Development of Detergent Sensitive Electrodes and Studies of the Charge Transfer Reaction at These Electrodes

A Thesis

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In Partial Fulfillment

of The Requirements for the Degree

Master of Science in Chemistry

by

Beniam Alemayehu

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To my Parents.

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1. INTRODUCTION

Detergency is a theory and practice of the removal of foreign material from solid surfaces by surface chemical means. Though many advantages are brought by the use of detergents, the adverse environmental effects arising from the use of detergents cannot be ignored. The practical advantage that detergents have over soap, i.e., high solubility in hard water must be balanced against the fact that some of these cleansing agents show a high resistance to biological degredation in sewage treatment plants and septic tanks. As a result, lakes and rivers etc. become contaminated with domestic and industrial detergents. Even if the problem of pollution has been minimized by the introduction of "soft detergents", the fact that even today non-biodegradable detergents are still being produced makes it necessary to have a means of controlling the detergent content in drinking water. Today direct and indirect determinations are employed using chemical and physico-chemical methods. It is the aim of this paper to present a method for the analysis of detergents by developing detergent sensitive electrodes.

We have developed a liquid membrane surfactant sensitive electrode which is selective for the dodecylsulfate ion. The liquid membrane that was used was crystal violet dodecylsulphate complex in nitrobenzene with carbon powder as a supporting matrix. The electrode response has been tested for varying concentrations of dodecylsulphate ions with and without interferring ions.

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We have developed a liquid membrane surfactant sensitive electrode which is selective for the dodecylsulfate ion. The liquid membrane that was used was crystal violet dodecylsulphate complex in nitrobenzene with carbon powder as a supporting matrix. The electrode response has been tested for varying concentrations of dodecylsulphate ions with and without interferring ions.

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To be able to understand the potential forming step at this electrode and further to account for the over-Nernstian behaviour that this electrode manifested, voltammetric investiga ion was chosen. Though it was not possible to fully explain the mechanism of the potential forming reaction at the electode, attempts have been made to study the charge transfer reaction of the detergent ion and the fluoride ion across the interface of two immiscible electrolytes using cyclic voltammetry with four electrode arrangements.

hexachlorobenzene had to be dissolved in the membrane phase, the advantages of these additives being to enhance the ionization of the ionogenic components. Such electrodes showed the slope expected from the Nernst equation upto the C.M.C.

Electrodes selective for different surfactants have been constructed by different workers. Birch and Clark used carrier complexes synthesized from the $C_{16}(CH_3)_3N^+$ salt. The anionic surfactants used were sodium n-alkylsulphonates with alkyl chain lengths from C_6 to C_{14}, sodium dodecylbenzenosulphate and the sodium salt of dodecyl ether sulphonate and dodecanoate. Electrodes sensitive to benzensulphonate, toluene sulphonate and α- naphathalene sulphonate ions have been constructed by Ishibashi et al (14) using crystal violet and some analogous of triphenylmethane derivatives (methyl violet and malachite green) as ion-exchange sites in the memberane. Each electrode had an approximately Nernstain slope (56 mv/decade) down to 10^{-4}M and was useful down to 10^{-5}M. Another group of workers, Tanake et al (15) were able to construct alkylbenzenesulphonate ion selective electrodes based on the incorporation of the sulphonate-ferroin complex into a poly-vinyl chloride matrix. The linear response range of the solid-state membrane electrode was 10^{-2}-10^{-5}M.

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The determination of detergents employing coated-wire ion-selective electrodes (16,17,18) has been applied and the linear response ranges and c.m.c. values for different detergents are given in parentheses: p-toluene sulphonate (57: $10^{-3.6}$-10^{-1}M) and Lauryl sulphate (89, $10^{-3.7}$-10^{-2}M).

The liquid membrane electrodes discussed above are not without limitations (19) . These electrodes are difficult to construct and frequently give irreproducible potentials. Often their lifetimes are quite brief and they have the added disadvantage that solubilization of the liquid membrane components into the surfactant solutions may take place at concentrations above the c.m.c. Culter and Meares (19) observed similar problems with coated wire electrodes.

From the above litrature review it is evident that different types of detergent sensitive electrodes have been produced based on liquid ion exchange electrodes. However, the potential forming mechanism of these electrodes has not been completely understood. The investigation of the ion transfer reaction across the interface of immiscible electrolytes using electronalytical techniques provides useful information about processes in biological systems, the kinetics of phase transfer catalysis and the charge transfer reaction occuring at liquid state ion sensitive electrodes (20). The organic solvents as well as the base electrolytes used in these methods are rather similar to those used in liquid membrane ion-selective electrodes. The appropriate

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polarographic current voltage curves can be used for a kinetic approach to the assessment of Nernstian, sub- and super-Nernstian behavior of similar ion-selective electrodes (21). The electrochemical processes involving the passage of ions across an interface between two immiscible solutions have been almost exclusively studied with a water-nitrobenzene system but using various different electroanalytical techniques namely: steady state polarization (22), chronopotentiometry (23,24,25), polarography with an orginal type of dropping electrode (26,27) and cyclic voltammetry (28-30). At the same time a basis has been formulated for the interpretation of electrochemical reactions taking place at the interface separating these electrolyte solutions (23,25,27).

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3. Experimental

3.1. Potentiometric Investigation with detergent sensitive carbon paste electrodes

3.1.1 Chemicals and Reagents

NaF(BDH), Nitrobenzene (Analar), sodium dodecyl sulphate (BDH) Tetrabutylammonium chloride (Fluka), crystal violet (BDH), LiCl (BDH), LiF (BDH), carbon powder (spectrograde). Sodium 2-(n-propyl)-5-(n-nonyl) benzene sulphontate, sodium 2-(n-butyl)-5-(n-decyl) benzene sulphonate, sodium 2-(n-heptyl)-5-(n-heptyl) benzene sulphonate, sodium 2-(ethyl)-5-(n-heptyl) benzene sulphonate.

Stock solutions were prepared at a concentration of 10^{-1}M for dodecyl sulphate and 10^{-2}M for all other detergents. They were diluted with redistilled water as necessary, immediately prior to use. For the concentrations 10^{-2}-10^{-3}M, dodecyl sulphate solution was found turbid a day after preparation.

3.1.2 The carbon paste electrode

A liquid ion exchange membrane is formed by dissolving a liquid ion exchanger in a water immiscible solvent. The ionogenic groups (sites) of a liquid ion exchange are mobile as opposed to solid ion exchangers which have their ionogenic

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groups fixed to the membrane matrix. Depending on the solvent used to form the ion exchange membrane, the sites would be completely dissociated (31,32) if the dielectric constant of the solvent is high or highly associated (33-35) if the dielectric constant of the solvent is low into ion pairs. The solvent, with which the membrane is saturated must be chosen so as to have certain properties of which immiscibility with water and high dielectric constant are the primary requirements. In the expriment, nitrobenzene has been chosen as the solvent on the grounds that it fulfills the above requirements particularly in its ability to dissociate the complex.

The carbon powder (graphite) with a liquid ion-exchanger in nitrobenzene forms the liquid ion exchange membrane. The carbon paste electrode has a number of characterstics which makes it useful for this purpose. It is a relatively inert electrode, whose surface can easily be renewed to give reproducible results. Above all it is easy to construct the electrode.

3.1.3 The cation-detergent complexes (active-sites).

The choice of the complex is made such that it should be sufficiently soluble in the membrane but minimally soluble in water. The cation part of the complex is a large organic molecule whereas the

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anionic part was determined by the nature of the species to which electrode reversibility (response) was desired. The general chemical equation for the complex formation is:

$$C^+ + A^- \longrightarrow CA$$

where C^+ is a big organic cation and A^- any organic anion e.g. detergent.

Preparation of complexes (electrode action)

In order to develop an electrode sensitive to the dodecyl sulphate ion (surfactant), the particular anionic surfactant chosen was sodium dodecyl sulphate. Crystal Violet-dodecyl sulphate (CVDS) complex was prepared by mixing equimolar amounts of aqueous solutions of sodium dodecyl sulphate (SDS) and crystal violet. A violet precipitate was formed which was extracted with chloroform. After evaporating the chloroform, the violet solid was further purified by extracting it with benzene in which it is soluble.

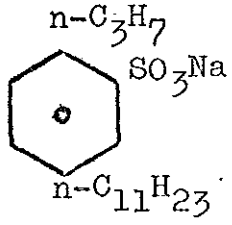
The complex tetrabutylammonium tetraphenylborate TBATPB was prepared by mixing an aqueous solution of tetrabutylammonium iodide (Fluka) with an aqueous solution of sodium tetraphenylborate (Fluka). The white precipitate, tetrabutylammonium tetraphenylborrate, was recrystallized from acetone (Analar) twice.

Crystal violet-tetraphenylborate (CVTPB) complex was was prepared by mixing equimolar amounts of crystal violet and tetraphenylborate that were dissolved in methanol. After evaporating the methanol the solid was extracted with benzene and then with n-hexane.

These complexes were dissolved in redistilled nitrobenzene to give a 10^{-2}M concentration.

Preparation of tetrabutylammonium alkybenzene sulphonate complexes

To gather some evidence as to the potential forming step in the electrode process, some complexes of tetrabutylammonium cation with detergents were prepared. The detergents used for this purpose were



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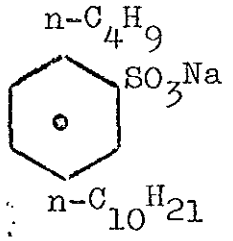

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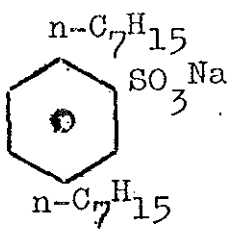

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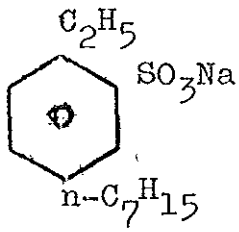

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A. Sodium 2-(n-propyl)-5-(n-nonyl)benzenesubphonate
B. Sodium 2-(n-butyl)-5-(n-decyl) benzene sulphonate
C. Sodium 2-(n-heptyl)-5-(n-heptyl) benzene sulphonate
D. Sodium 2-(ethyl)-5-(n-heptyl)benzene sulphonate.

Each complex was prepared by mixing equimolar amounts of hot solutions of the detergent and tetra-butylammonium chloride. A white precipitate was formed immediately. After filtration, the complex was washed with redistilled water several times to remove the sodium chloride and then left to dry for several days in the open air.

3.1.4 Preparation of detergent sensitive electroes

The detergent sensitive electrode pastes prepared by dissolving 10^{-2}M concentration of each of the respective complexes in nitrobenzene. The paste was then prepared by mixing 2 grams of the nitrobenzene complex solution with 5 grams of graphite powder in a mortar. Mixing of the materials for 5 minutes gave a homogenous paste.

The electrode was constructed by pushing the carbon-paste into a commercially available methrom-CP-electrode. Before use the electrode was given a smooth surface, by polishing it against another smooth surface.

3.1.5 Potentiometric Measurement

All the potentiometric measurements have been carried out with a Philips digital PH-meter PW 9409 using the following cell arrangement.

Hg	Hg_2Cl_2	KCl (Sat)	Test Solution X mole/l	Detergent Sensitive Carbon Paste electrode

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3.2 Voltammetric studies of the ion transfer across the interface water - nitrobenzene

In order to study the charge transfer reaction taking place at detergent sensitive electrodes, voltammetric investigation in the system nitrobenzene-water seem to be promising. Salt like compounds of detergent anions and a large organic cation were employed as electrode active materials and the same complexes were used as supporting electrolyte in the organic phase. In this section the charge transfer of the dodecyl sulphate ion across the water/nitrobenzene interface has been studied for different aqueous and non-aqueous supporting electrolytes. The method employed was cyclic voltammetry with a four electrode arrangement.

3.2.1 The Experimental set-up

The studies were made using an apparatus and vessel similar to that of Koryta and Samec. Initial compositions of the solutions investigated (before matual saturation and equilibrium) were the following

Aqueous Solution	Nitrobenzene Solution
A^+B^- C $\leq 10^{-4}$	$R^+R'^-$, 10^{-2}M
MX, C=10^{-1}-10^{2}	

Where A^+B^-, is any test ion (salt), $R^+R'^-$ any complex or organic supporting electrolyte and M^+X^- any hydrophilic pair (supporting electrolyte).

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Voltammetric cell: The electrolytic cell was constructed in our laboratory. It consisted of the working space where the interface to be studied was located and of two compartments for the platinium wire counter electrodes, separated from the working space by sintered glass and of one compartment for the elimination of diffusion of ions. The compartments for the counter electrodes contained a 0.1 M aqueous solution of NaF and and the working space was filled by an aqueous test solution containing sodium Dodecyl sulphate (NaDS) + 0.01M LiF and 0.01 M nitrobenzene solution of the base electrolyte.

The boundary of the aqueous and the nitrobenzene phases in the working space had an area of 0.33 cm^2. The Ag/AgCl reference electrode (fig. 10, RE 1 and RE 2) was connected to each phase close to the interface by means of the Luggin capillary. The four electrode arrangement is shwon in fig. 10.

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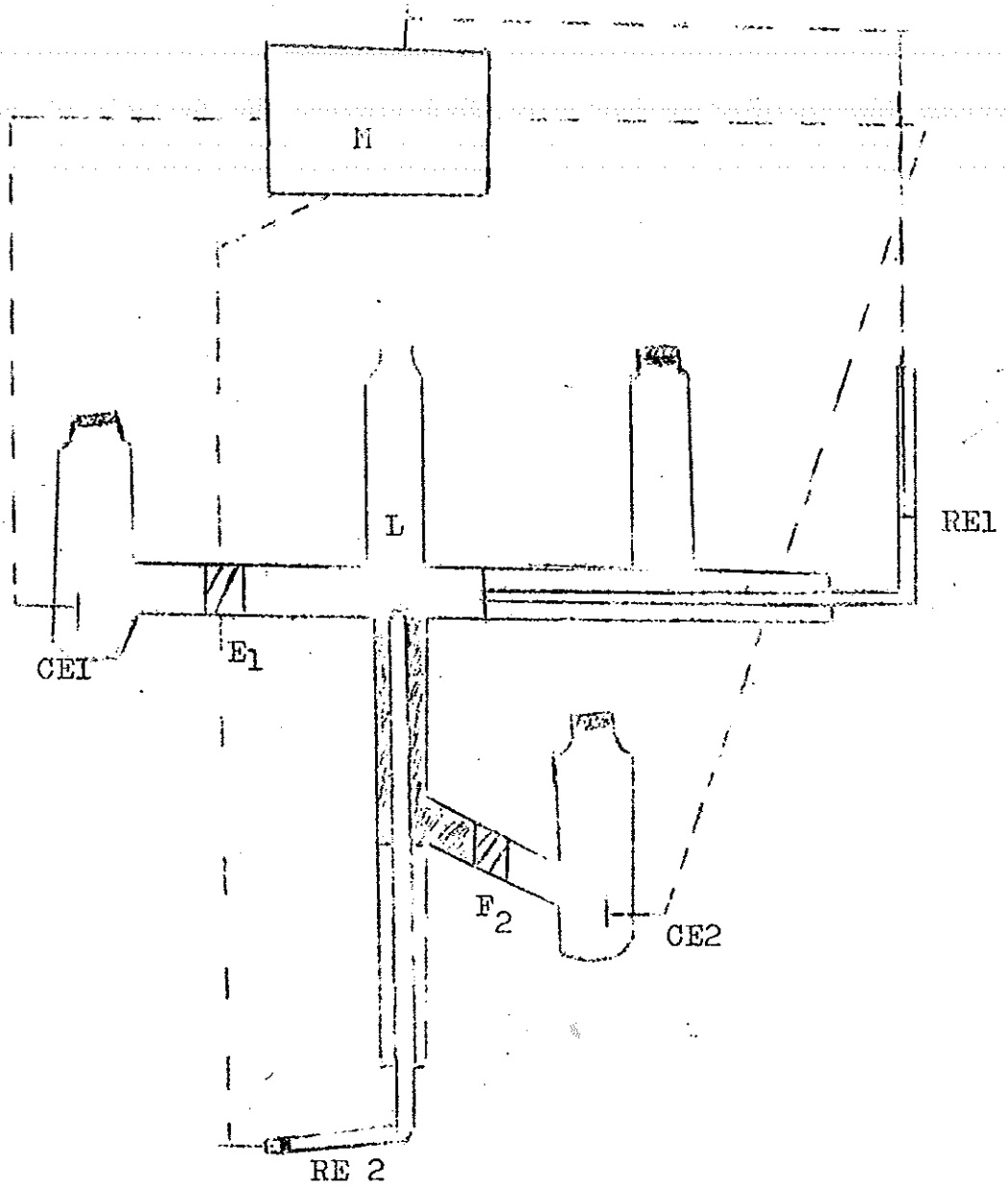

Figure 10: Scheme of the electrolytic cell. Ref 1 and Ref 2, Ag/AgCl reference electrodes; CE 1 and CE 2, counter plantinium wire electrodes. Sheded area represents the nitrobenzene solution F_1, F_2 sintered glass disks. L is the Luggin capillary connecting organic solution (NB) to an aqueous reference electrodes. M is both the pulse generator and the potentiostat.

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Electronic circuit: The potential E vs is applied to the contacts of the reference electrodes RE 1 and RE 2 from a generator of triangular voltage pulses through the four-electrode potentionstatic circuit. It is equal to the potential difference $\Delta\varphi_{nB} = \varphi_{(W)} - \varphi_{(nB)}$ across the interface.

