PRELIMINARY INVESTIGATION OF POTEMTOMETRIC STRIPPING ANALYSIS AT THE GEL STABILIZED OIL-WATER INTERFACE

By

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TO MY FATHER, MOTHER,

SISTER & BROTHERS

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ABBREVIATION

ACH^+ = Acetylcholine

ac = alternating current

ASV = anodic stripping voltammetry

CVTPB= Crystal violet tetraphenylborate

ITIES= Interfaces between two immiscible electrolyte solution

PSA = Potentiometric stripping analysis

μ_i° = Standard chemical potential for ion i

$\Delta G^{\circ}_{tr,i}$ = Standard Gibbs energies of transfer for ion i

TBATPB= Tetrabutylammonium tetraphenylborate

TBA(p-ClTPB) = Tetrabutyl ammonium parachloro-tetraphenylborate

TPAsDCC = Tetraphenylarsonium dicarbollyl cobaltate(III)

TPAsTPB = Tetraphenylarsonium tetraphenylborate

TPAsDPA = Tetraphenylarsonium dipicrylaminate

PNPDCC = p-nitrido-bis (triphenylphosphorus) 3,3-como-bis (undecahydro-1,2-dicarba-3-cobalta closodo decarbor)ate.

s.d. = Standard deviation

i = current at any point of the current-potential polarographic wave

i_d = diffusion limiting current in polarography

PVC-nb= Polyvinylchloride-nitrobenzene

ABSTRACT

Potentiometric stripping analysis (PSA) was applied to the interface between two immiscible electrolyte solutions (ITIES). The analysis was done on anions of thiocyanate, perchlorate and nitrate.

Polyvinylchloride-nitrobenzene (PVC-nb) gel was prepared following the procedure introduced by Senda et al [Bunseki Kagaku, 33 (1984) E 371] and the PVC-nb gel electrode was constructed using polytetrafluoroethylene (PTFE) tubing as a main cell body.

The behaviour of the cell was characterized by ac and dc cyclic voltammetry and reproducible voltammograms were obtained showing that the ion transport processes in both phases is diffusion controlled. The reversibility of the system was also tested using current reversal techniques.

The dependence of transition time (τ) on deposition time and deposition (or enrichment) potentials was qualitatively studied. From this preliminary study the method (PSA) was found to be quite applicable for the electrolysis of ions across the ITIES,

1. INTRODUCTION

Electrolysis at the interface of two immiscible electrolyte solutions (ITIES) is relatively recently developed as a new electroanalytical method [1, 2]. Particularly, since the first review by Koryta [1] in 1979 on electrolysis at the interface between two immiscible electrolyte solutions, this topic has been characterized by an increase in the number of groups working in this field and a rapid growth of publications concerned with both experimental, as well as theoretical aspects [3]. Even though the investigation of the polarization of the interface between two immiscible electrolyte solutions has been comparatively small in scope as compared to metal/electrolyte solution interface, there is a widespread interest on ITIES since it gives an insight on the processes taking place in biological systems, liquid-liquid extraction, phase transfer catalysis and in liquid state ion-selective electrodes.

The first paper describing the electrical properties of the interface between two immiscible liquid electrolyte phases is the regularly quoted work by Nernst and Riesenfeld [4] which dates back to 1902. They theoretically predicted and experimentally proved the effect of accumulation and depletion of the transported salt at ITIES depending on the direction of the current and on the values of transport numbers.

For about eight decades investigations of ITIES were, more or less, restricted to the study of equilibrium potential differences between aqueous and organic phases in contact in the presence of various electrolytes [5].

As mentioned in reference [6] Guastalla and Gavach, in 1968, showed that the water-nitrobenzene interface could be polarized. Since then a number of publications have been dedicated to the study of polarization phenomena and charge transfer reactions at the ITIES. Thus, the amount of information gathered has permitted the elaboration of a rather well-defined model of the interface. Surface tension [7] and capacitance measurements [8,9] have given access to the important interfacial quantities such as surface excess concentrations. The use of the Gouy-Chapman theory has indeed confirmed [10] that the Galvani potential difference between two phases *was* spread entirely within the two back-to-back double layers, while the interface can be regarded as a mixed solvent layer no more than *two* or three molecular diameter thick with a negligible contribution for the Galvani potential gradient [11]. All the chemical potential gradient $[\Delta G_{tr}^{0,1\to 2} = \mu_2^0 - \mu_1^0]$ is expected to take place within this thin mixed solvent layer.

Although both ion and electron transfer can occur across an ITIES, much attention has been given to the study of ion transfer. Early experimental kinetic studies by Gavach {as mentioned in Ref. (6) and more recent work by Samec, et al (12) and Senda, et al (13), have clearly shown that ion transfer reactions are fast $k_{app} > 10^{-2}$ cm s^{-i}). On the other hand, the investigation of electron transfer at the ITIES seems to be particularly important since electron transfer processes across biological membranes have paramount importance in living systems (1).

In many works it has been shown that the interface between two immiscible liquids is, with proper experimental setup, an analog of the metal electrode/electrolyte solution interface (1,5,14-18) and that this interface can be studied by the method, analogous to those used with metallic electrodes. Experimentally, the most extensively used techniques for the investigation of ITIES and ion transfers across the interface have been chronopotentiometry by Gavach and his co-workers (15,19-24), polarography with electrolyte dropping electrode (16,25-28), cyclic voltammetry (29-33) and impendance measurements (34-39).

The three most important criteria to choose an organic phase for the investiaation of ITIES are very low mutual solubility with water large difference in density as compared to water in order to have a stable interface, and high permitivity to ensure the dissociation of the supporting electrolyte (40). Based on this, nitrobenzene has been the most frequently used organic solvent. Besides the well-established oil-phase solvents like nitrobenzene and

1,2-dichloroethane, acetophenone [41], 0-nitrophenyloctylether [42], 0-nitrotoluene [83], dichloromethane [84], aniline, 0-dichlorobenzene, 0-chloroaniline, nitropropane and benzonitrile [43], chloroform [44] and solvent mixtures like nitrobenzene + chlorobenzene [45], nitrobenzene + benzonitrile and nitrobenzene + benzene [46] have also been used. For the solvent systems studied the kinetic parameters and Gibbs energies of transfer of ions have been successfully evaluated.

