0.4661)
$71 \pm 1$	0.2826	0.2624	(0.2690)
	0.3425	0.3194	(0.3258)

\*Calculated for  $2HgI_2 + C_4H_4O_4$ .

reactants of particle size  $> 140$  mesh. The results given in Table 1 show that mercury(I) succinate and iodine react in a 1 : 2 molar ratio.

In order to analyse the final reaction products, the fractional separation and analysis of the reaction products were carried out by an experimental set up shown in Fig. 1. The mixed reaction product was kept in tube A and the assembly was kept in an electric tube furnace at  $220 \pm 10^\circ C$  for 3–4 hr in such a way that tubes B, C and D were outside the furnace. A white needle shaped crystalline substance got condensed in tubes C and D; it was found to be succinic anhydride by its melting point (Found:  $120 \pm 0.5^\circ C$ ; reported<sup>3</sup>: 119.6) and also by powder X-ray diffraction pattern which was in agreement with that reported in ASTM file. A yellow compound was found in tubes A and B. On cooling, this yellow compound changed into a red one which was collected and identified to be mercury(II) iodide by DTA (endotherm for phase transition, found:  $127.5^\circ C$ ; reported<sup>4</sup>:  $127^\circ C$ ) and also by the powder X-ray diffraction pattern which was in good agreement with that reported for mercury(II) iodide in the ASTM file.

The product was also quantitatively analysed. A known amount of the product was shaken well with distilled water. The white product dissolved in water while the red one settled down. The red product was filtered, dried and weighed (Table 2). The solution containing the white soluble compound was treated with mercury(I) nitrate solution and the precipitate obtained was filtered, washed, dried and then weighed (Table 2). Thus, on the basis of DTA, powder X-ray diffraction pattern, and chemical analyses, the reaction product has been established to be a mixture of mercury(II) iodide and succinic anhydride in 2 : 1 molar ratio.

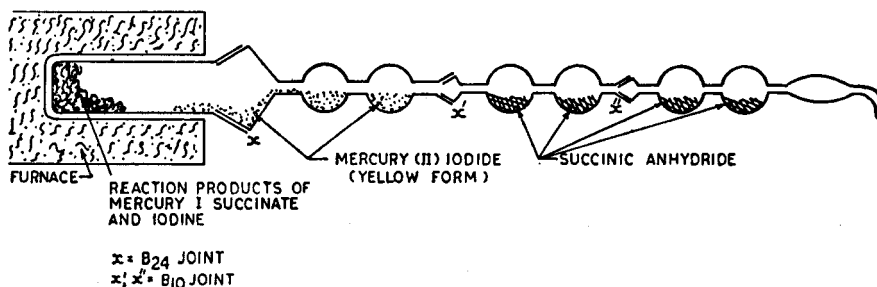


Fig. 1 — Experimental set-up for the analysis of the reaction products.