The electronic circuit for the voltammetric measurements with the four-electrode system was similar to that of Samec (30). The block diagram is given in fig. 11. The potentio-state are represented by the operational amplifiers OA 1-2. The differential amplifier was taken from the negative feedback of the current follower OA 2 with the feedback resistor R_2 which can be interrupted in the external connections. This makes it possible to transform the circuit of the potentiostat into a four-electrode configuration. Because each reference electrode is connected to the high impedance input of the operational amplifier (OA 1 and OA 2) only negligible current can flow through each of them. The potential difference between the tips of the Luggin capillary is then controlled in a defined manner. The current flowing through the interface is supplied by the outputs of the operational amplifiers OA 1 and OA 2 by means of the counter electrodes CE 1 and CE 2.

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Its value can be measured as the floating voltage drop across the resistor R_2. The output of the operational amplifier OA 3 was connected to the imput of XY recorder.

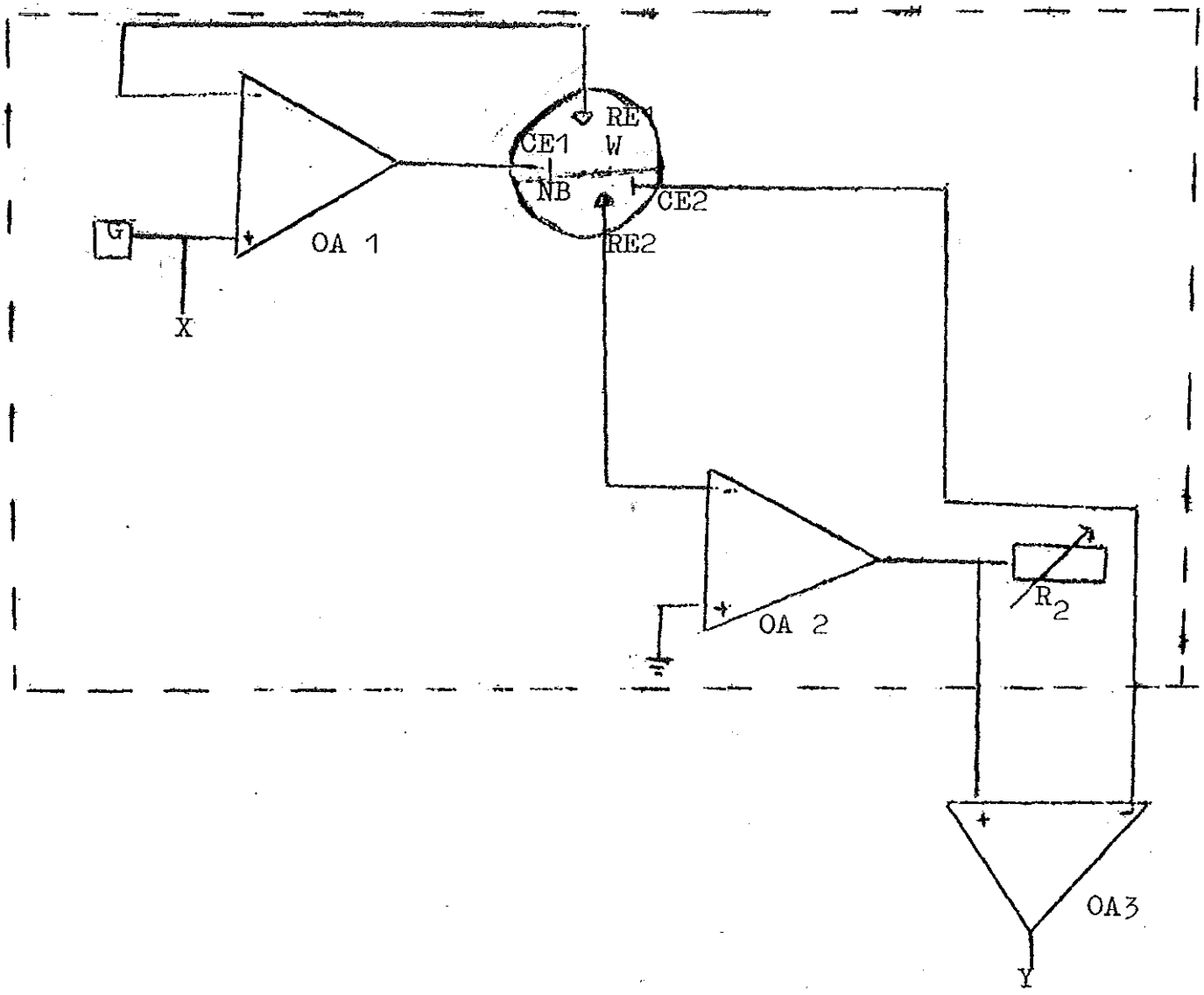

Figure II: Block diagram of the electronic curcuit, G pulse generator X and Y, imputs of recorder; RE 1 and RE 2, reference electrodes; CE 1 and CE 2, counter electrodes; R_2, floating resistor. Part of circuit bordered by dotted line in block diagram of MPI. MP1012 A potentiostat. Symbols NB and (W) are for nitrobenzene and aqueous phase respectively.

4. Results and Discussion

4.1 Potentiometric Studies

The response of the CVDS-carbon paste electrode to the varying dodecyl sulphate concentration have been studied under two experimental conditions i.e. keeping the ionic strength constant and without the supporting electrolyte. The sets of measurements taken is shown in table 1. The variation in the potentials of this specific electrode are represented as a function of the detergent concentration and not of the average activity. The concentrations used are sufficiently low that it may be assumed that these are equal to the activity.

Plots were prepared for the measured potentials verus the negative logarithm of the variable concentration of SDS. Fig. 1 shows a sample plot. The curve representing the variation in electrode potential is composed of two parts. In the low concentration region the electrode potential increases with the detergent concentration. The electrode response was found to be super-Nernstian with a slope of 80 mv. This over-Nernstian behavious has been observed by other workers (16,17,36) using different complexes. The reason is not completely understood.

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Table 1

Concentration (M)	Potential in mv sodium dodecyl sulphate				Potential in mv sodium dodecyl sulphate in supporting electrolyte, NaF (0.1M).			
10^{-5}	90	70	80	96	70	69	64	53
5×10^{-5}	25	32	39	30	21	26	23	25
10^{-4}	11	6	16	23	11	3	0	2
5×10^{-4}	-54	-67	-50	-51	-44	-43	-47	-43
10^{-3}	-78	-83	-69	-69	-54	-52	-58	-54
5×10^{-3}	-92	-80	-79	-79	-55	-60	-63	-59
10^{-2}	-80	-76	-66	-74	-57	-59	-63	-59

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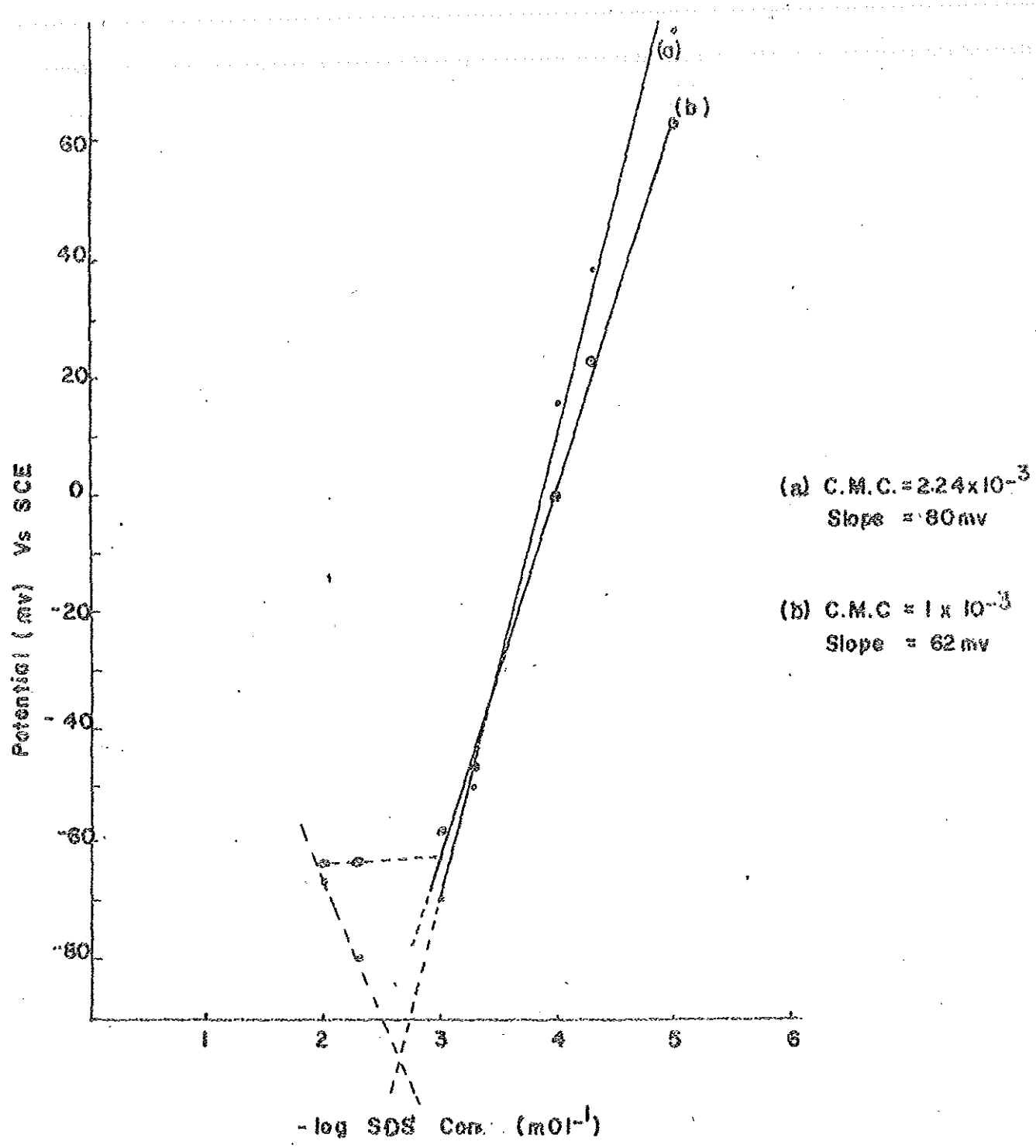

Fig. 1 - Response of dodecylsulphonate electrode in SDS solution.
(a) without supporting electrolyte
(b) with 0.1M NaF supporting electrolyte.

Ionic detergents in aqueous solution are known to be almost completely dissociated at low concentrations. But in areas of high concentration there solutions contain free ions as well as micelles formed by the association of a certain number of long chain ions and partially neutralized by counter ions. The break in the plot of EMF verus log C_{SDS}, where C_{SDS} , is the concentration of sodium dodecyl sulphate, indicates that the c.m.c lies at a value of 2.2×10^{-3}M. This value differs significantly from the accepted limits for the c.m.c. These limits are $8.0\text{-}8.4 \times 10^{-3}$M (37). The lower c.m.c value obtained can be ascribed to the interaction of the carrier liquid, nitrobenzene with the detergent and also to the impure materials that may present with the surfactant. The surfactant had not been further purified. The possibility that some impurities may exist is shown by the change to turbidity of these solutions on standing (10^{-2}-10^{-3}M). Gavach at al and Clark et al have also reported (12,11) the effect that impurities and nitrobenzene may have on the lowering of the c.m.c.

In Figure 1(a) , at high concentrations, i.e. in the micelle areas, the electrode potential decreases slightly as the detergent concentration increases. It appears that one could relate this decrease to the fact that the electric charge on the organic ions constituting the micelle is not completely compenseted for by the inorganic ions which are bound in a stable manner to the surface of the micelle (3).

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From can be shown that the useful
concentratic n which the electrode may be used
extends from 10^{-5}M.

From the otential vs log concentration plot (fig.1b), the slope was calculated to be 62 mv. The critical micelle concentration, c.m.c, lies at 1.0×10^{-3}M. The useful concentration range extends from 10^{-3}-10^{-5}M. Below the c.m.c the values of the electrode potential of a DS^- selective electrode in contact with a solution containing the surfactant and the supporting electrolyte at the same time, are less than the values obtained with solutions of SDS in pure water (fig. 1a and 1b). The reduction in the activity coefficient of the DS^-, estimated by the method of approximation using the limiting Debye-Huckel formula is not sufficient to account for this effect. Since the specific electrode responds only to the activity of the monomeric form of the surfactant (11), the difference in potential of the DS^- selective electrode in the presence and absence of NaF may be due to the dimerization of dodecyl sulphate ion in the solution (38,39). This very fact may also account for

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the shift in the position of the c.m.c. from 2.2×10^{-3} to 10^{-3}M. This behivor has been observed by other workers (11,12) .

Table 2

Concentration (M)	Potential in mv (Cl^-)				Potential in mv Pb^{2+}		Potential mv (NO_3^-)
10^{-6}	142	155	139	142	189	179	51
10^{-5}	142	138	134	122	187	199	61
10^{-4}	137	136	130	122	156	124	64
10^{-3}	120	124	120	112	110	128	69
10^{-2}	116	115	118	98	74	96	66
10^{-1}					56	96	57

Concentration (M)	Potential in mv (Ni^{2+})			Potential in mv (SO_4^{2-})			Potential mv Cu^{2+}	
10^{-6}	94	147	175	153	214	196	189	174
10^{-5}	94	157	175	154	155	150	165	172
10^{-4}	106	145	152	204	212	202	174	176
10^{-3}	106	132	116	222	225	219	165	171
10^{-2}	96	119	84	245	247	228	192	214

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Table 3

Concentration in (M)	Potential in mv Detergent B				Potential in mv Detergent D			
10^{-6}					41	38	26	11
5×10^{-6}	95	103	43	29	56	55	60	52
10^{-5}	90	110	68	67	32	41	39	40
5×10^{-5}	44	61	20	20	-25	-19	-8	-22
10^{-4}	33	44	-1	-1	-40	-39	-30	-32
5×10^{-4}	-5	5	-50	-47	-87	-84	-65	-75
10^{-3}	-10	-9	-63	-61	-99	-90	-75	-86
2.5×10^{-3}	-13	-20	-66	-65	-98	-88	-76	-90
10^{-2}	-16	-26	-68	-69	-94	-88	-77	-96

Table 4

Concentration in (M)	Potential in mv Detergent C				Potential in mv Detergent A			
10^{-6}	59	42	37	12	30	26	13	6
5×10^{-6}	70	53	46	40	20	31	30	32
10^{-5}	48	36	34	27	4	19	20	22
5×10^{-5}	-7	-8	-16	-18	-48	-35	-34	-30
10^{-4}	-31	-35	-39	-45	-67	-59	-57	-52
5×10^{-4}	-68	-75	-82	-92	-104	-98	-99	-92
10^{-3}	-87	-88	-100	-105	-104	-101	-102	-100
2.5×10^{-3}	-109	-99	-107	-107	-103	-101	-100	-100
10^{-2}	-117	-100	-100	-105	-103	-101	-102	-102

The response of this detergent sensitive electrode towards certain cations and anions has been studied, table 2. Curves were obtained for the measured potentials vs log concentration for a series of concentrations of these anions and cations as shwon in fig. 2,3,4 and 5. From the distribution of the points and the calculated slopes, it can be concluded that Cl^-, NO_3^-, Cu^{2+}, Pb^{2+}, SO_4^{2-} and Ni^{2+} show insignificant interference in the concentration range of 10^{-2}-10^{-5}M.

Table 3 and 4 show measurements taken for detergents A,B,C and D using the corresponding detergent complex electrode. Fig. 6-9 represent the plots prepared for the

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measured potential with respect to the logrithm of the varying concentration of each detergent. From these figures the slopes were calculated to be 64,64,65 and 60 mv and the critical micelle concentrations were found to lie at 5.62×10^{-4}, 1.1×10^{-3}, 1.4×10^{-3} and 7.1×10^{-4}M for detergents A,B,C and D respectively.

Detergents A,B and C have 14 carbon atoms as side chains which approximately corresponds to the number in dodecyl sulphate, neverthless the results indicate that the slopes for these detergents show Nernstian behavior unlike SDS. Detergent D with less carbon atoms than the others still shows a Nernstian behavior. From the above findings it therefore appears that the shape of the molecule and the number of carbon atoms probably does not affect the electrode process in the potential forming step for this type of ion selective electrode.