Transfer of quaternary ammonium ions 126], picrate [31, 47] thiocyanate (SCN), dodecylsulphate [27], cations of choline and acetylcholine [47, 48], cesium [30] and iodide, nitrate, thiocyanate and perchlorate [51, 53] ions transfer across the interface of water/nitrobenzene has been investigated using different electroanalytical techniques. In most cases the supporting electrolytes employed in the organic phase were TBATPB, TPAsTPB, TPAsDCC, TPAsDPA, PNPDCC, PNPTPB, TBAtP-ClTPB) and CVTPB while the sulphates, fluorides, chlorides or bromides of lithium, sodium and magnesium have been widely used in the aqueous phase. In general, a highly hydrophobic (lipophilic) salt in the oil phase and a highly hydrophilic one in the aqueous phase would provide a wider working potential range or "potential window" for the investigation of individual ion transfer without interference of the transfer of the ions of the base electrolytes, In order to extend the potential window towards negative potentials the tetraphenylarsonium [49] and Crystal Violet [50] cations have been used. The system with which an extremely negative potential can be reached contains NaF in the aqueous phase and Crystal Violet in nitrobenzene [51, 52].

The standard Galvani potential differences across the water-oil interface for some cations such as alkali, alkaline earth metal ions and proton are so positive that they cannot be determined in simple ion transfer processes across the ITIES. They can, however, be investigated if their transfer is facilitated by the presence of an ionophore (complex former) in the organic phase.

An ionophore is a hydrophobic (lipophilic) substance that possesses acceptor properties for cations; the resulting ionophore-ion associate must also be hydrophobic. For the lower concentration of ionophore as compared to the concentration of the transferred ion, the current is controlled by the diffusion of ionophore to ITIES and of the complex formed from the ITIES to the organic bulk solution. The current is controlled by the diffusion of metal from the aqueous to the ITIES and the diffusion of the complex formed from the ITIES to the bulk of the organic phase for low concentrations of metal ion 152].

In the investigation of ITIES, a very important improvement of the analytical instrumentation has been the introduction of polymer-electrode gel in 1984 by Senda, et al [54] (see Ref. [3, 55, 57] in order to avoid mechanical instability of the interfaces between two immiscible electrolyte solutions. Marecek and Colombini [55] and Janata, Marecek, Gratzl and Pungor [56] tried to investigate the properties of polyvinylchloride-nitrobenzene gel/water interface using dc cyclic voltammetry and fluctuation analysis employing a four-electrode arrangements with positive feedback.

Besides the intensive research of electrolysis at the interface between two immiscible electrolyte solutions, there is a well established method in trace analysis-the potentiometric stripping analysis (PSA) - which was introduced and described by Jagner and Graneli [68] in 1976. The basic principles of PSA are, the deposition of the ions to be determined on a suitable working electrode which is kept at a fixed potential and the dissolution (stripping) of the metals from the deposit. The stripping is either realized by an appropriate oxidizing agent such as oxygen and mercuric ion [69-73] or by a constant current applied to the electrode. The determination of ions is based on the evaluation of the potential-time curves monitoring the course of the dissolution process. The transition times obtained at a certain potential (which is related to the standard redox potential of the respective ion) is proportional to the concentration of the reactive ion.

Jagner & Graneli [68] used mercury-film coated glassy carbon (MFGCE) as the working electrode, SCE and olatinum foil as reference and counter electrodes, respectively. The working electrodes generally used in PSA are MFGCE [68,74] noble metals and graphite electrodes [69,75], and the carbon fiber electrodes (CFE) [76.79]. The CFE have recently been used for ASV and PSA and its incredible properties, uses, applications and advantages is reviewed by Edmonds [79].

PSA has got an important position for trace metal analysis over the other electroanalytical techniques because of its unique properties [70,80,81] such as sensitivity, simplicity, cost and above all its accuracy and precision.

But this electroanalytical techniques (PSA) has not been applied yet to the interface between two immiscible electrolyte solutions. Thus, in order to investigate the possibility whether the potential stripping analysis technique could be applied for the determination of anions employing the interface between two immiscible electrolyte solution (ITIES) as working electrode, the organic phase has, in the present work, been "solidified" as PVC-gel.

The organic phase (nitrobenzene) was "solidified" as PVC-gel and the respective anions were transferred to the organic phase by applying a potential difference sufficiently negative to work in the limiting current region of the ion under investigation. Stripping out the anions from the organic phase was done galvanostatically.

2. THEORY

In the last few years considerable effort has been made in the utilization of the polymer gel-liquid interface in analytical chemistry [54, 58-60] (cf. [60]). Senda and co-workers [54] first used cyclic voltammetry to study an ion transfer across the polymer gel/liquid interface in a two-electrode arrangement. The solidification of one side (organic or aqueous) of the interface by a polymer gel simplifies the experimental arrangement and extends the possibilities of its utilization in analytical chemistry.

Marecek, et al [60] have constructed a polyvinylchloride-nitrobenzene (PVC-nb) gel electrode and tried to test its performance using electrochemical pulse methods. They found a sensitivity increase of over one order of magnitude and a fast response time was obtained as compared to ion-selective and enzyme electrodes for acetylcholine (ACH+). They also compared the cyclic voltammograms of ACH+ in simple water-nitrobenzene and water/PVC-nb gel interfaces at different polarization rates. It was found that ACH+ transfer in the former is simple with apparent transfer rate constant $k_{app} = 1.6 \times 10^{-2}$ cm/sec, while in the latter the mechanism of transfer seems to be more complicated. The peak potentials at low polarization rates differ slightly from those obtained at a simple liquid-liquid interface and their dependence on the polarization rate indicates a partially kinetic and diffusion controlled process.