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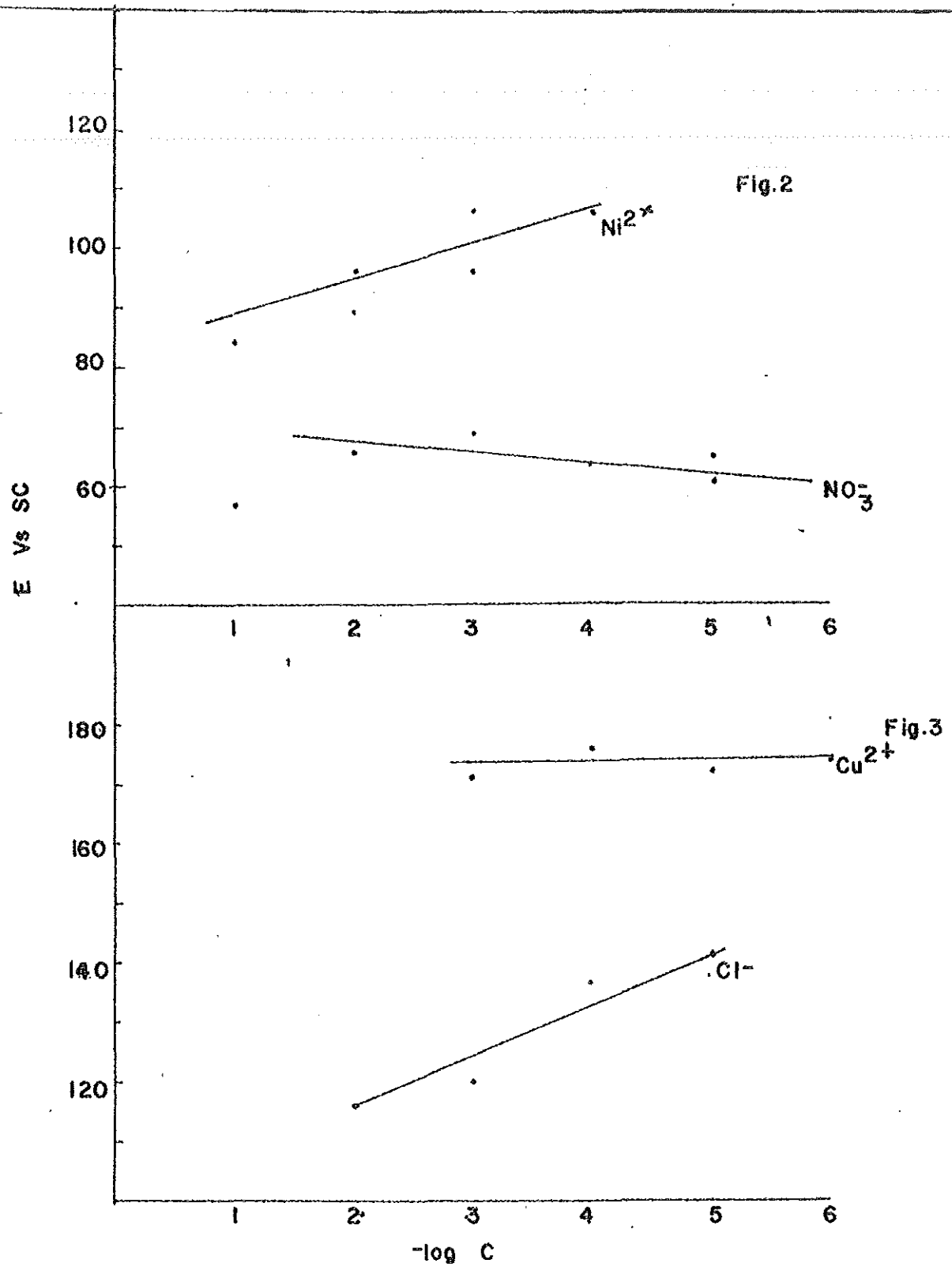


Slope $\frac{17}{1.5}$

Fig. 2 and 3 Effect Of The Interfering Ions On The Response Of The Electrode

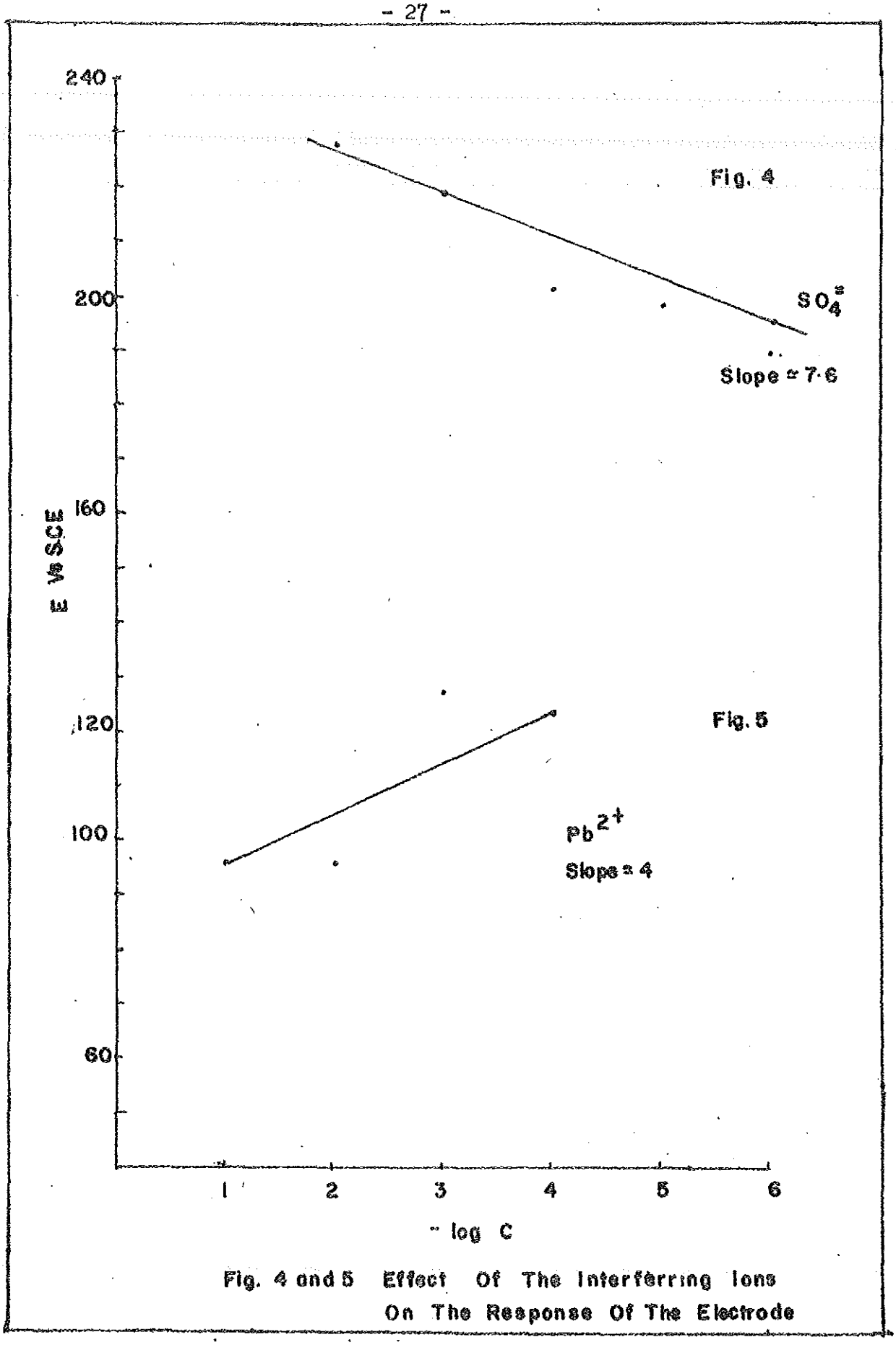


Fig. 4 and 5 Effect Of The Interferring Ions On The Response Of The Electrode

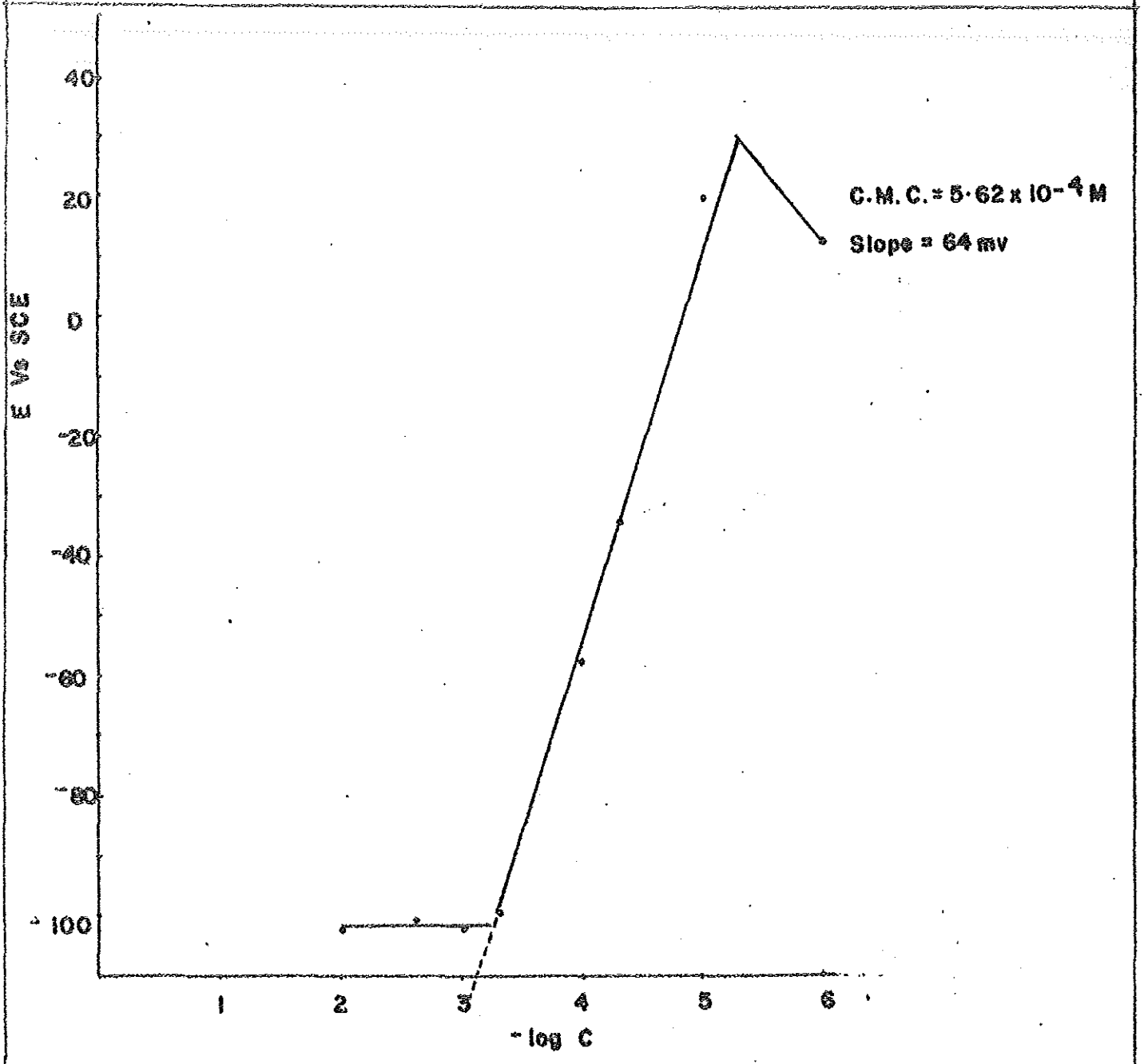


Fig. 6 : Response Of The Detergent (A) Electrode In The Detergent A Solution.

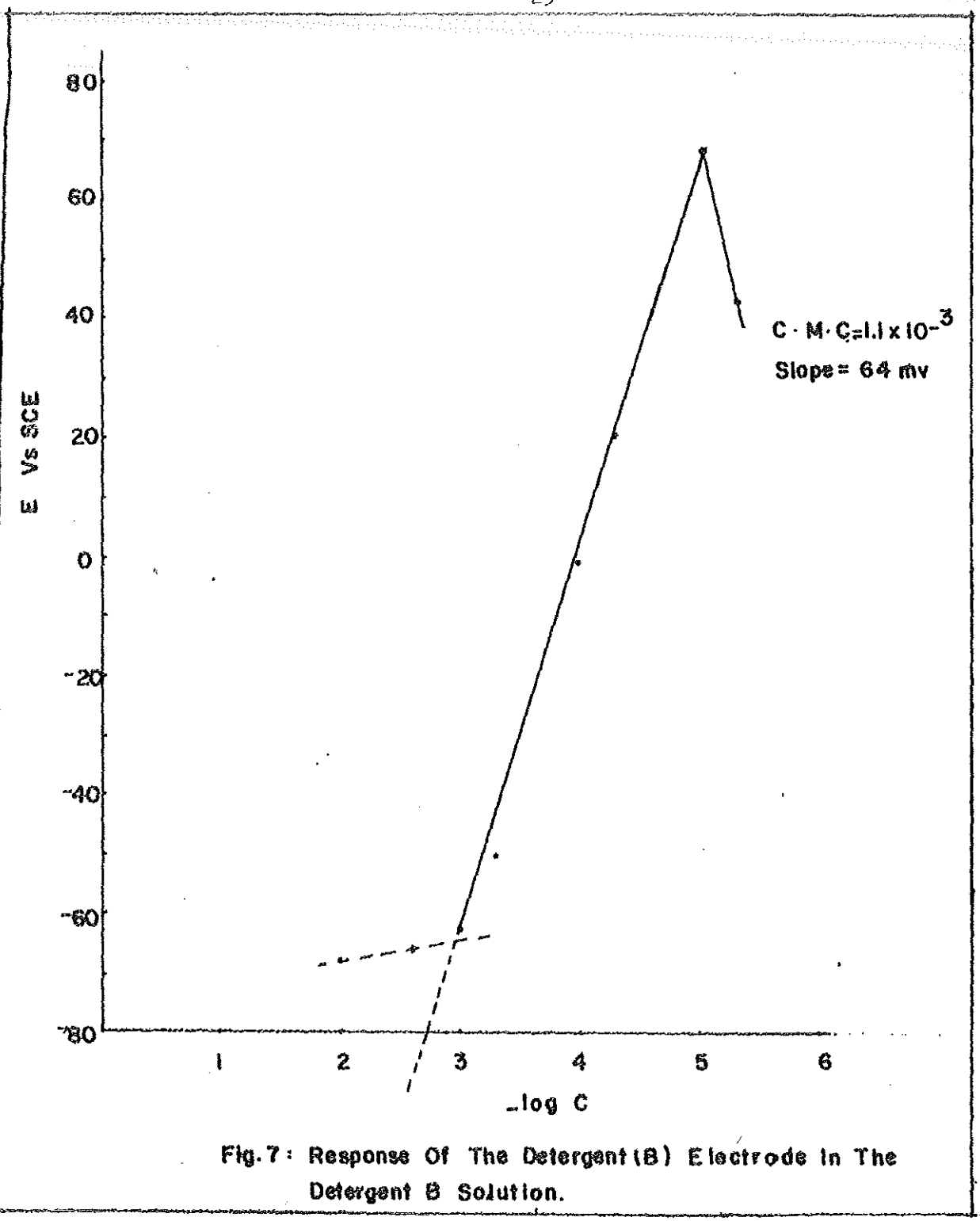


Fig. 7 : Response Of The Detergent (B) Electrode In The Detergent B Solution.

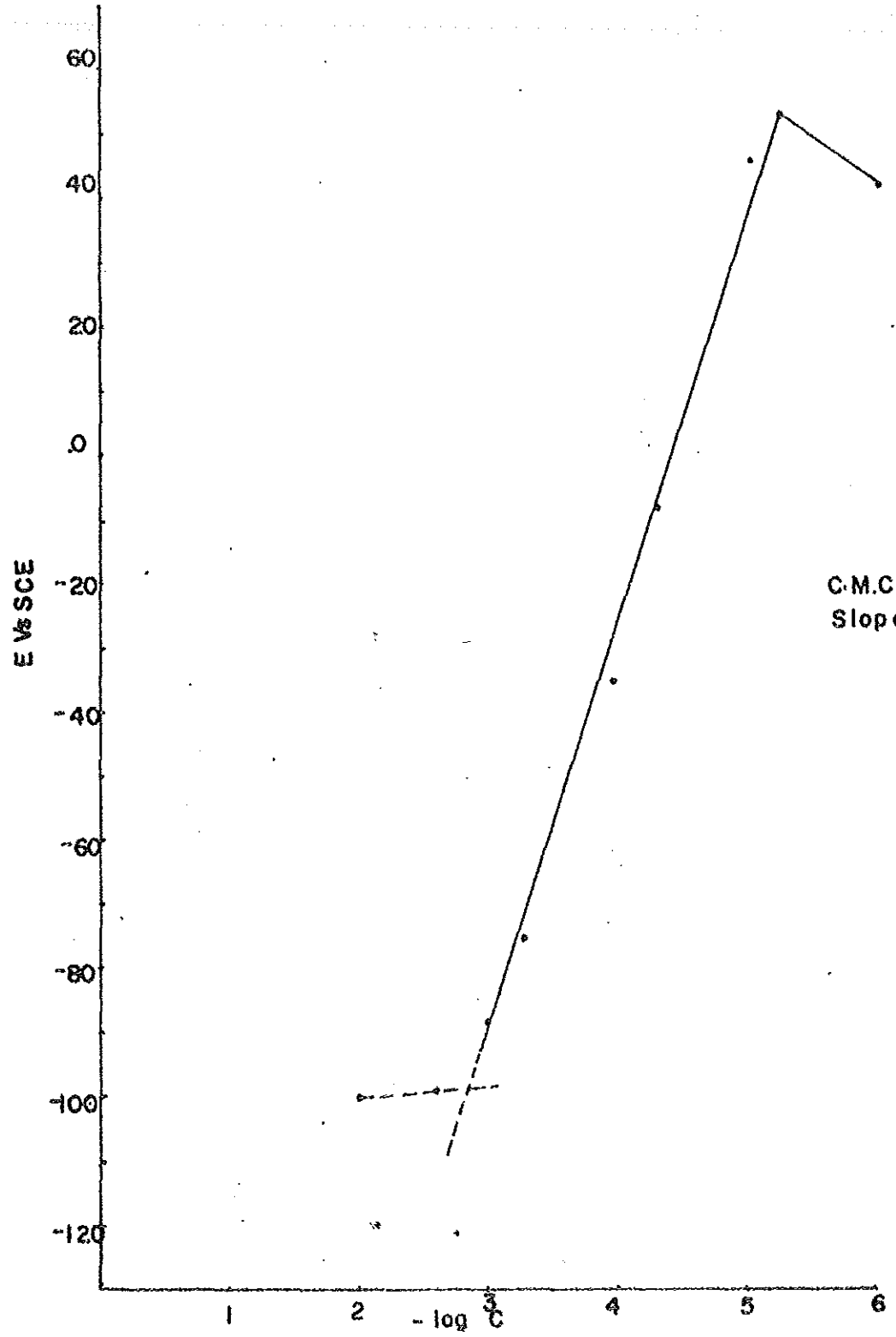
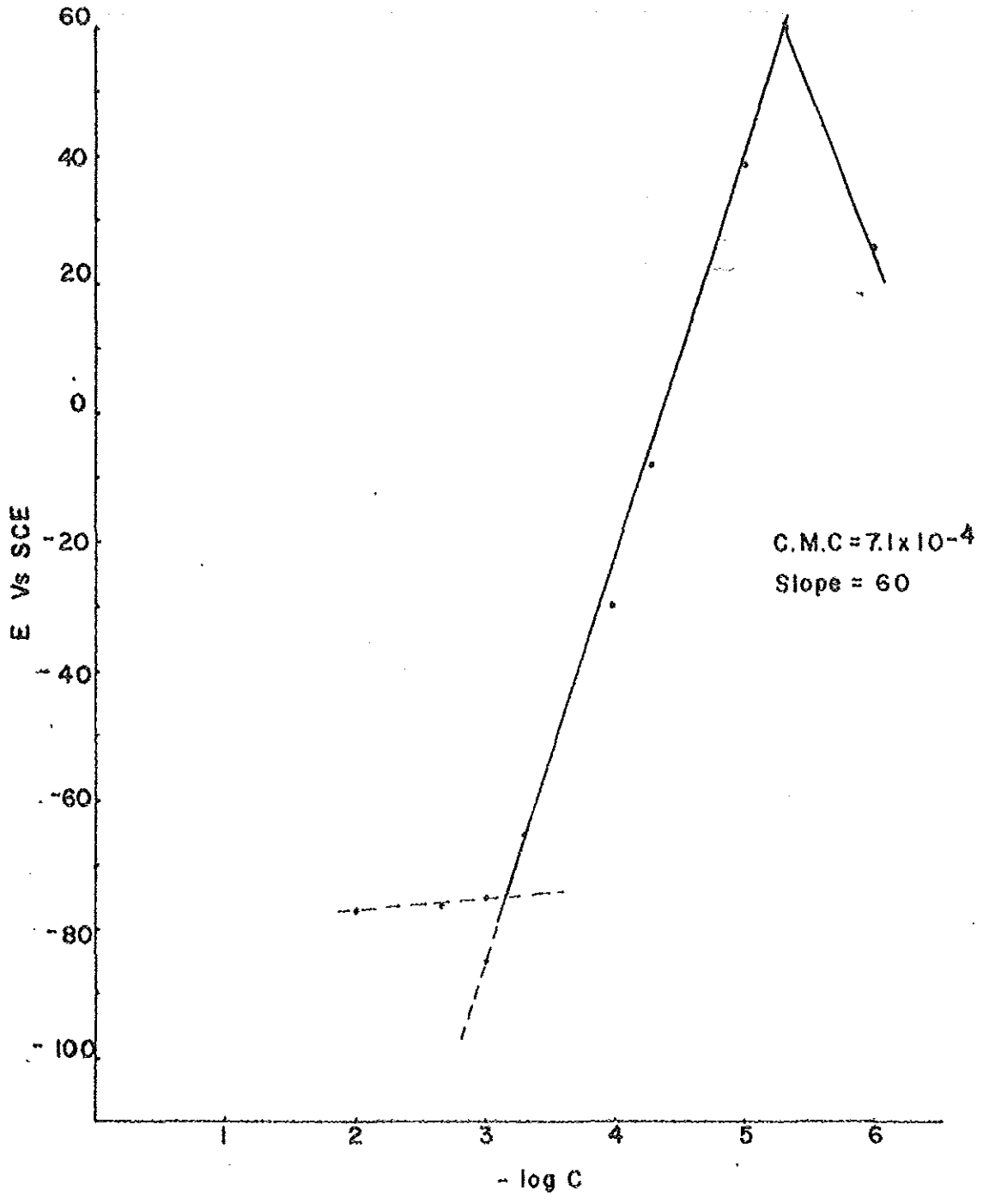