Polarization measurements at the polymer gel-liquid boundaries were employed for an analysis of the behavior of the ISE [58] and for direct evaluation [55, 58] or monitoring [60] of the ion concentrations. In contrast to the first experiments with a two-electrode system [54, 58], more accurate measurements using a four-electrode arrangement [55] have indicated that the ion transfer across a polymer gel/liquid boundary shows little difference from that occurring at an ITIES.

On introduction of a charge to one of the phases from an external source (and simultaneously, of a charge of opposite sign to the other phase), two processes can take place; either the transfer of ions whose equilibrium potential due to charge injection does not coincide with the equilibrium value $\Delta_o^w\Psi_{eq}$ (rather $\Delta E = \Psi_o^w + \Delta V$) or the charging of the electrical double layer present at ITIES.

When the electrolyte of the aqueous phase consists of very hydrophilic ions ($\Delta_o^w \Psi_i^o$ very positive for cation and very negative for the anion) while the organic phase only contains very hydrophobic ions ($\Delta_o^w \Psi_i^o$ very negative for the cation and very positive for the anion) then there exists a potential range ("a potential window") where the ITIES behaves like an ideally polarized electrode, ie. the injected charge is used only for double layer charging [1, 16].

The chronopotentiometric method was extensively used for the study of electroanalytical processes at metal-solution interfaces by different researchers [64-68]. Delahay and his co-workers [63,64,67] have had an immense contributions to the application of this technique for different types of electrode processes (reversible, quasi-reversible and irreversible) using three-electrode system in which mercury pool served as working electrode. As the name implies, chronopotentiometry utilizes the measurement and interpretation of the potential-time curves. It is frequently mentioned that interfaces between two immiscible electrolyte solutions have several basic features analogous to the interface metallic electrode/electrolyte solution [1,61]. Thus, we extrapolate (or transpose) PSA techniques in metal electrode/electrolyte solution to the ITIES.

A potentiometric stripping analysis (PSA) in its common form consists of two steps- concentration and stripping steps. Its application at the ITIES in particular is a combination of a concentration step, in which an ion in an aqueous solution is transferred into the organic phase or gel through the application of an appropriate potential from an external source for a specified period of time, followed by a stripping process in which the ion is stripped back to the aqueous phase. Thus the potential-time characteristic is registered using Y-t recorder from which one can extract both the quantitative (from transition time) and qualitative ($E_{\tau/4}$) informations.

When two immiscible electrolyte solutions are in contact there is established an electric potential difference which in case where both phases contain a common ion i with a charge number Z follows the Nernst-Donnan equation

$$\Delta_o^w \Psi_{eq} = \Psi(w) - \Psi(o) = \frac{\mu_i^o(0) - \mu_i^o(w)}{ZF} + \frac{RT}{ZF} \ln \frac{a_i(o)}{a_i(w)}$$

$$= \frac{\Delta G_{tr,i}^{o,0\to W}}{ZF} + \frac{RT}{ZF} \ln \frac{f_i(0)}{f_i(w)} + \frac{RT}{ZF} \ln \frac{C_i(0)}{C_i(w)}$$

$$\Delta_o^w \Psi_{eq} \simeq \Delta_o^w \Psi^o + \frac{RT}{ZF} \ln \frac{C_i(0)}{C_i(w)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where the Ψ's are the inner electrical potentials, μ^o's the standard chemical potentials which include the terms describing the ion-solvent interactions, a's activities of the ion i in each phase and are functions of only concentrations and of inter ionic interactions, f's the activity coefficients and C's the concentrations of ion i in each phase. The quantity $\Delta G_{tr,i}^{o,0\to w}$ is the standard Gibbs energy of transfer of the ion i from the organic to the aqueous phase and it is, in fact, the difference of standard Gibbs energies of solvation of i in the phase w (aqueous) and 0 (organic) respectively. In order to attribute a definite value to this quantity an extrathermodynamic approach has to be used, eg. the"TATB assumption" stating that the standard transfer Gibbs energies of $TPAS^+$ cation and of TPB^- anion are equal for any pair of solvents [62]. On the basis of this assumption $\Delta G^{o,0\rightarrow w}_{tr,i}$'s and $\Delta^{w}_{o}\,\Psi^{o}_{i}$'s can be composed [52].

When the interfacial potential between the two non-miscible solution have the value different from the equilibrium potential ($\Delta^{o}_{o}\,\Psi_{eq}$), an ion transfer will occur in the available potential ranges. Let us assume that ion i is the only ion that crosses the interface. The passage of this ion from the organic solution to the aqueous phase can simply be written as:

$$i(o) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} i(w) \quad \ldots\ldots \qquad (2)$$

It is assumed that the transport of ion i from the bulk of the organic phase to the interface is governed by diffusion. Under constant current conditions $C_i(o)$, the interfacial concentration of the ion i at the organic side of the interface is given by

$$C_i(o) = C^{o}_{i}(o) - \frac{2i_o t^{\frac{1}{2}}}{ZFA(\pi D_i(o))^{\frac{1}{2}}} \qquad (3)$$

where $C^{o}_{i}(o)$ is the bulk concentration in organic phase, i_o the current density, $D_i(o)$ the diffusion coefficient of ion i in the organic phase, t the electrolysis time, A the area of the interface and F faraday constant. The expression of the transition time τ follows immediately when $C_i(o) = 0$

$$\tau^{\frac{1}{2}} = \frac{C_i^{o}(o)\,ZAF(D_i(o)\pi)^{\frac{1}{2}}}{2i_o} \quad .... \quad (4)$$

Equation (4) shows that there is a direct relationship between the transition time τ and the bulk concentration in the organic phase.