Fig. 8 : Response Of The Detergent (C) Electrode In The Detergent C Solution.



Fig·9 : Response Of The Detergent (D) Electrode In The Detergent (D) Solution.

4.2 Voltammetric studies of the ion transfer across the interface water - nitrobenzene

4.2.1

In principle there are two types of charge transfer across the interface of two immiscible electrolyte solutions α and β(38).

a. The transfer of an ion X^z, with a charge number Z, from the phase α to the phase β and the reverse.

$$X^z(\alpha) \rightleftarrows X^z(\beta)$$

b. The electron transfer between the particle in the phase α and the particles in the phase β, which can be written as

$$Red_1(\alpha) \quad OX_2(\beta) \rightleftarrows OX_1(\alpha) + Red_2(\beta).$$

At the interface a Galvanic Potential difference $\Delta\Psi = \Psi(\beta) - \Psi(\alpha)$ is formed. Under equilibrium conditions the sum of the electrochemical potentials of the reactants in a transfer reaction, which takes place at the phase boundary, must be equal to the sum of electrochemical potentials of the products. Or, at equilibrium, the electrochemical potential $\tilde{\mu}$ of every ion is the same in both phase α and β.

$$\tilde{\mu}^{\alpha} = \tilde{\mu}^{\beta} \qquad (3)$$

or

$$\mu_i^{o\alpha} + RT \ln a_i^{\alpha} + zF\phi^{\alpha} \quad \mu_i^{o\beta} + RT \ln a_i^{\beta} + z_i F\phi^{\beta}$$

where $\mu_i^{o\alpha}$ and $\mu_i^{o\beta}$, are standard chemical potentials of the ion X_i^z in α and β. From equation (4) we have

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$$\Delta_{\beta}^{\alpha}\varphi = \varphi^{\alpha} - \varphi^{\beta} = (\mu_i^{o\beta} - \mu_i^{o\alpha})/ZF + \frac{RT}{ZF} \ln \frac{a_i^{\beta}}{a_i^{\alpha}} \quad (5)$$

here, $\Delta_{\beta}^{\alpha}\varphi$ is called the Galvani potential differences between phase α and β.

Equation (5) can be written in the form

$$\Delta_{\beta}^{\alpha}\varphi = \Delta_{\beta}^{\alpha}\varphi^{o} + \frac{RT}{ZF} \ln \frac{a_i^{\beta}}{a_i^{\alpha}} \quad (6)$$

where

$$\Delta_{\beta}^{\alpha}\varphi^{o} = (\mu^{o,\beta} - \mu_i^{o,\alpha})/ZF = \Delta G^{o,\ \alpha\rightarrow\beta}/Z_i F \quad (7)$$

where $\Delta G^{o\alpha\rightarrow\beta}$ is the standard Gibb's energy of transfer of ion X^z from α to β and $\Delta_{\beta}^{\alpha}\varphi_i^{o}$ is the standard Galvani Potential difference of the ion X_i^z between the phase α and β.

In order to attribute a definite value to the standard Gibbs energy of transfer an extrathermodynamic approach has been used, for example, the TPATPB assumption, stating that the standard transfer Gibbs energies of tetraphenylarsonium cation and tetraphenylborate anion are equal for any pair of solvents(39) . On the basis of this assumption, scales for the standard Gibbs energies of transfer of ions from one solvent to another can be constructed by using standard Gibbs energies of transfer of salts calculated from Partion Coefficients (40) .../

The standard Galvani Potential difference of ions can be then calculated from equation 7, as shown in table 5.

When the interface of an aqueous and an organic electrolyte is electrochemically polarized from an external source, two processes can take place. One of these is the transfer of ions whose equilibrium potential (equation 6) due to charge injection doesn't coincide with the actual value of $\Delta_{\beta}^{\alpha}\varphi$. The other one is the charging of the electrical double-layer present at ITIES(Interface of two immiscible electrolyte solution).

In the presence of semi-hydrophobic ions in a considerable lower concentration than the base electrolytes, the interoduction of charge to a phase can cause their transfer to occur in the 'potential window'. However if the organic phase only contains very hydrophobic ions and the aqueous phase only consists of hydrophilic ions then there exists a potential range where ITIES behave like an ideally polarized electrode, i.e. the injected charge is used for the charging of the double layer (20). Furthermore the transfer of these ions across the interface can be followed by the same methods as in the case of electron transfer in the system metallic electrode/electrolyte solution, for example voltammetry and chromopotentiometry as stated earlier.

Table 5

Standard Gibbs energies of transfer from water to nitrobenzene, $G_{tr}^{o,\ w \rightarrow nB}$, and of the standard electrical potential difference between these phases (44).

Ion	$G_{tr}^{o,w\rightarrow nB}$ / kj mol^{-1}	$\Delta_{V}^{nB}\psi_{T}$
Li^+	+38.2	0.395
Na^+	+34.2	0.354
K^+	+23.4	0.242
TBA^+	+24.0	-0.248
TPB^-	-35.9	0.372
I^-	-18.8	-0.195
Br^-	+28.4	-0.295
Cl^-	+31.4	-0.324
DS^-	+ 5.0	-0.052

The potential difference $\Delta\psi$ is defined by

$$\Delta\psi = \psi_{(w)} - \psi_{(o)}$$

So that the electrical potential of the organic phase is subtracted from the potential of the aqueous phase. The flow of positive charge from the aqueous to the organic phase corresponds to positive electrical current.

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4.2.2 Results and Discussion of the voltammetric studies

In order to study the charge transfer of the dodecyl sulphate ion different organic and aqueous supporting electrolytes have been used.

Fig. (12) shows the cyclic voltammogram of the base electrolyte, 0.01 M LiF in water and 10^{-2}M TBATPB in nitrobenzene. In the potential range from 120 mv to 300 mv the current is controlled mainly by the charging of the interface while at more positive or negative potentials the current is controlled by the transfer of the base electrolyte ions from one phase to the other. Based on the standard free energy of transfer of the individual ions (Table 5) present in the system, it can be said that the increasing negative current at potentials more negative than 110 mv corresponds to the transfer of TBA^+ ion from nitrobenzene phase to the aqueous phase (water). The transfer of TBA^+ ion from water back to nitrobenzene is shown from the peak at 0.025 v when the scan is reversed. In a similar manner, it can be conculded that the rising positive current at a potential more positive than 0.3 v was due to the transfer of TPB^- ion from nitrobenzene to the aqueous phase and the peak at

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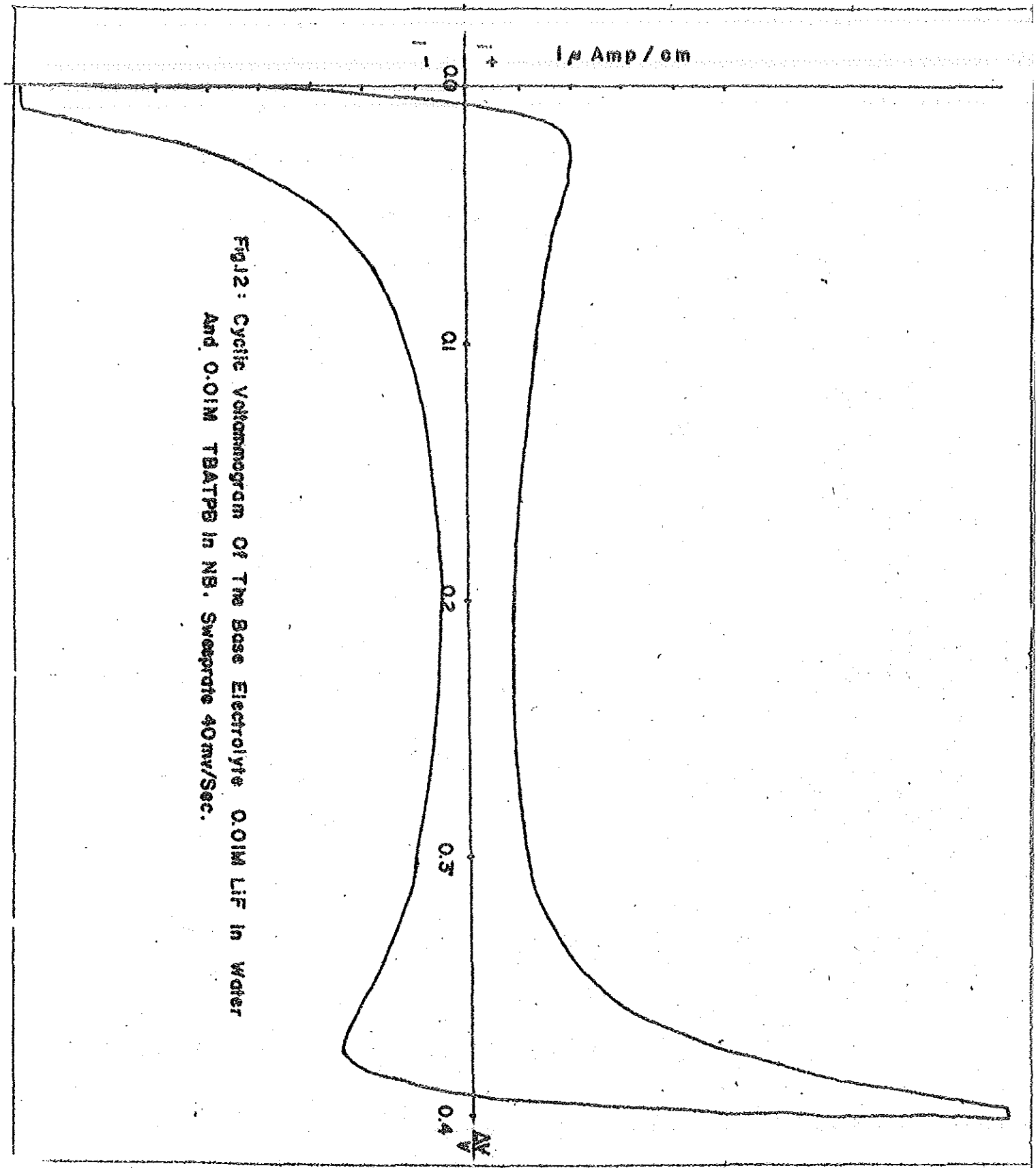

Fig.12 : Cyclic Voltammogram Of The Base Electrolyte 0.01M LiF in Water And 0.01M TBATPB in NB. Sweeprate 40mv/Sec.

0.375 v corresponds to its transfer from aqueous back to the nitrobenzene phase upon scan reversal.

Fig. 12, the cyclic voltammogram of the base electrolyte is very similar to that obtained by Samec et al, who used the same base electrolyte for the organic phase. This similarity has greatly supported us in the assumption that the set up we were using was acceptable.

Fig. 13 is the cyclic voltammogram showing the transfer of the organic base electrolyte ions and the detergent ion in 2 x 10^{-4}M concentration. The two peaks at the extremes of the voltammogram are due to the transfer of TBA and Na^+ ions. While the peaks between belong to the transfer of DS^- ion. The peak at 0.190 v corresponds to the transfer of DS^- ion from water to the nitrobenzene phase while the other peak at 0.225 v corresponds to the transfer of DS^- ions from nitrobenzene back to the aqueous phase on reverse polarization.

A number of voltammograms have been taken for 2 x 10^{-4} DS^- ion in the same base electrolytes by varying the polorization rate. The peak current for each sweep rate and the peak potential and the half-peak potential have beem measured from these cyclic voltammograms.

Table 6

Variation of the peak current and peak potential with the change of polarization rate

2×10^{-4}M Dodecyl sulphate

Organic base electrolyte: 0.01M TBATPB

Aqueous base electrolyte: 0.01 LiF

Peak current (i_p)	Sweep rate (V)	$V^{1/2}$	peak potential $E_p(H_2O \rightarrow NB)$	$E_p - E_{p/2}$	E_p (Reverse)
11.6	0.06	0.245	0.185	0.0570	0.240
13.8	0.08	0.283	0.190	0.057	0.245
14.5	0.10	0.316	0.195	0.058	0.245
17.0	0.12	0.346	0.190	0.055	0.250
18.5	0.14	0.374	0.190	0.057	0.250
20.0	0.16	0.4	0.195	0.055	0.245
21.5	0.180	0.424	0.190	0.057	0.250

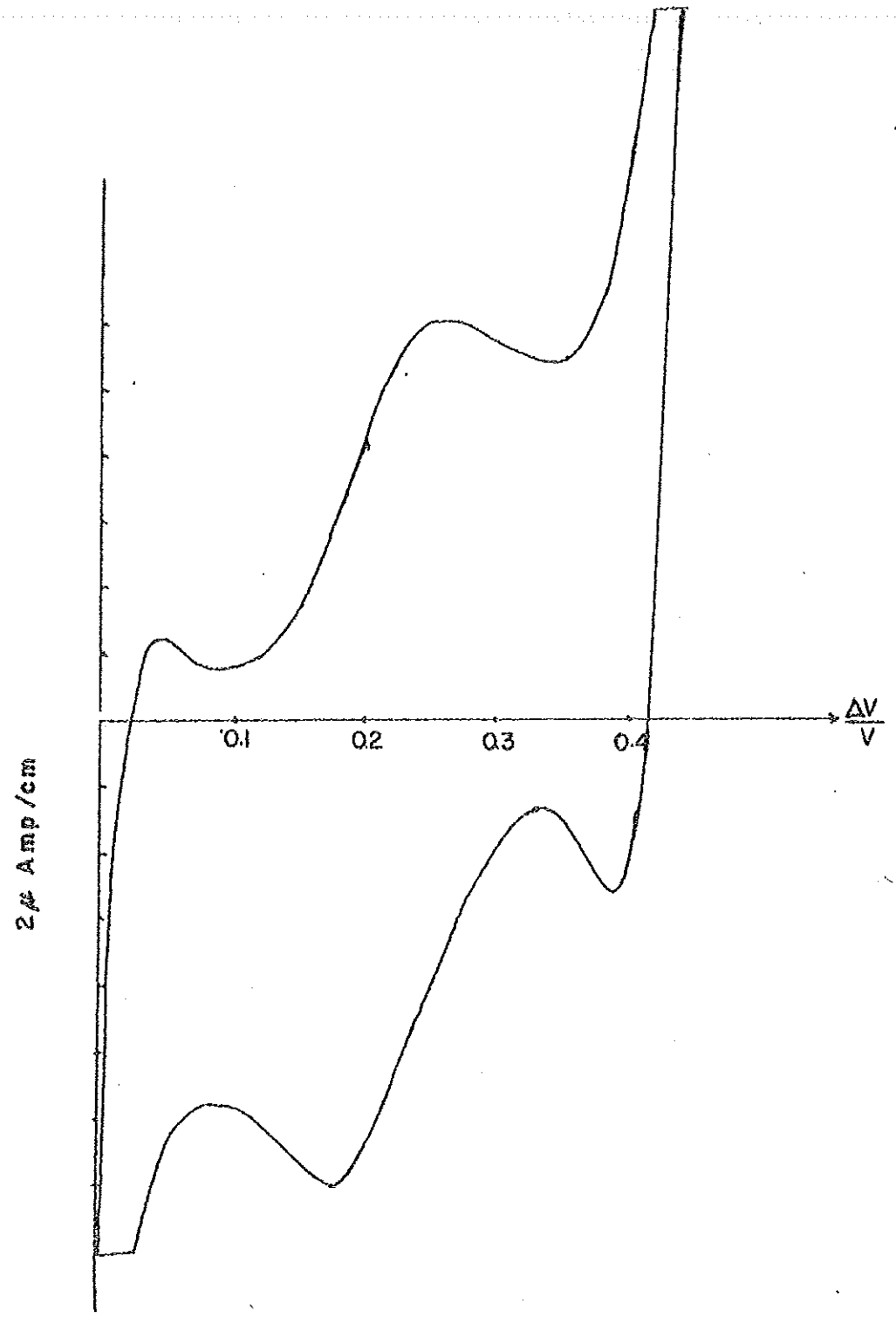

Fig.13: CYCLIC VOLTAMMOGRAM OF 2×10^{-4} M AQUEOUS SOLUTION OF DS^- ION BASE ELECTROLYTE 0.01 M LIF IN WATER AND 0.01M TBATPB. SWEEPRATE 40 mv/Sec.