For a reversible ion transfer across the ITIES, the Galvani potential difference across the interface obeys the Nernst equation

$$\Delta_o^w \Psi = \Delta_o^w \Psi^o + \frac{RT}{ZF} \ln \frac{C_i(o)}{C_i(w)} \quad .... \quad (5)$$

During potentiometric stripping from the organic to the aqueous phase, the concentration of the species i in the aqueous side of the interface can be given by

$$C_i(w) = \frac{2i_o t^{\frac{1}{2}}}{ZFA(\pi D_i(w))^{\frac{1}{2}}} \quad .... \quad (6)$$

Noting that $C_i = a_i f_i$ and using equations (3)-(6) one can obtain the potential-time relationships as follows

$$\Delta_o^w \Psi = \Delta_o^w \Psi^o + \frac{RT}{ZF} \ln \frac{f_i D_i^{\frac{1}{2}}(w)}{f_i D_i^{\frac{1}{2}}(o)} + \frac{RT}{ZT} \ln \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}}$$

$$\Delta_o^w \Psi = \Delta_o^w \Psi_{\tau/4} + \frac{RT}{ZF} \ln \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}} \quad .... \quad (7)$$

where $\Delta_o^w \Psi_{\tau/4}$ corresponds to a value of t equal to one-fourth of the transition time and is identical to the reversible half wave potential. $t^{\frac{1}{2}}$ and $\tau^{\frac{1}{2}}$ are thus analogous to i and i_d in polarographic theory. At the transition time, when $t = \tau$, the potential in equation (7) theoretically goes to infinity. Actually the potential at time τ increases towards more positive potential relatively rapidly in the PSA of ions from the organic (PVC-nb gel) to the aqueous phase.

The reversibility of the system can be tested by plotting $\Delta_o^w \Psi$ vs. $\log \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}}$. A straight line with a slope equal to 2.303 RT/nF is indicative of a reversible process. The reversibility of the ion transfer across the PVC-nb gel/water interface has been proved by Marecek and his colleagues [57].

In current reversal chronopotentiometry, the direction of the current is changed at the instant when a pre-arranged potential is reached so that the species is subjected to a reverse transfer, provided that the ion transfer process is reversible. Thus, current reversal analysis is another test for reversibility of the system.

For a totally irreversible transfer process, the rate expression (k_s) is introduced in the normal way to give the end result.

$$\Delta_o^w \Psi = \Delta_o^w \Psi^o + \frac{RT}{\alpha nF} \ln \frac{FnAC_i k_s}{i_o} + \frac{RT}{\alpha nF} \ln \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{\tau^{\frac{1}{2}}} \quad \ldots \qquad (8)$$

where α is the transfer coefficient and other symbols have their usual meanings.

In potentiometric stripping analysis, the sensitivity and the detection limit is dependent on the concentration of the ion in the organic phase and therefore on the current density, length and efficiency of the controlled-potential electrolysis step (enrichment step). It is expected that, at a lower current density, by keeping small the size of the organic phase as compared to the aqueous phase one can obtain an extremely low detection limit of this PSA of the anions from the organic to aqueous phase.

3. EXPERIMENTAL

Measurements were carried out with a four-electrode potentiostat or/and galvanostat with automatic IR compensation by means of positive feed-back [30]. The IR compensation was set to the nearest point before the potentiostat starts oscillating. In the four-electrode system the two auxiliary silver wire electrodes work as a source and drain of currents while the potential difference across the interface is controlled (in the potentiostatic case) or measured (in the chronopotentiometric case) by means of two $Ag/AgCl/Cl^-$ reference electrodes. The voltammograms and chronopotentiograms were recorded with an X-y and Y-t recorder, respectively. The experiments were carried out at room temperature of $22\pm2.^{\circ}C$ in air-saturated solutions.

All solutions were prepared from alkali and alkaline earth metal salts of analytical reagent grade with twice-distilled water. The nitrobenzene was washed with 0.1N sulfuric acid to remove impurities and then with 0.1N potassium hydroxide to neutralize the acid, and finally with distilled water until it become neutral towards litmus-paper. The nitrobenzene was then distilled at a reduced pressure and only the middle of the distillate was collected and stored in a brown bottle.

3.1 Preparation of polyvinylchloride-nitrobenzene gel electrode

The polyvinylchloride-nitrobenzene (PVC-nb) gel was prepared by dissolving 1g of high molecular weight PVC powder in 8 ml of nitrobenzene which contained 10 mM crystal violet tetraphenylborate (CVTPB) that would serve as a supporting electrolyte in the organic phase. The whole mixture was left in a boiling water bath until it "liquified." When the amount of PVC powder increased, the phase behaviour of the PVC-nb gel changed from a viscous liquid to a "plastic type" solid.

The PVC-nb gel was injected into a PVC-tubing which contained a glass tube (see Fig. 1). However, it was found that the resistance of the membrane was too high. Furthermore, there was a leakage of the magnesium sulfate (bridge electrolyte for the counter electrode of the organic phase) solution through the PVC-nb gel. To avoid this leakage problem, the magnesium sulfate solution was substituted with agar agar-water gel, which was prepared by dissolving 3g of agar agar powder in 100 ml of 10 mM boiling magnesium sulfate solution. However, the electrode was not stable and its response was not reproducible.

After several trials, it was possible to construct a working electrode using a polytetraflouroethylene (PTFE)

Table 1: Data of the sweep rate dependence of peak currents using 10^{-5} M $LiClO_4$ with (10 mM $MgSO_4$) and without supporting electrolyte in the aqueous phase

Sweep Rates (mv/s)	Peak currents in μA with base electrolytes		Peak currents in μA without base electrolyte	
	i_p(w→nb)	i_p(nb→w)	i_p(w→nb)	i_p(nb→w)
25	4.25	3.90	2.90	2.70
36	4.70	4.50	3.40	3.20
40	5.80	5.60	3.70	3.50
60	6.70	6.50	4.50	4.30
80	7.40	7.30	5.95	5.75

4.3 Calculation of the Area of the Interface

Fig. 5 illustrates the dependence of peak current on sweep rates using 10^{-5} M $LiClO_4$ in the aqueous solution when perchlorate ion is transferred from the aqueous phase to PVC-nb gel (organic phase). From the plot of peak current vs. square root of sweep rate one can calculate the area of the electrode using the relationship ($i_p = 269.Z^{3/2}A.D^{\frac{1}{2}}C^o\nu^{\frac{1}{2}}$). The area of the interface (A) was found to be 0.785 cm^2 which is a bit higher as compared to the area (.70 cm^2) calculated from the measurement of the internal diameter of the PTFE tube. The cause of this discrepancy may be the surface roughness due to pores and spherical nature of the interface. In this calculation, diffusion coefficient of perchlorate ion in water was taken as 1.79×10^{-5} cm^2/s (82).