Table 7

Variation of the peak current with the change of polarization rate

10^{-4}M Dodecyl sulphate

Organic base electrolyte: 0.01 TBATPB

Aqueous base electrolyte: 0.01 LiF

Corrected peak current (i_p)	Sweap rate V	$V^{1/2}$
2.5	0.02	0.141
3.5	0.028	0.167
4	0.036	0.190
5.1	0.04	0.2
6.2	0.06	0.245
7.4	0.08	0.283
8.8	0.1	0.316
10.4	0.12	0.346
11.6	0.14	0.374
12.8	0.16	0.4
14.2	0.18	0.424

Table 8

Variation of the peak current with the change of polarization rate

5×10^{-5} M Dodecyl sulphate

Organic base electrolyte: 0.01 TBATPB

Aqueous base electrolyte: 0.01 LiF

Peak current (i_p)	Sweep rate V	$V^{1/2}$
3.4	0.04	0.2
4	0.06	0.245
4.6	0.08	0.283
5.2	0.10	0.316
5.9	0.12	0.346
7.2	0.14	0.374
7.6	0.16	0.4
8	0.18	0.424

Table (6) contains these values. The same has been repeated for 10^{-4}M and 5 x 10^{-5}M concentrations of dodecyl sulphate ion as shown in table (7,8).

The effect of the polariztion rate on the peak current is shown in fig. 14,15,16 for 2 x 10^{-4}, 10^{-4}, 5 x 10^{-5} molar concentrations of DS^- ion respectively.

The dependance of the peak current on DS^- ion concentration is depicted in fig.17. The plot of the peak potential and the half peak with change in the polarization rate for reverse and forward scanning is shown in fig. 18.

For the interpretation of the above results, the charge transfer reaction across the interface of two immiscible electrolytes is treated in a manner similar to metallic electrode/solution interfaces to which the classical electrochemical kinetics equations are then applied. Hence the theory of the stationary electrode voltammetry is used as our tool. The current is related to the potential and other variables by

$$i = n^{3/2} C_o^b F^{3/2} D^{1/2} V^{1/2} \eta^{1/2} A \chi(at)$$

where i = current in amps, V = polarization rate, V/sec. D = Diffusion coefficient, A = area in cm^2

C_o^b = bulk concentration ../

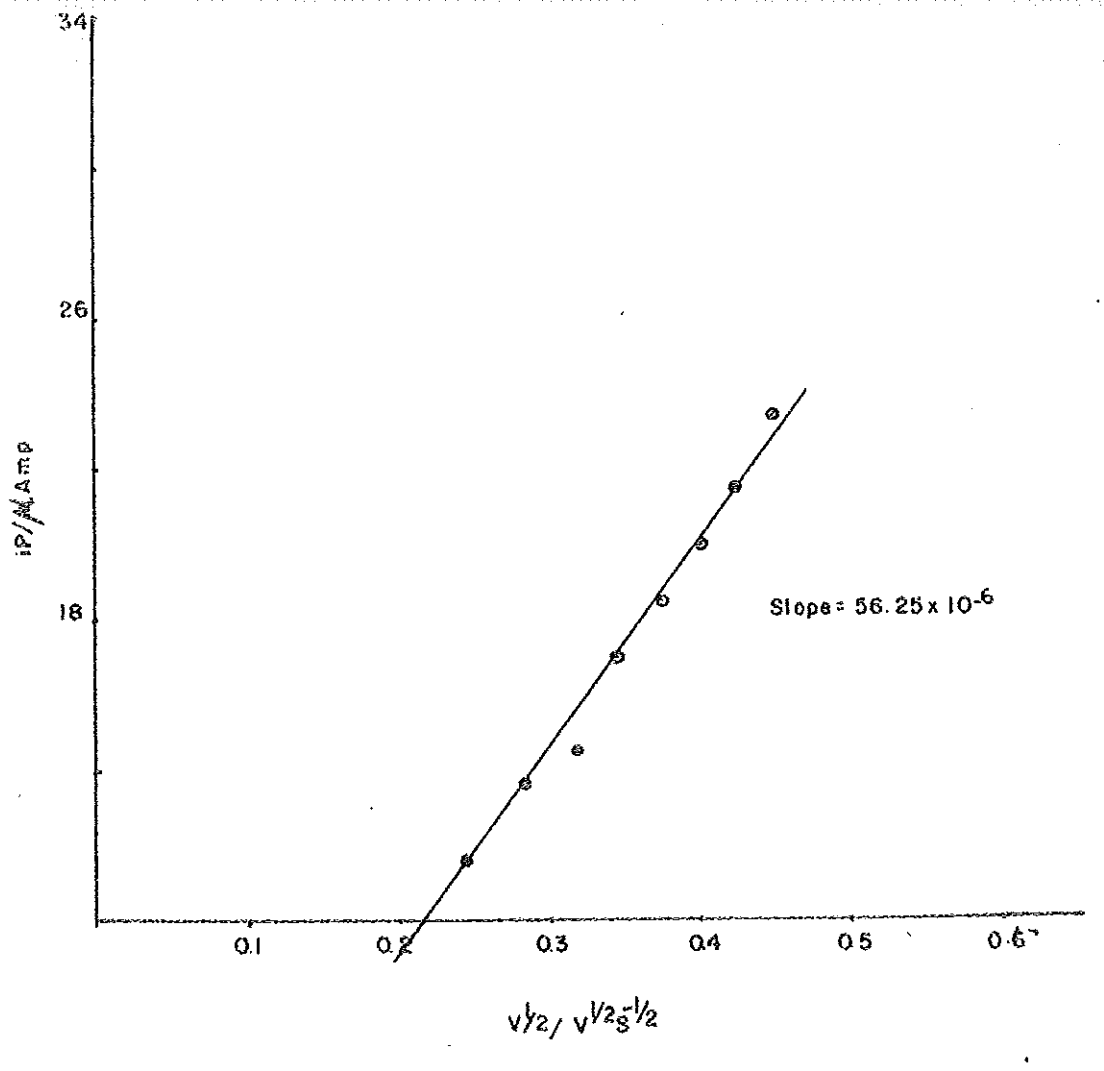

Fig.14 The Dependance Of The Peak Current ip Correspondeng To The Transfer Of DS^- From Water To NB On Squareroot Of The Polarization Rate ($V^{1/2}$), Concentration Of DS^- Is 2×10^{-4} M.

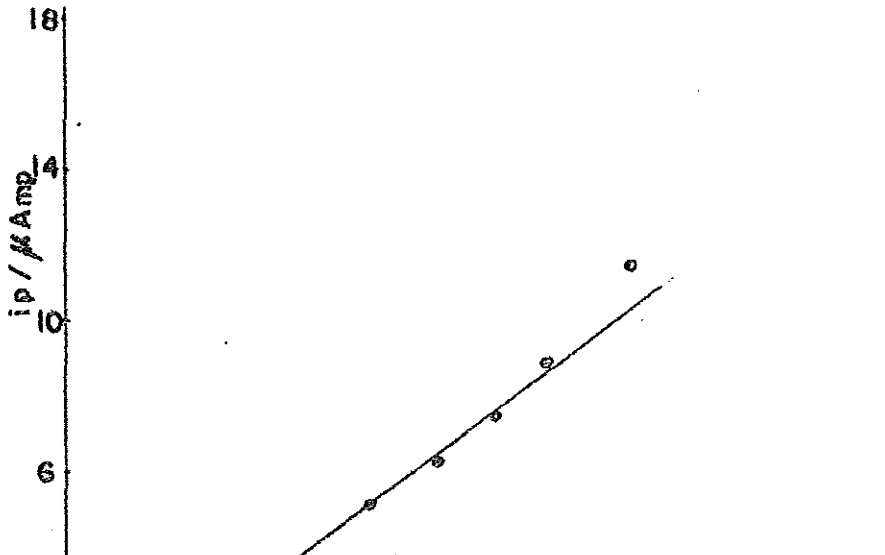

Fig. 15 The dependence of the peak current Ip corresponding to transfer of DS^- ion from water to NB on $V^{1/2}$

C_{DS^-} is 10^{-4} M.

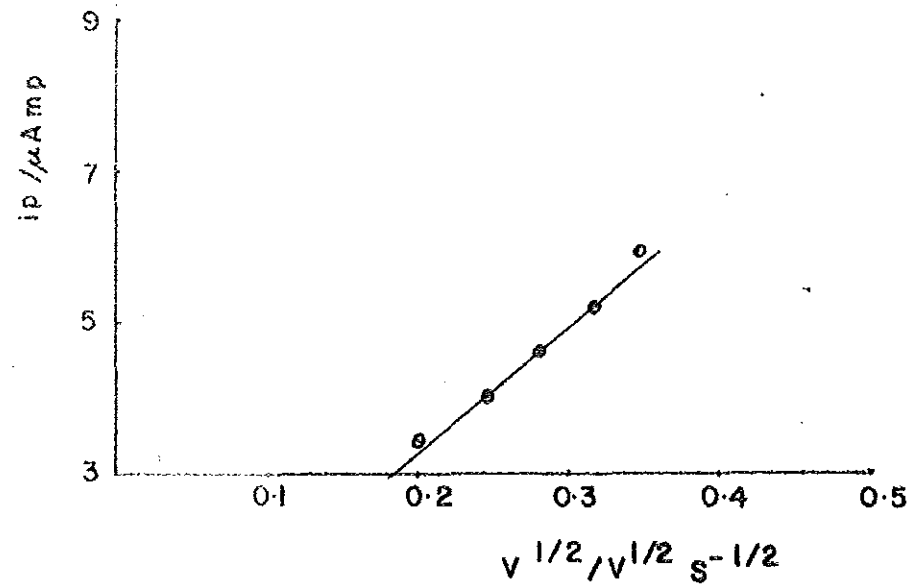

Fig. 16 The dependence of ip on $V^{1/2}$

C_{DS^-} is $5 \times 10^{-5} M$,

From fig. (14-16) it can be concluded that the peak current (i_p) is proportional to the square root of the polarization rate ($V^{1/2}$) up to 0.160 V/sec and in addition to that the i_p varies linearly with concentration changes ($0.5 \times 10^{-4} - 2 \times 10^{-4}$) . The position of the peak and the half peak potential for the forward and the reverse transfer of DS^- ion from the aqueous phase to nitrobenzene does not shift with change in the polarization rate below 0.160V/sec (fig.18). This behavior of the dodecyl sulphate ion indicates that the transfer of this ion across the interface aqueous nitrobenzene is controlled by diffusion in the range of the polariz tion rate from 0.001 to 0.160V. This conclusion can be supported further by the diagnostic criteria laid down for the diffusion controlled charge transfer process (41) .

These are:

1. It follows from fig.18 that the half-peak potential ($E_{p/2}$) preceeds the peak potential for the forward polarization by 0.057 V which is in very good agreement with the theoretical value, i.e. 0.0565 V (41) .

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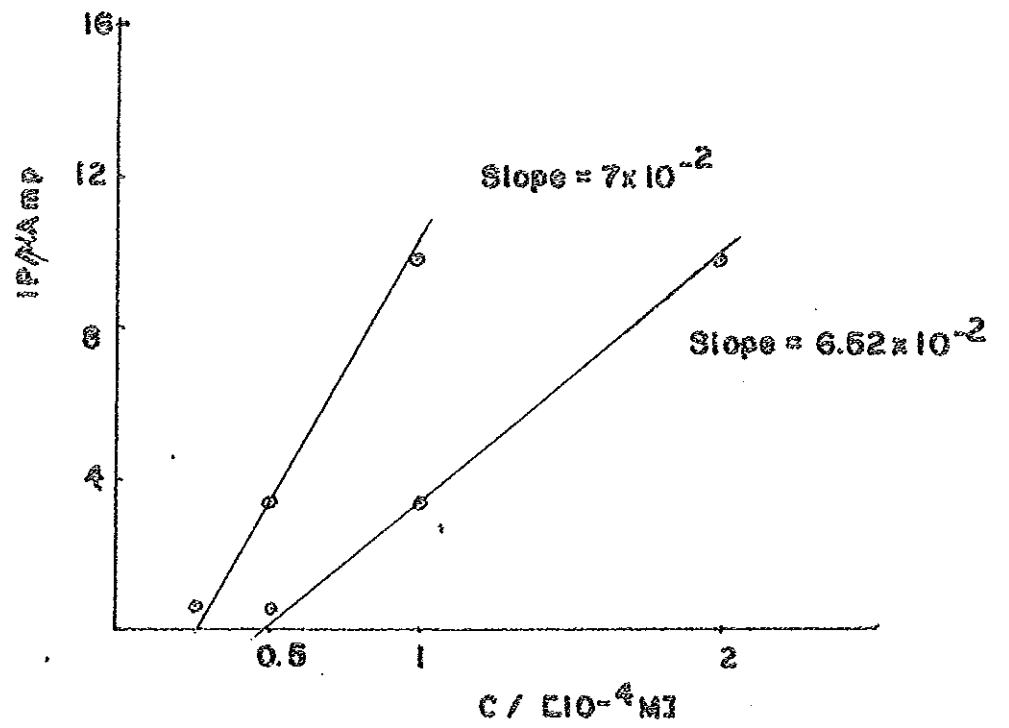

Fig. 17 The Dependance Of The Peak Current (ip) Corresponding To The Transfer Of DS^- From Water To NB On Concentration Of DS^- In The Aqueous Phase. Sweeprate 80 mv/Sec

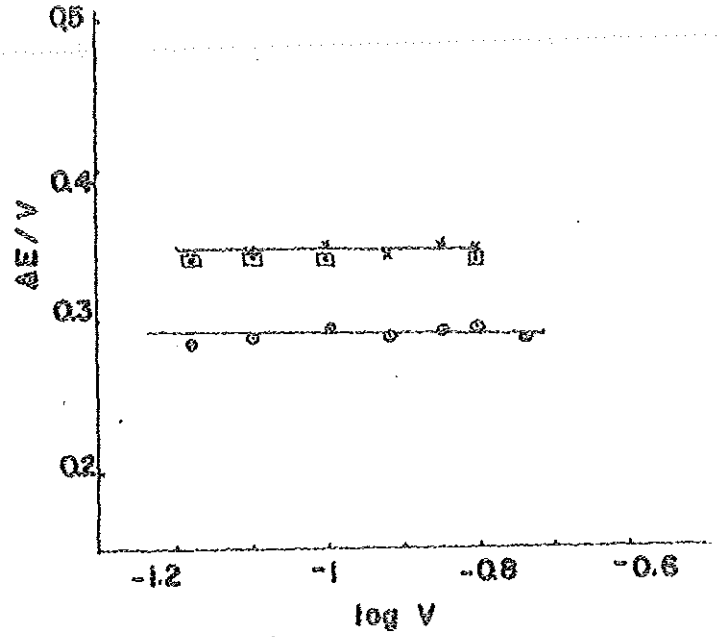

Fig. 18 The Effect Of The Polarization Rate On The Position Of The Peak $\Delta Ep(\bullet)$ Or Half-Peak $\Delta Ep/_2(\times)$ Forward Polarization On The Position Peak Potential (ΔEp) For Reverse Polarization (⊡)

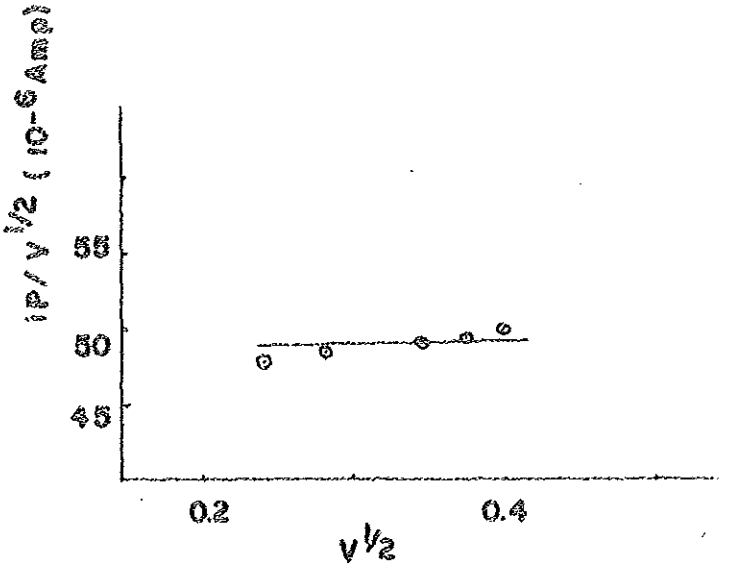

Fig.19 Cyclic Voltammetry Behavior Of DS^- In The Transfer Reaction From Water To NB $C_{DS} = 2 \times 10^{-4}$ M Base Electrolyte [TBA TPBI.

2. For a reversible process involving one electron transfer the peak potential separation for forward and reverse polarization was found to be 0.06 V. From table (6) or fig. (18), the peak separation was observed to have an average value of 0.055 V which is in close agreement with the theoretical value.

3. The variation of $i_p/V^{1/2}$ vs $V^{1/2}$ is shown in fig. (19). A horizontal line indicates that the process is diffusion controlled and furthermore that the rate of the charge transfer is rapid. This criterion was first suggested by Galus and Adams in connection with the preceeding chemical reactions (42) . Koryta et al (43). have pointed out that charge transfer across the interface of two immiscible electrolyte solution is usually rapid. This may support the above observation.

Once the reversibility of the process i.e, the transfer of dodecyl sulphate ion from water to nitrobenzene is established then two important values can be obtained from the voltammetric measurements. First the diffusion coefficient can be calculated from the slope of the dependence of the peak current (i_p) on the square root of

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the sweep rate ($V^{1/2}$) based on the theory of stationary voltammetry i.e. equation 8. The calculation yielded the average value $D_{DS^-}(W) = (1.11 \pm 0.07) \times 10^{-5}$ $cm^2 S^{-1}$ at three different concentrations of DS^- ion. Alternatively, the diffusion ocefficient has been evaluated using the dependance of peak current on concentration (Fig.17) which was found to be $D_{DS^-}(W) = 7.8 \times 10^{-6}$ cm^2/sec. These two values are comparable to the value of $D_{DS}(W)$ i.e. 9×10^{-6} cm^2/sec. obtained (calculated) from conductance at infinite dilution (45).

The second important quantity which is inferred from the cyclic voltammetric measurements is the half-wave potential of $E_{1/2}$, which is analogous to the reversible polarographic half-wave potential. This value can be obtained using the assumption that $\Delta E_{1/2}$ should precede the peak potential difference E_p by 0.0285/Z volts(41). Hence from the value of $\Delta E_p = 0.192$ for the DS^- ion the half-wave potential was obtained to be 0.221V. Alternatively the $\Delta E_{1/2}$ value can be estimated from the previous assumption but considering the standard free energy of transfer of ions between the interface (30). The half-wave potential is related to the standard potential (E^Θ) such that:

$$E_{1/2} = E^\Theta + \frac{RT}{ZF} \ln \left(\frac{D_{DS^-}(W)}{D_{DS}(N)} \right)^{1/2} \qquad (9)$$

where D(NB) and D(W) are the diffusion coefficients of the transferred ion in nitrobenzene ahd

in the aqueous phase respectively and ΔE^{Θ} is the formal potential difference ${}_{\Delta}{}^{W}_{nB}\varphi^{o}_{i}$ for the transferred ion (DS^- ion) related to the formal potential difference for TBA^+ ion, ${}^{W}_{nB}\varphi^{o}_{TBA^+}$, i.e.

$$\Delta E^{\Theta} = {}_{\Delta}{}^{W}_{nB}\varphi^{o}_{DS^-} - {}_{\Delta}{}^{W}_{nB}\varphi^{o}_{TBA^+} \qquad (10)$$

After having estimated the ratio of the viscosity coefficient of nitrobenzene to that of water, $D_{DS}-(W)/D_{DS}(.B)$ to be 1.95(58) using standard potential, ΔE^{o} = 0.196 V from table (5), the $\Delta E_{1/2}$ value was calculated thus:

$$\Delta E_{1/2} = 0.196 + 0.059 \log (1.95)^{1/2} = 0.205 \text{ V}.$$

As may be seen from the result, the half wave potential obtained from the voltammetric measurrements is comparable to the value of $\Delta E_{1/2}$ calculated using the extraction data. The small difference between the two values may be accounted for by the activity coefficient terms involved in E^{Θ} and may moreover be due to uncertainity in the estimation of the diffusion coefficients.

In this series of experiments the organic base electrolyte was changed to crystal violet-tetraphenylborate, whereas the base electrolyte for the aqueous phase remained unchanged.

Fig.(20) shows cyclic voltammogram obtained using the base electrolytes 0.01MLiF in the water phase and 10^{-2}M CVTPB in the nitrobenzene phase. In the potential range from-0.25V to 0.25V the current is controlled by the charging of the interface while at more positive or negative potentials the current is controlled by the transfer of the base electrolytes from one phase to another. The peak at-0.35Vcorresponds to the transfer of F^- ion from nitrobenzene to water and the peak at the other extreme at 0.3V corrosponds to the transfer of tetraphenylborate (TPB^-) from water to nitrobenzene. This assignement is based on the standard free energies of transfer of the individual ions (Table 5).

A sample voltammogram for the transfer of DS^- ion from the aqueous to the nitrobenzene phase and for the reverse transfer upon scan reversal is given in Fig. 21. At a much more negative potential at the extreme end of the voltammogram, the transfer of flouride ion is observed. A number of voltammograms have been taken using different scan rates.

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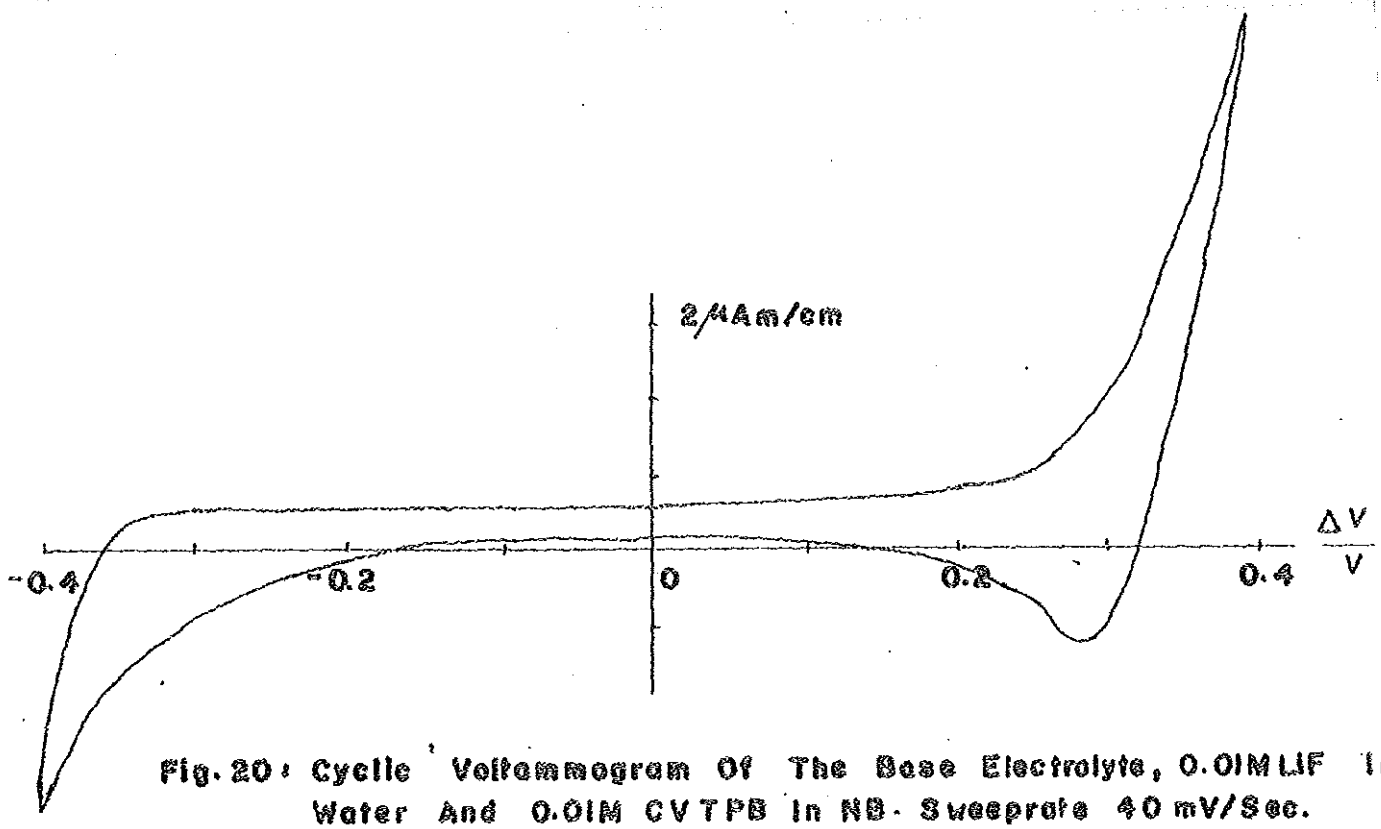

Fig. 20: Cyclic Voltammogram Of The Base Electrolyte, 0.01M LiF In Water And 0.01M CVTPB In NB. Sweeprate 40 mV/Sec.

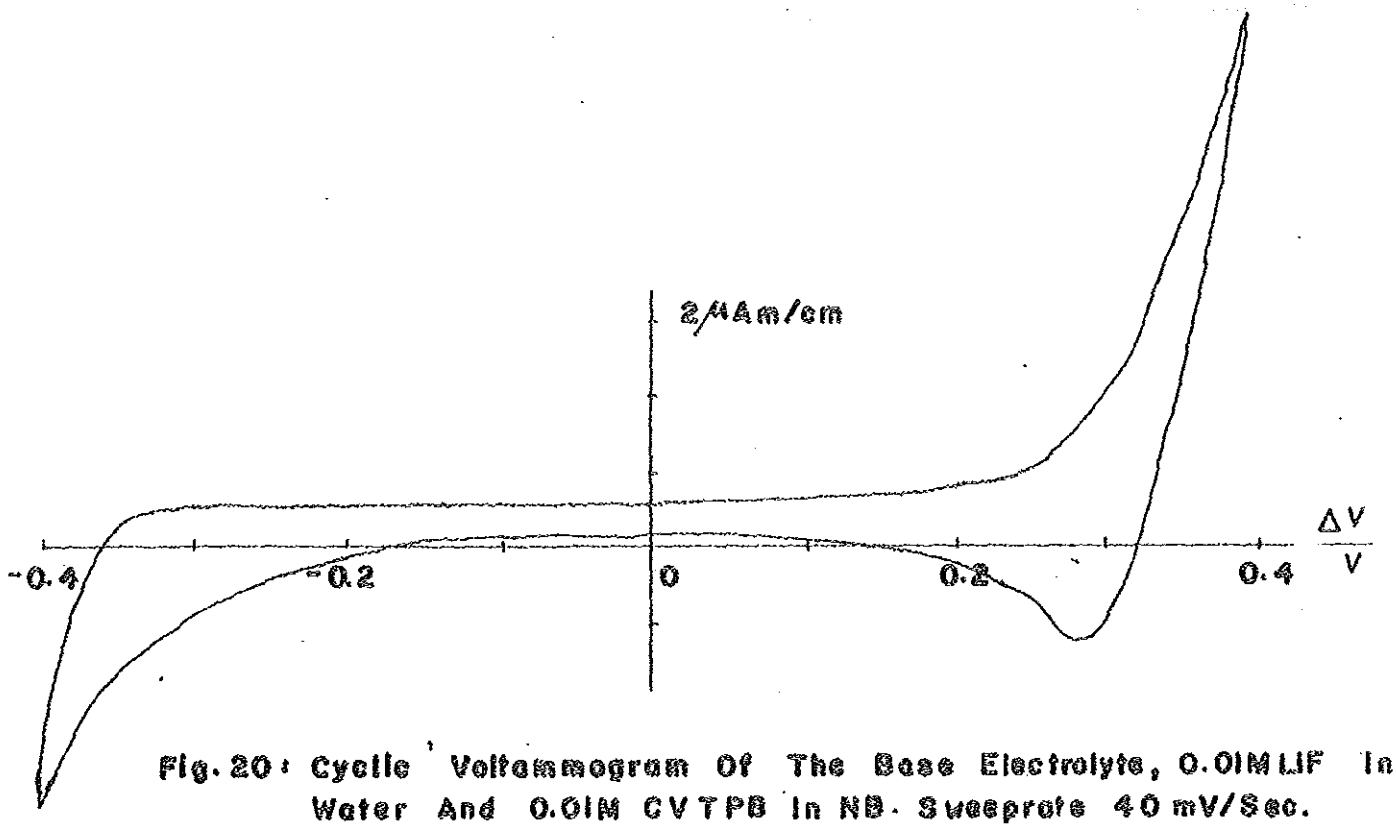

Fig. 20: Cyclic Voltammogram Of The Base Electrolyte, 0.01M LiF In Water And 0.01M CVTPB In NB. Sweeprate 40 mV/Sec.

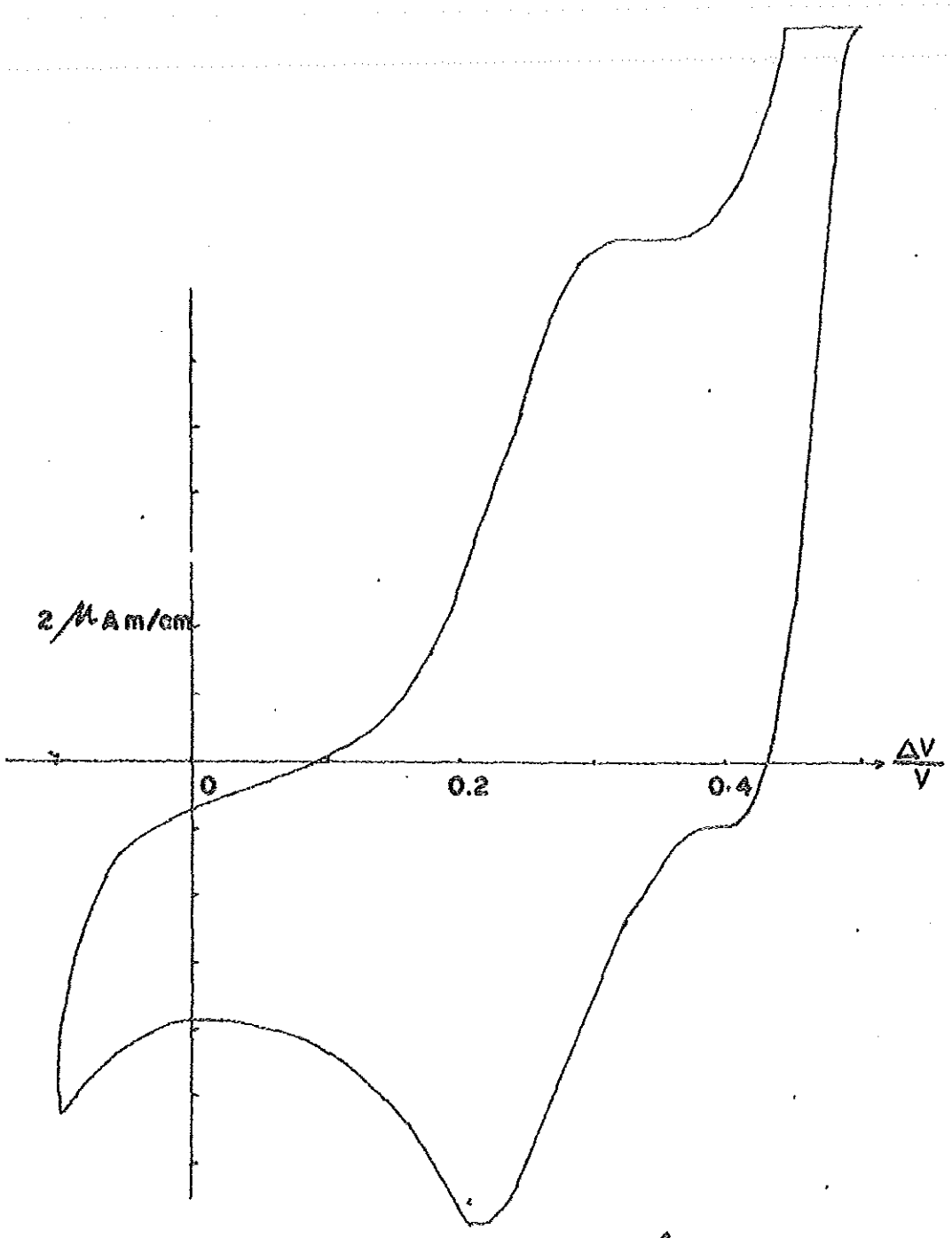

Fig. 21 : Cyclic Voltammogram Of 2.5×10^{-4} M Aqueous Solution Of DS^{-} Ion Base Electrolyte 0.01 LiF In Water And 0.01M CVTPB. Sweeprate 40 mV/Sec

Table 9

Variation of the peak current and peak potential with the change of polarization rate

$2.5\ 10^{-4}$M Dodecyl sulphate
Organic base electrolyte: 0.01M CV TPB
Aqueous base electrolyte: 0.01M LiF

Peak current i_p corrected	Sweep rate (V)	$V^{1/2}$	$E_p - E_{p/2}$	Peak Potential difference (ΔE_p)	Peak Potential W--> NB E_p
10.2	0.040	0.2	0.060	0.060	0.205
12	0.060	0.245	0.0575	0.062	0.205
15	0.080	0.283	0.055	0.055	0.205
16.5	0.10	0.316	0.0575	0.060	0.205
18	0.12	0.346	0.060	0.060	0.205
20	0.14	0.374	0.575	0.060	0.205
21	0.16	0.4	0.055	0.060	0.205

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Table 10

Variation of the peak current with the change of polarization rate

10^{-4}M Dodecyl sulphate

Organic base electrolyte: 0.01M CVTPB

Aqueous base electrolyte: 0.01M LiF

Peak current (i_p)	Sweep rate (V)	$V^{1/2}$
7.5	0.04	0.2
9.4	0.06	0.245
10.6	0.08	0.283
11.6	0.10	0.316
12.8	0.12	0.346
14	0.14	0.374
15	0.16	0.4

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Table 11

Variation of the peak current with the change of polarization rate

5×10^{-5}M Dodecyl sulphate

Organic base electrolyte: 0.01M CVTPB

Aqueous base electrolyte: 0.01M LiF

Peak current (i_p)	Sweep rate (V)	$V^{1/2}$
0.6	0.02	0.141
2.95	0.028	0.167
3.25	0.032	0.179
3.9	0.04	0.2
4.4	0.06	0.245
5.1	0.08	0.283
6	0.1	0.316
7.8	0.12	0.346
8.6	0.14	0.374
9.6	0.16	0.4
10.2	0.180	0.424

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The effect of the polarization rate on the peak current, peak potential, and half-peak potential has been studied for different molar concentrations of the dodecyl sulphate ion. Table (9,10,11) contain these values for 2.5×10^{-4}, 10^{-4}, 5×10^{-5}M concentration of DS^- ion respectively.