4.4 Reproducibility of Measurements

To test the reproducibility of potentiometric stripping measurements using interfaces between two immiscible electrolyte solutions (the PVC-nb gel/water interface), ten replica of the potentiometric stripping measurements were taken at a deposition time of 20 seconds and zero deposition potential using 10^{-5} M potassium thiocyanate in 10 mM magnesium sulfate. Quite reproducible results were obtained with standard deviation of 1.44 seconds (20.5 + 1.44) for the transition time (τ) and 2.35 mV (182.5 ± 2.35) for that of the half-wave potential ($E_{\tau/4}$) of thiocyanate. The same half-wave potential was obtained by phase-selective fundamental harmonic ac cyclic voltammetry.

Table 2: Potentiometric stripping measurements of 10^{-5} M KSCN in a continuously stirred solution (1500 rpm) and at a deposition time of 20 seconds

	Transition Time (τ/s)	Half-wave Potential ($E_{\tau/4}$/mV)	Deposition Potential (mV)
	18.0	185.0	0
	22.2	185.0	0
	20.7	185.0	0
	22.2	185.0	0
	21.0	182.5	0
	21.9	182.5	0
	19.05	180.0	0
	21.3	180.0	0
	19.2	180.0	0
	20.25	180.0	0
mean	20.58	182.5	0
s.d.	1.440	2.350	0

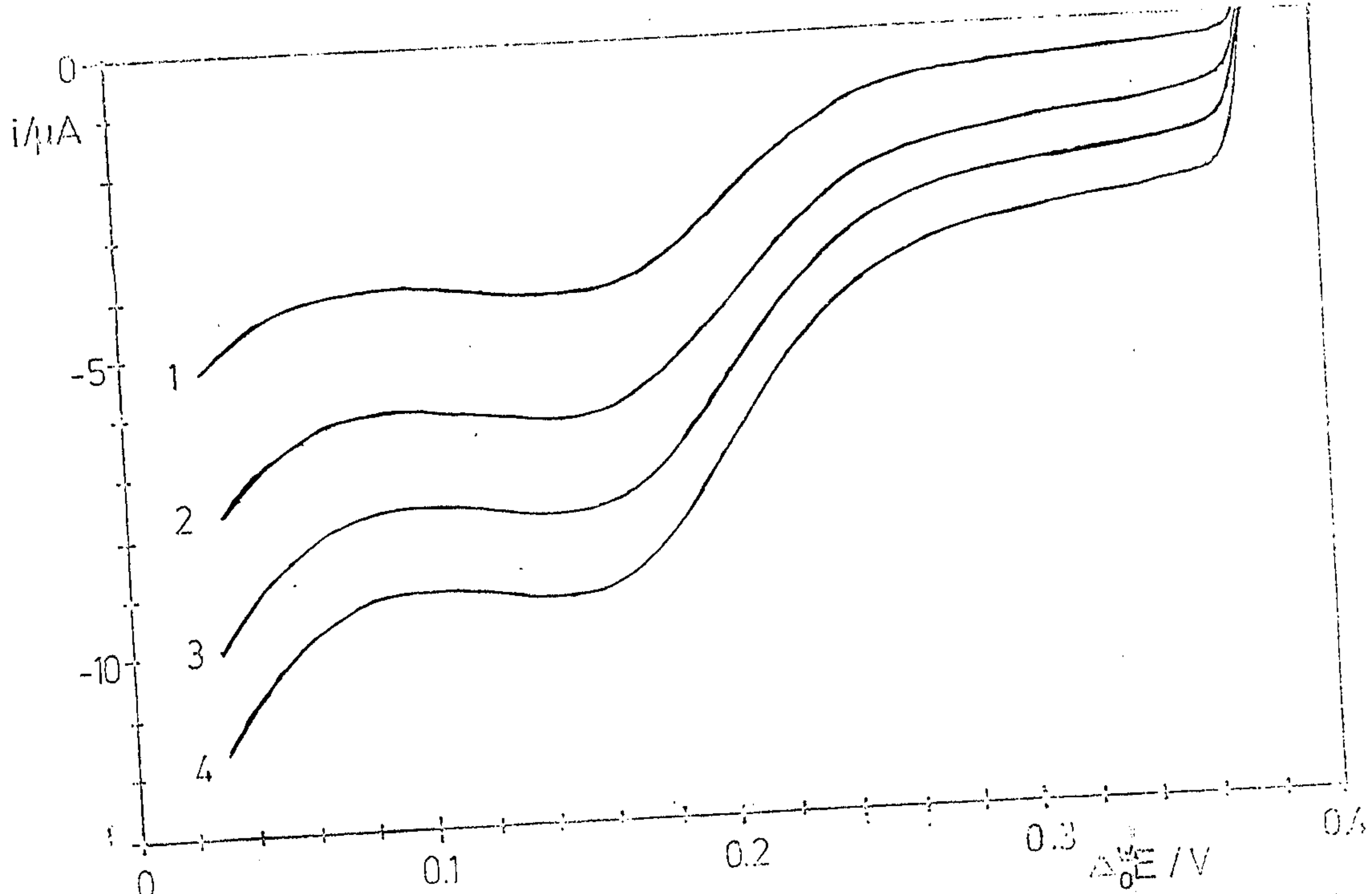

Fig. 5: Sweep rate dependence of the transfer of the ions (10^{-5}M $LiClO_4$) from the aqueous to the PVC-nb gel. Sweep rates 25 (1), 50 (2), 75 (3) and 100 mV/s (4). The aqueous and organic phases contain 10 mM $M_{\mu}SO_4$ and CVTPB, respectively.