For the interpretation of the above results the interface of two immiscible electrolyte is treated in a manner similar to a metallic electrode/solution interface as was done for systems using other electrolytes. From the plot of the peak current versus the square root of the polarization rate (Fig. 22-24), it can be concluded that the peak current(i_p) is proportional to the square root of the polarization rate upto o.16 v/sec. A straight or a horizontal line obtained from the plot of the peak potential vs log V(Fig.25) shows that the position of the peak and the half-peak potential for the transfer of DS^- ion from aqueous to nitrobenzene does not shift with the change in the polarization rate below 0.16v/sec. As in the previous system, this behaviour of the dodecyl sulphate ion indicates that the transfer of this ion across the aqueous-nitrobenzene interface is controlled by diffusion in the range of polarization rates 0.01 to 0.16 v/sec.

Further confirmation has been obtained regarding the reversibility of the process (charge transfer) applying

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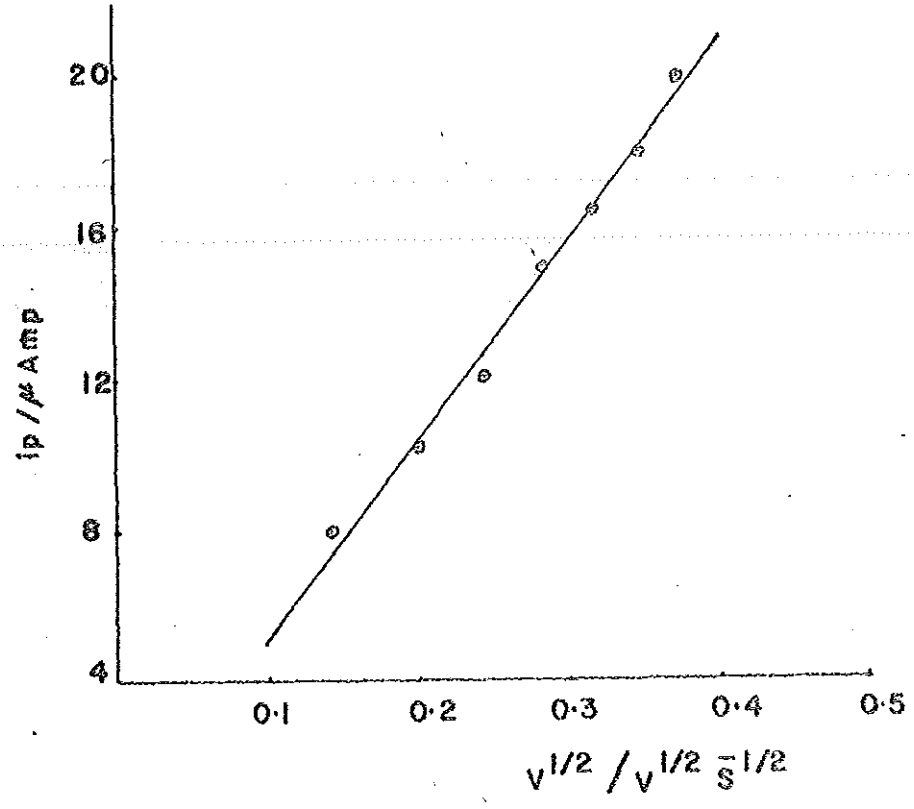

Fig. 22 The dependence of the Ip corresponding to the transfer of DS^- from water to NB on $V^{1/2}$

$C_{DS^-} = 2{\cdot}5 \times 10^{-4}$M,

CVTPB base electrolyte.

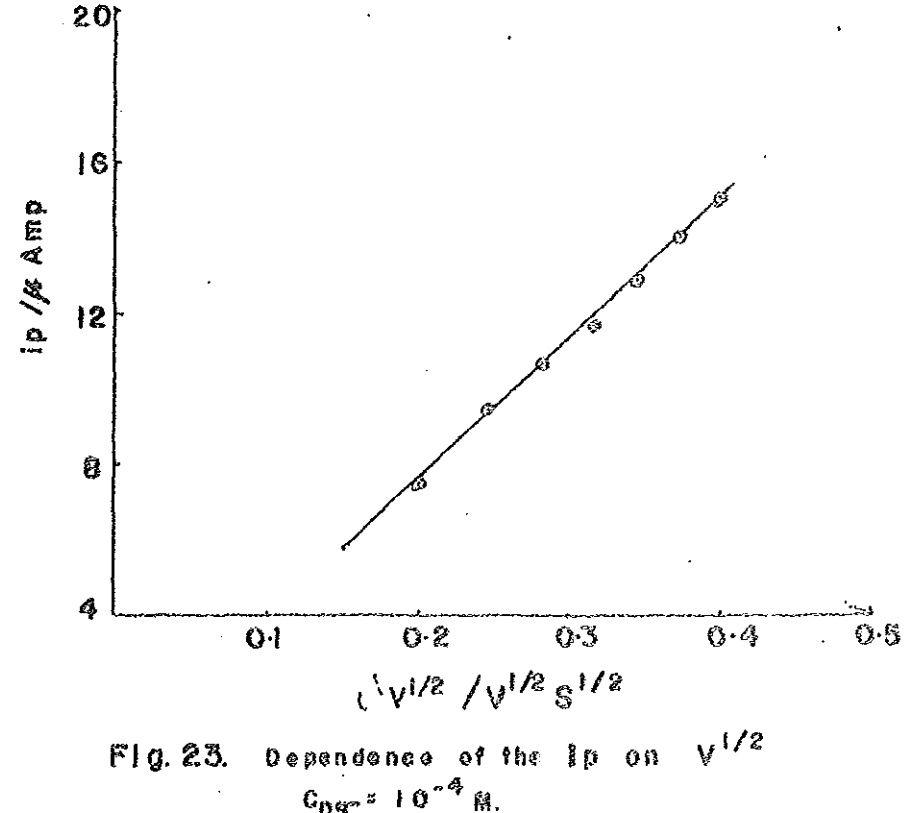

Fig. 23. Dependence of the Ip on $V^{1/2}$

$C_{DS^-} = 10^{-4}$ M.

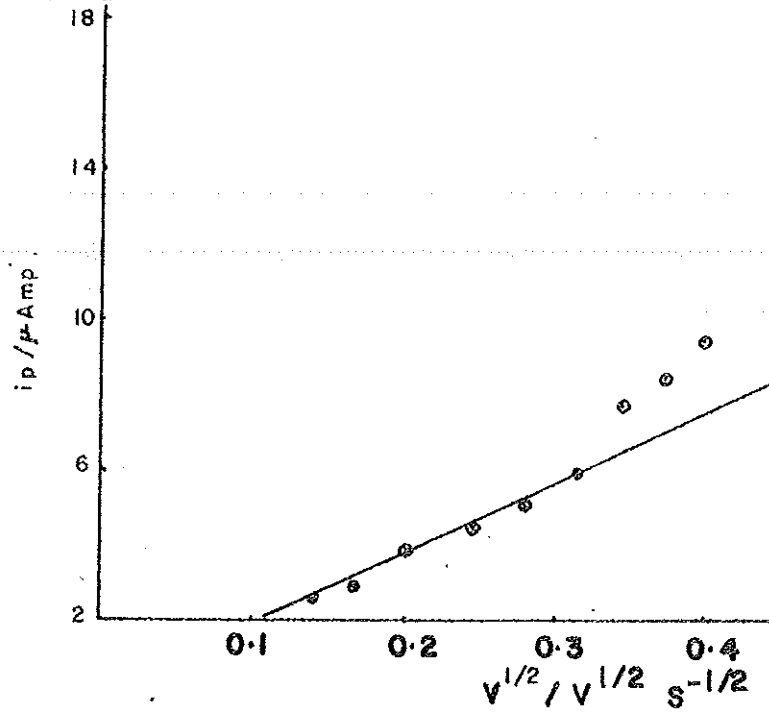

Fig. 24 The dependence of ip on the $V^{1/2}$

$C_{DS^-} = 5 \times 10^{-5} M$

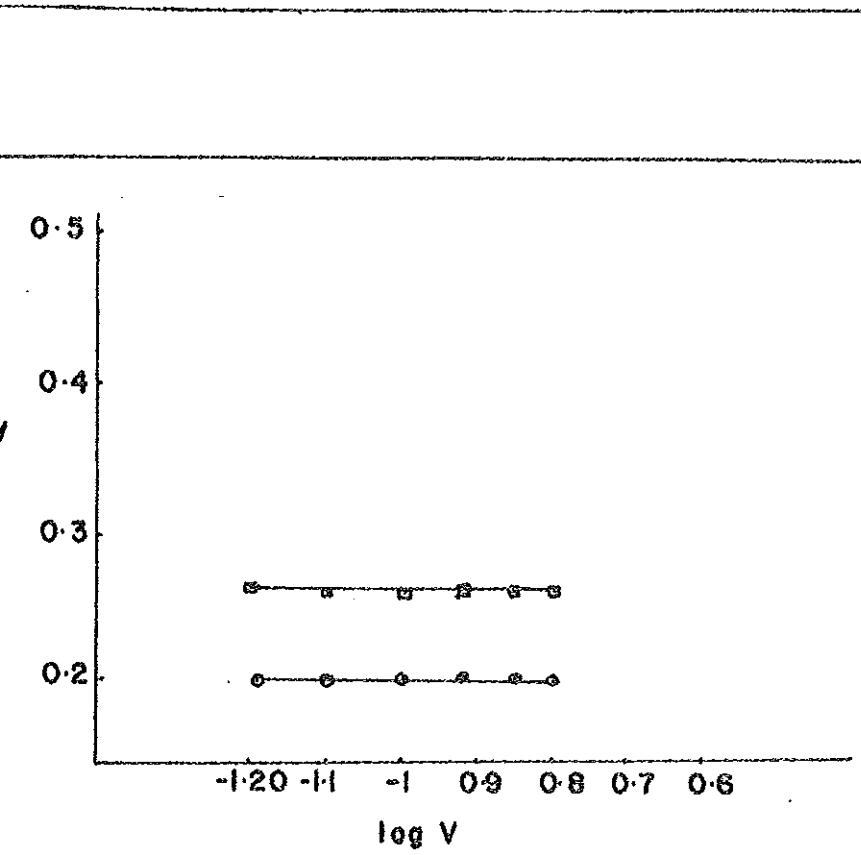

Fig. 25 Effect of the polarization rate on the position of the Peak ΔEp (○) or the half-peak Potential, $E_{p/2}$ (⊡). $C_{DS^-} = 2 \cdot 5 \times 10^{-4} M$

the same diagnostic criteria that were used in the previous systems. Thus the half-peak potential ($E_{p/2}$) preceeds the peak potential by 0.0575(Fig.25) which is in accord with the theoretical value. From table 9, the peak potential separation for forward and reverse polarization was found to be 0.06 mv which again conforms well with the theoretical value. The variation of $i_p/V^{\frac{1}{2}}$ with respect to $V^{\frac{1}{2}}$ gave a horizontal line as depicted in Fig. 26, confirming that the process is rapid and reversible.

The diffusion coefficient of dodecyl sulphate ion in the aqueous phase has been calculated from the slope of the dependance of the peak current on the square root of the sweep rate (Fig. 22-24). The calculation gave an average value $D_{DS^-}(W) = 1.49 \pm 0.49 \times 10^{-5}$ cm^2S^{-1} at three different concentrations of DS^- ion. This value is comparable to the values obtained using the TBATPB supporting electrolyte and to the value of D_{DS^-} calculated from the conductance at infinite dilution..

In the previous system, the half-wave potential of dodecyl sulphate was evaluated with respect to the transfer of TBA^+ ion. In that system the agreement of the voltammetric measurement with the extraction data was verified. A similar relationship is applied to evaluate the standard potential of the floride ion in this system. Figure 21 shows two peaks, in which the peak at about 0.240 potential corresponds to the transfer

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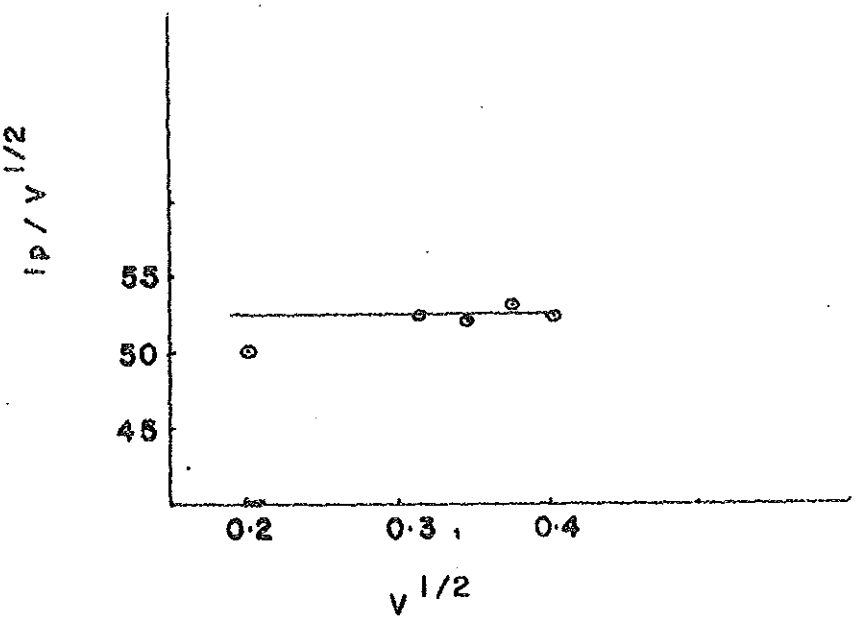

Fig. 26 Cyclic Voltammetry behaviour of DS^- ion in the transfer RXn from water to NB
$C_{DS^-} = 2{\cdot}5 \times 10^{-4}M$ base electrolite (CVTPB)

of DS^- ion from the aqueous to the nitrobenzene phase while the peak at-0.10V corresponds to the transfer of F^- ion from the aqueous to the nitrozenzene phase. The peak difference was found to be 0.340 V. Combining the results from voltammetric measurements with the given extraction data, the standard potential or half-wave potential of flouride was evaluated using the relationship,

$$\Delta E_{1/2} = E^{\Theta} + 0.059 \log \left(\frac{DW}{DnB}\right)^{1/2} \qquad (9)$$

where ΔE^{Θ} is the formal potential difference of floride ion, $\Delta^{W}_{B}\varphi^{o}_{F^-}$ related to the formal potential of DS^- ion, $\Delta^{W}_{nB}\varphi^{o}_{DS^-}$ i.e.

$$\Delta E^{\Theta} = \Delta^{W}_{nB}\varphi^{o}_{F^-} - \Delta^{W}_{HB}\varphi^{o}_{DS^-}$$

where ΔE^{o} is the standard potential difference.