4.5 The Relationship between Deposition and Transition times in PSA

In a solid electrode such as noble metals and glassy carbons or in electrodes coated with a thin film of mercury on an appropriate material it is found that the square root of transition time ($\tau^{\frac{1}{2}}$) is directly proportional to the concentration in solution and the deposition time (t_{dep}). To test the applicability of these fact on ITIES and then to apply the potentiometric stripping analysis to the interface, the measurement of transition times were taken at different deposition times using nitrate, perchlorate and thiocyanate ions both in stirred and quiscent solutions. From the plot of deposition time versus transition time, a linear relationship was found between these quantities (Fig. 6). One can therefore use interfaces between two immiscible electrolyte solutions for the analysis of ions using potentiometric stripping techniques. Table 3 shows the data of the PSA of perchlorate (10^{-5}M), thiocyanate ($5x10^{-5}$M) and nitrate (10^{-4}M) in a continuously stirred solution at the rate of 1500 rpm. In all cases the deposition potential was set at zero volt.

Table 3: Transition time dependence on deposition time in PSA

Deposition time/s	Transition time/s		
	Perchlorate	Thiocyanate	Nitrate
10	9.0	-	-
20	15.0	25.5	10.05
30	15.6	33.6	14.7
40	20.4	45.6	17.4
50	25.1	52.8	21.6
60	-	64.8	24.0
70	-	-	25.2

4.6 Effect of Stirring and Deposition Potential on PSA

The effect of stirring during potentiometric stripping and the influence of deposition potential on transition time (τ) was also tested using $5x10^{-5}M$ potassium thiocyanate and the results are tabulated in Tables 4 and 5, respectively. It is a well known fact that the deposition or enrichment time can be made shorter either by stirring a solution with a magnetic bar or by rotating an electrode since in a stirred solution, the electro-active species is transported towards an electrode or interface both by convection and diffusion. As can be seen from Table 4 τ is a bit smaller in stirred solution during stripping as compared to the analysis in a quiscent solutions. This is theoretically expected, since the thiocyanate ion is continuously removed from the interface as it is stripped from the organic to the aqueous phase, a factor which is absent in an unstirred solution (see Fig. 7 and Table 4).

Table 4: Effect of Stirring on PSA using 5×10^{-5}M KSCN at zero Deposition Potential

Deposition time (seconds)	Transition time (τ/s) Stirred Solution (1500 rpm)	Transition time (τ/s) quiscent solution
20	21.2	25.8
30	28.8	33.6
40	43.2	45.6
50	53.2	53.8
60	63.2	64.8

Table 5: Influence of deposition potential on τ in PSA using 5×10^{-5}M KSCN. The solution was stirred at 1500 rpm

V_{dep}/mV	t_{dep}/s	τ/s
0	60	64.80
50	60	59.20
75	60	41.40
100	60	36.00
125	60	15.30

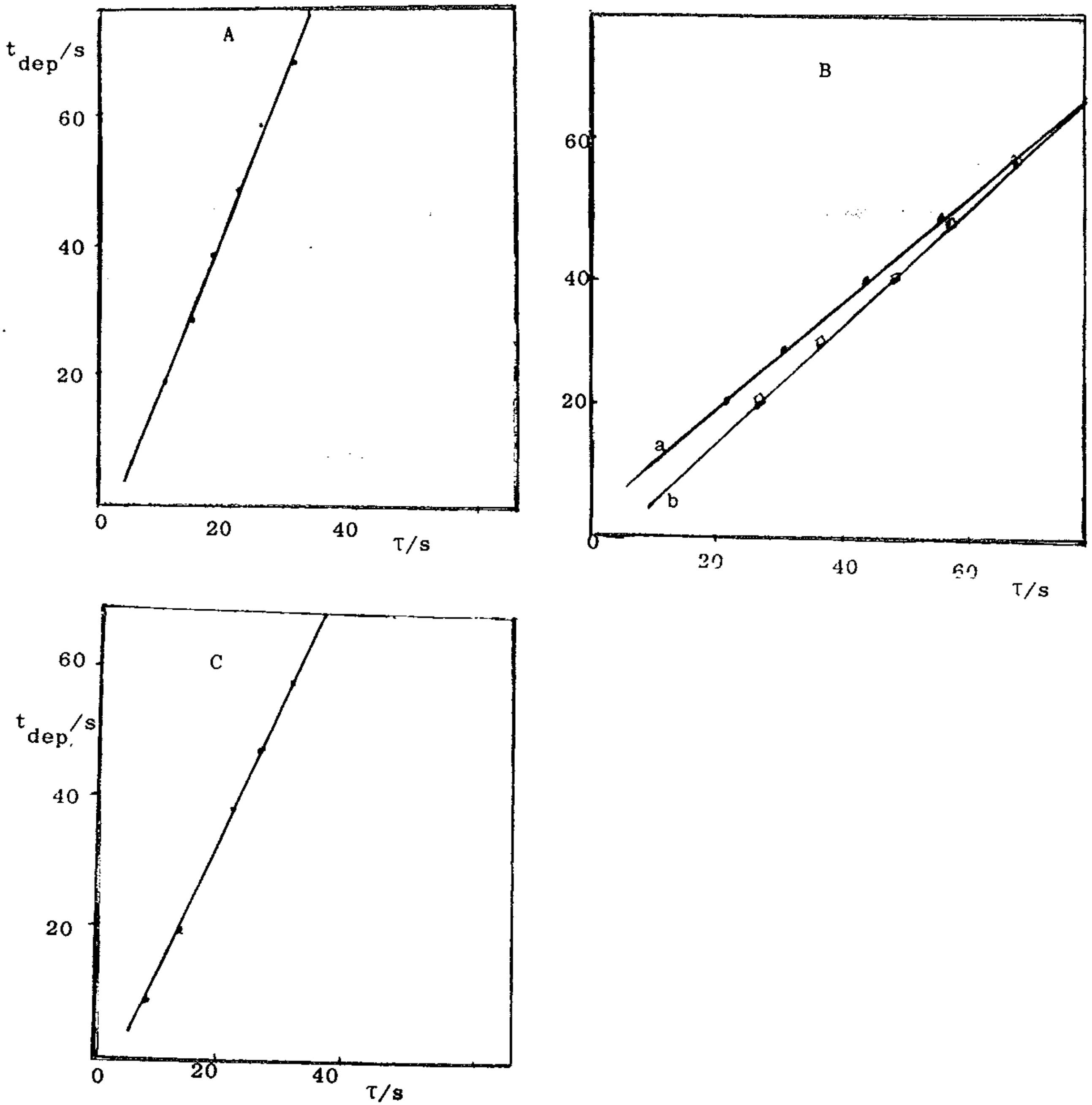

Fig. 6: Plot of deposition time (t_{dep}/s) versus transition time (τ/s) for 10^{-4} M KNO_3(A), 5×10^{-5} M KSCN (B) and 10^{-5} M $LiClO_4$ (C) solutions. Except curve b (in B) all measurements were done in a stirred solution (1500 rpm). Aqueous and organic phases contains 10 mM $MgSO_4$ and 10 mM CVTPB in PVC-nb gel, respectively.

From Table 5 it is clear that the transition time grows smaller (the amount of ion transferred from the aqueous to the organic phase decreases) with an increase in the deposition potential (see Fig. 7c).

As is shown in Fig. 7, especially at a longer deposition time (when a relatively large amount of thiocyanate ion is transferred from the aqueous to the organic phase) there is a distortion of the potential-time curves at the beginning of the chronopotentiogram. This peak-like distortion may be due to the formation of an insoluble salt of crystal violet thiocyanate at the interface.

Potentiometric stripping analysis across the PVC-nb gel/water interface was also performed using different concentrations of perchlorate, nitrate and thiocyanate. The method was found to be quite applicable for the determination of anions both qualitatively and quantitatively. For example, potential-time curves of perchlorate (10^{-5}M) and nitrate (10^{-4}M) are shown in Fig. 8 which are obtained during PSA of respective anions from the organic to the aqueous phase. The deposition or enrichment times for each case are indicated on the curves.

4.7 Effect of Current Density on Transition Time (τ)

Current reversal stripping analysis has also been made employing 5×10^{-5}M KSCN in 10mM magnesium sulfate in the aqueous phase while the organic phase contains 10mM

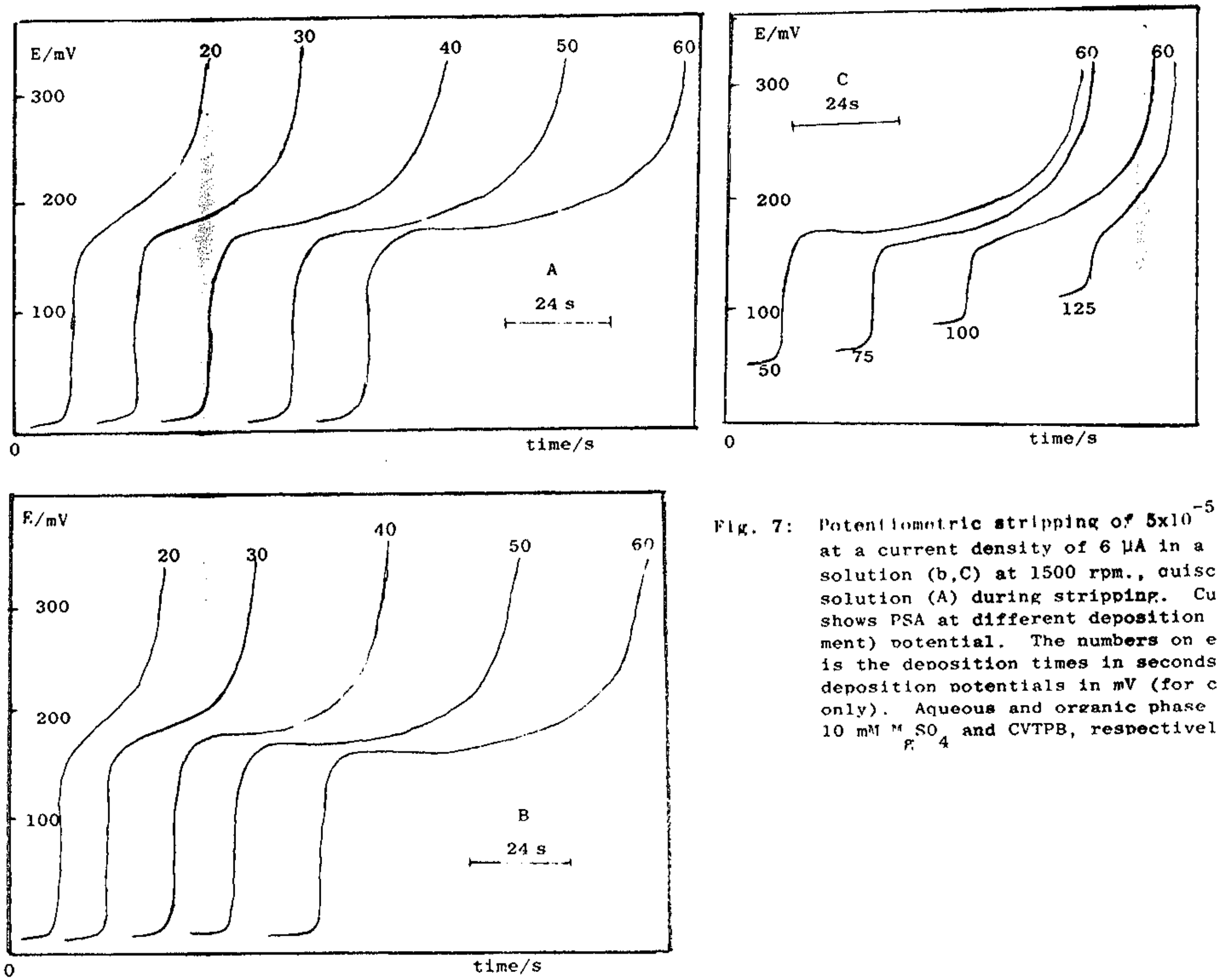

Fig. 7: Potentiometric stripping of 5×10^{-5} M KSCN at a current density of 6 μA in a stirred solution (b,C) at 1500 rpm., quiscent solution (A) during stripping. Curve C shows PSA at different deposition (enrichment) potential. The numbers on each curve is the deposition times in seconds and deposition potentials in mV (for case C only). Aqueous and organic phase contains 10 mM $MgSO_4$ and CVTPB, respectively.