The formal potential difference of dodecyl sulphate $\Delta^{W}_{NB}\varphi^{o}_{DS^-}$ is obtained from table (5) and the standard potential difference, ΔE^{o} , is measured , from the peak potential difference of the two ions on the voltammogram. The formal potential difference of the floride ion $\Delta^{W}_{NB}\varphi^{o}_{F^-}$ is then calculated

$$-0.340 = \Delta^{W}_{nB}\varphi^{o}_{F^-} + 0.52$$

$$\therefore \quad {}^{W}_{nB}\varphi^{o}_{F^-} = -0.392$$

The half-wave potential of F^- ion is calculated to be -0.402 v using equation (9). Furthermore the free energy of the transfer of flouride ion from water to nitrobenzene

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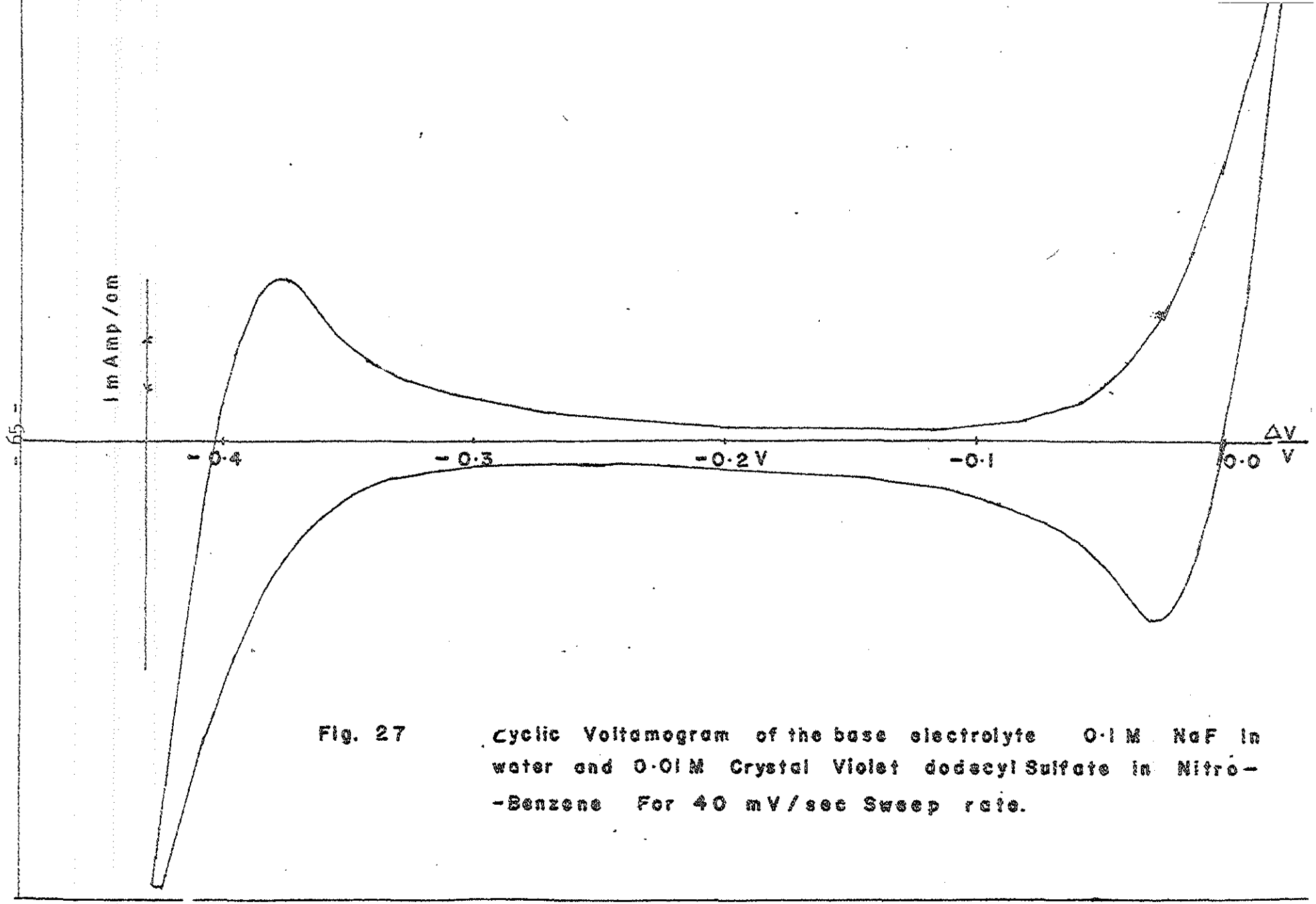

Fig. 27 Cyclic Voltamogram of the base electrolyte 0·1 M NaF in water and 0·01 M Crystal Violet dodecyl Sulfate in Nitro-Benzene For 40 mV/sec Sweep rate.

is calculated to be +37.83 KJ/mole using the relation(7).

The third system that has been studied is the charge transfer of ions in which 0.1M NaF was used as base electrolyte for the aqueous phase while 10^{-2}M crystal violet dodecyl sulphate was used as base electrolyte for the organic phase (nitrobenzene). Fig. 27 shows the voltammogram of such a system. In the potential region from 0.08 to 0.3v the current is controlled mainly by charging of the interface. At potentials more negative than 0.3Vthe current is controlled by the transfer of F^- ion across the interface, while at potentials more positive than 0.08Vthe current is controlled by the transfer of DS^- ion from one phase to the other. The rising postitive current beyond 0.08v corresponds to the transfer of the DS^- ion from nitrobenzene to the aqueous phase. A peak at 0.024V corresponds to the transfer of DS^- ion from water to nitrobenzene upon scan reversal. The peak at 0.36 v belongs to the transfer of F^- ion from the nitrobenzene to the aqueous phase. The peak difference is found to be 0.330V. This same potential difference was also obsserved in the previous experiment. The present findings therefore support the validity of the assumptions and calculations made using this value in the evaluation of the standard potential of flouride ion.

Fig. 28 shows the effect of using a different supporting electrolyte on the working potential range or

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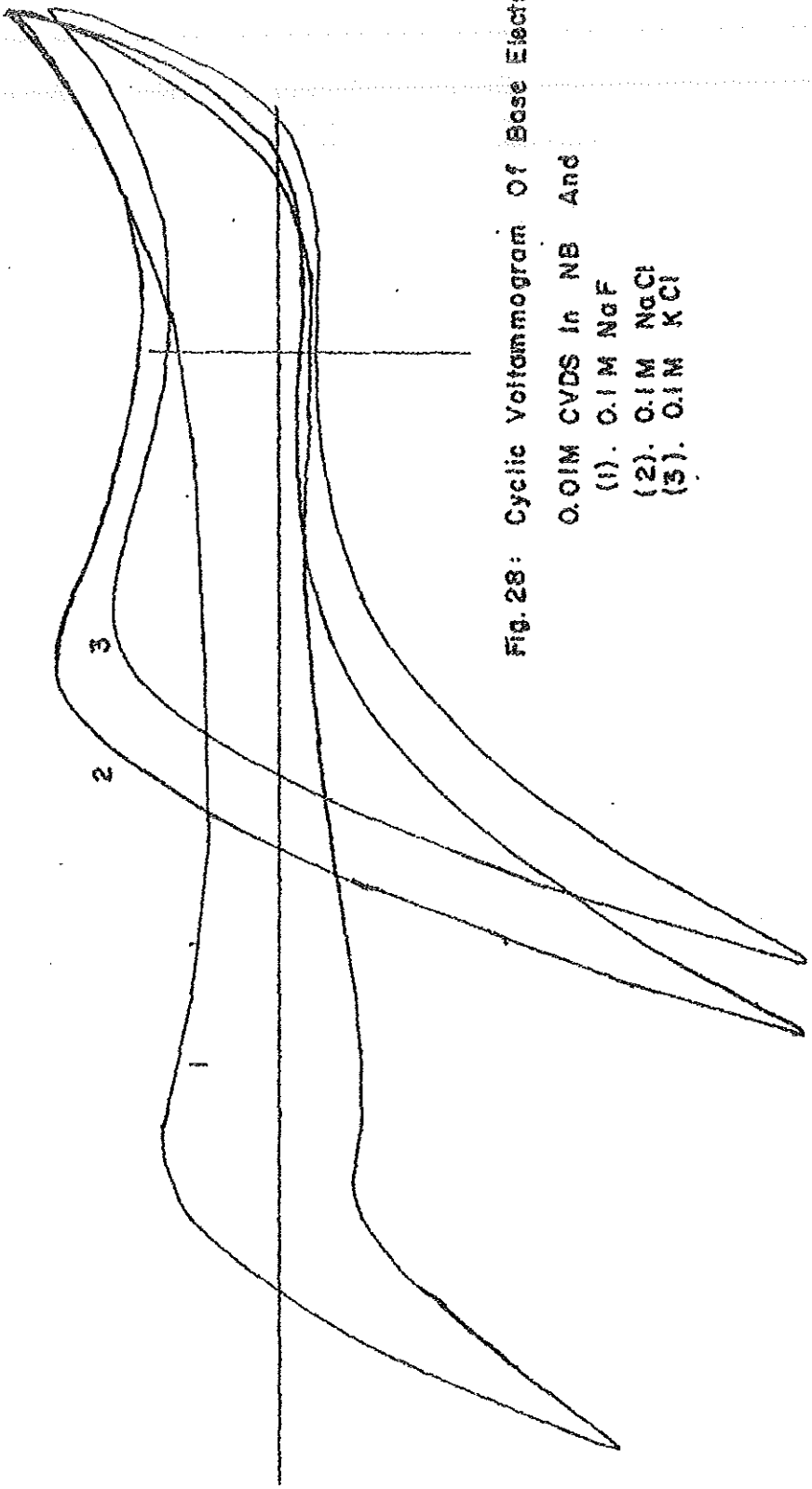

Fig. 28: Cyclic Voltammogram Of Base Electrolyte 0.01M CVDS In NB And
(1). 0.1 M NaF
(2). 0.1 M NaCl
(3). 0.1 M KCl

"potential window" of the voltammogram. From this figure it can be concluded that at one end of the voltammogram the current is governed by the transfer of DS^- ion from aqueous to nitrozenzene phases and the reverse is true upon scan reversal, while the other end is controlled by the base electrolyte chosen. The transfer of DS^- ion from the nitrobenzene phase to the aqueous phase was found to be reversible in this system. This has been established from the comparison of the experimental current-potential curve with the theoretical current-potential curve. Fig. 29 shows the theoretical curve obtained using equation 8.

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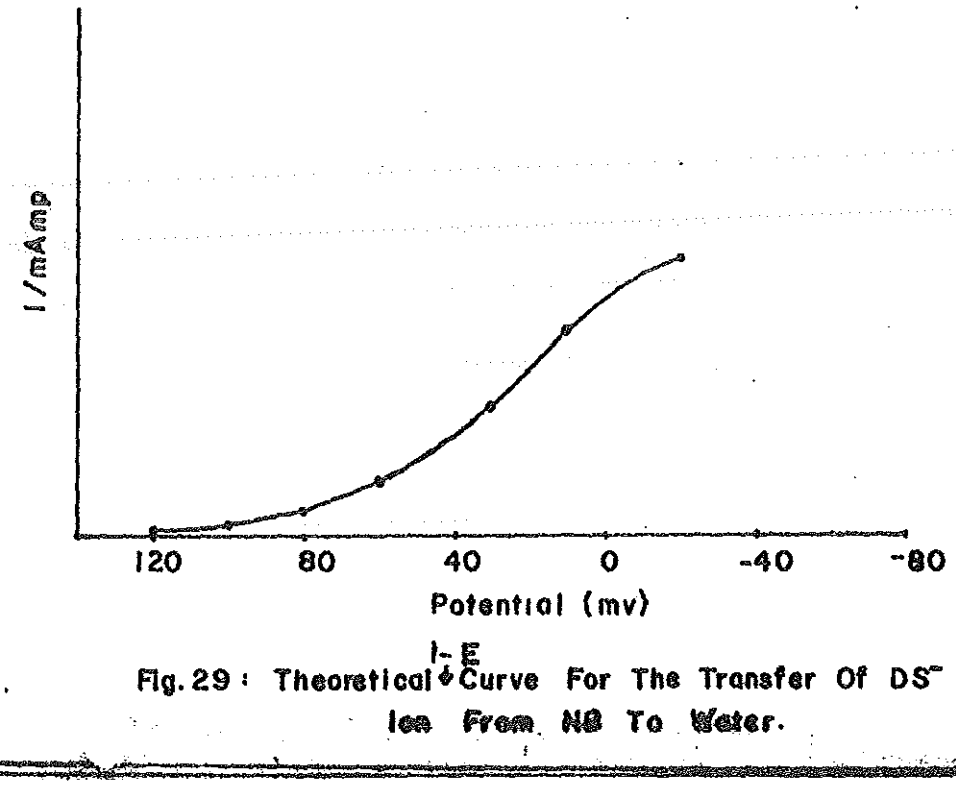

Fig. 29 : Theoretical I-E Curve For The Transfer Of DS^- Ion From NB To Water.

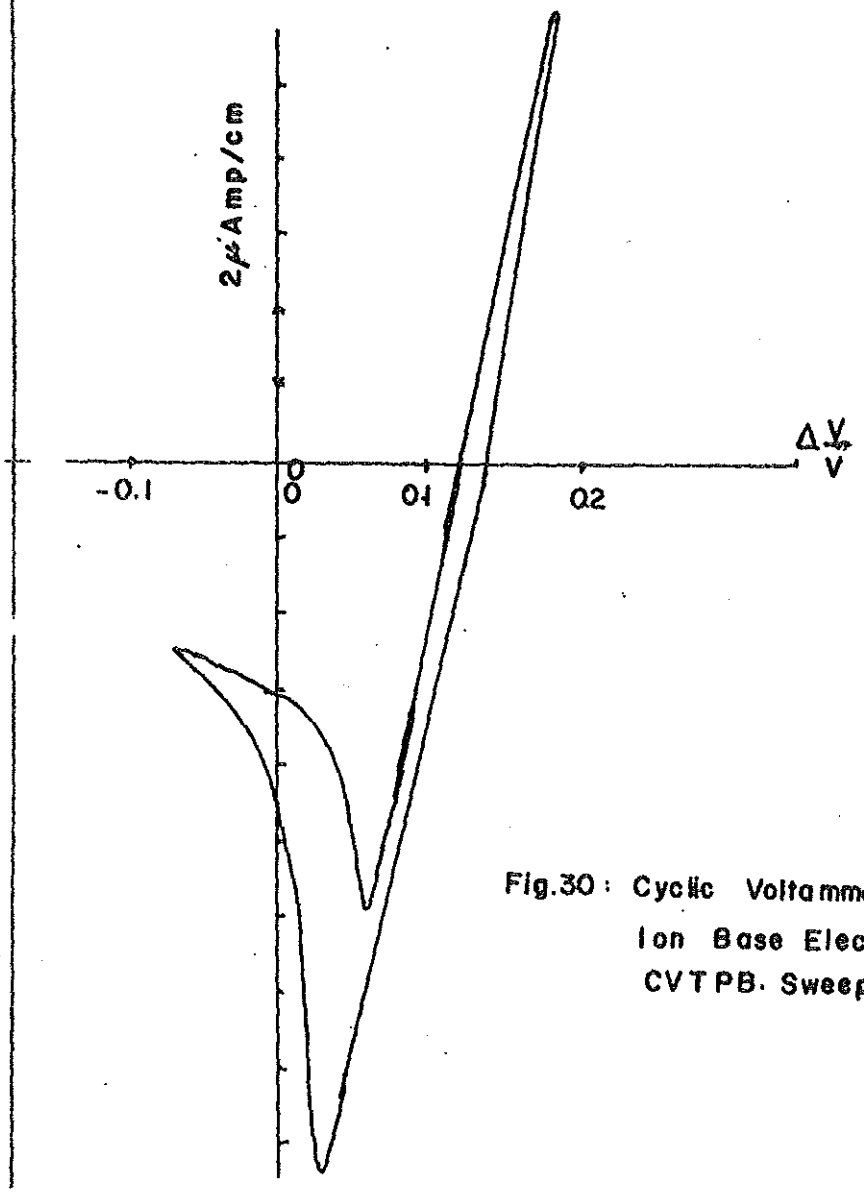

Fig.30 : Cyclic Voltammogram Of 1mM Aqueous Solution Of DS^- Ion Base Electrolyte 0.01M LiF In Water And 0.01M CVTPB. Sweeprate 40 mv/Sec.

SUMMARY

In the above series of experiments tetrabutylammonium tetraphenylborate, crystal violet tetraphenylborate and crystal violet-dodecyl sulphate were used as base electrolytes for the organic phase, while 0.01M LiF and 0.1M NaF were used as base electrolytes for the aqueous phase. In these systems, the transfer of dodecyl sulphate ion across the interface of two immiscible electrolyte solutions has been studied employing cyclic voltammetry. The results of these studies show a rapid and reversible transfer of dodecyl sulphate ion both from the nitrobenzene phase to the aqueous phase and also for the transfer in the opposite direction upon the reversal of the polarization.

This behaviour requires that the potential forming step is established immediately and that there is a 60 mv potential change per decade concentration change in the potentiometric measurment. The over-Nernstian behaviour that was exhibited by the carbon paste electrode does not appear to be accounted for by the cyclic voltammetric studies. The effect of the carbon powder on the electrode process needs to be investigated as this substance has not been included in the voltammetric studies.

The diffusion coefficient of dodecyl sulphate in aqueous solution has been evaluated from the voltammetric measurements. The values, D_{DS^-} were found to be $1.1 \pm 0.07 \times 10^{-5}$ cm^2 s^{-1} and This value conform well with a value,

$D_{DS}(W)$, 9 x 10^{-6} cm^2 S^{-1} calculated from conductance measurment at infinite dilution.

The quantity $E_{1/2}$, which is analogous to the reversible polarographic half-wave potential, was obtained for the transfer of dodecyl sulphate ion across the water-nitrobenzene interface. The value estimated from the voltammetric measurment i.e.0,221 V is comparable to the value obtained using the extraction data which was 0.205 V when TBA^+ was taken as a reference. The free energy of transfer of the DS^- ion from water to nitrobenzene, $\Delta G^{W\rightarrow nB}_{tr,DS^-}$ was calculated to be 19.68 kJ/mole.

The type of base electrolyte employed in the voltammetric studies have made it possible to evaluate the formal potential difference of F^- ion, $\Delta^{W}_{nB}\varphi^{o}_{F^-}$. The value was estimated to be 0.392 V and the $\Delta G^{W\rightarrow nB}_{tr,F^-}$ was calculated to 37,83 kJ/mole.

It is evident from the results given above, that reproducable and reasonable values have been obtained even without IR-drop compensation and using a relatively simple electronic circuit.

Below the critical micelle concentration, the transfer of dodecyl sulphate across the nitrobenzene/water interface has been reported to be reversible. However above this concentration (10^{-3}M) the voltammogram obtained appears to show an unexpected pattern as shown in Figure 30.

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