CVTPB as base electrolyte. In this current reversal PSA, a constant current was applied at the interface until a prearranged or selected potential was attained at which point the direction of the current was changed so as to get a well-defined chronopotentiogram. This current reversal technique can also be used as a test of the reversibility of the system. In our case, the anions were first transferred from the aqueous phase to the PVC-nb gel (organic) phase by the application of constant current until the potential was equal to zero. Then the polarity (direction) of the current was reversed in order to get potential-time curves when the anions were stripped back from the PVC-nb gel to the aqueous phase. The data that shows the dependence of transition time on current density are tabulated in Table 6 while the corresponding chronopotentiograms are shown in Fig. 9.

Table 6: Influence of Current Density on Transition time using 5×10^{-5}M KSCN

$\pm\ i_o/\mu A$	t_{dep}/s	τ/s
5	116.4	43.5
10	18.0	5.10
15	7.88	1.37
20	3.96	0.60

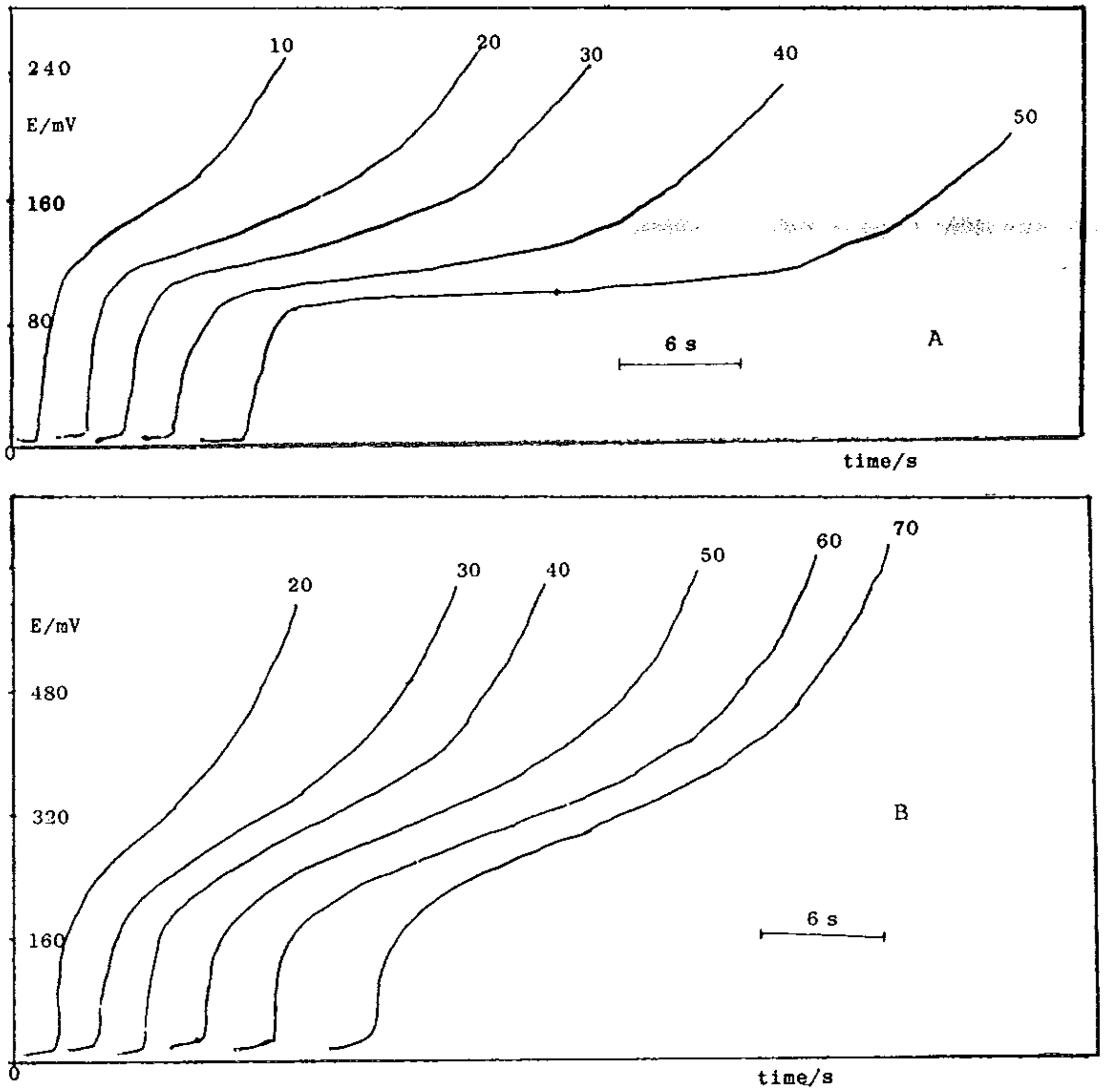

Fig. 8: PSA (potential-time curves) of 10^{-5} M $LiClO_4$(A) in a quiscent solution and 10^{-4} M KNO_3 (B) in a stirred solution which is agitated at a rate of 1500 r.p.m. Aqueous phase: 10 mM M_gSO_4 and organic phase: 10 mM CVTPB in the PVC-nb gel.

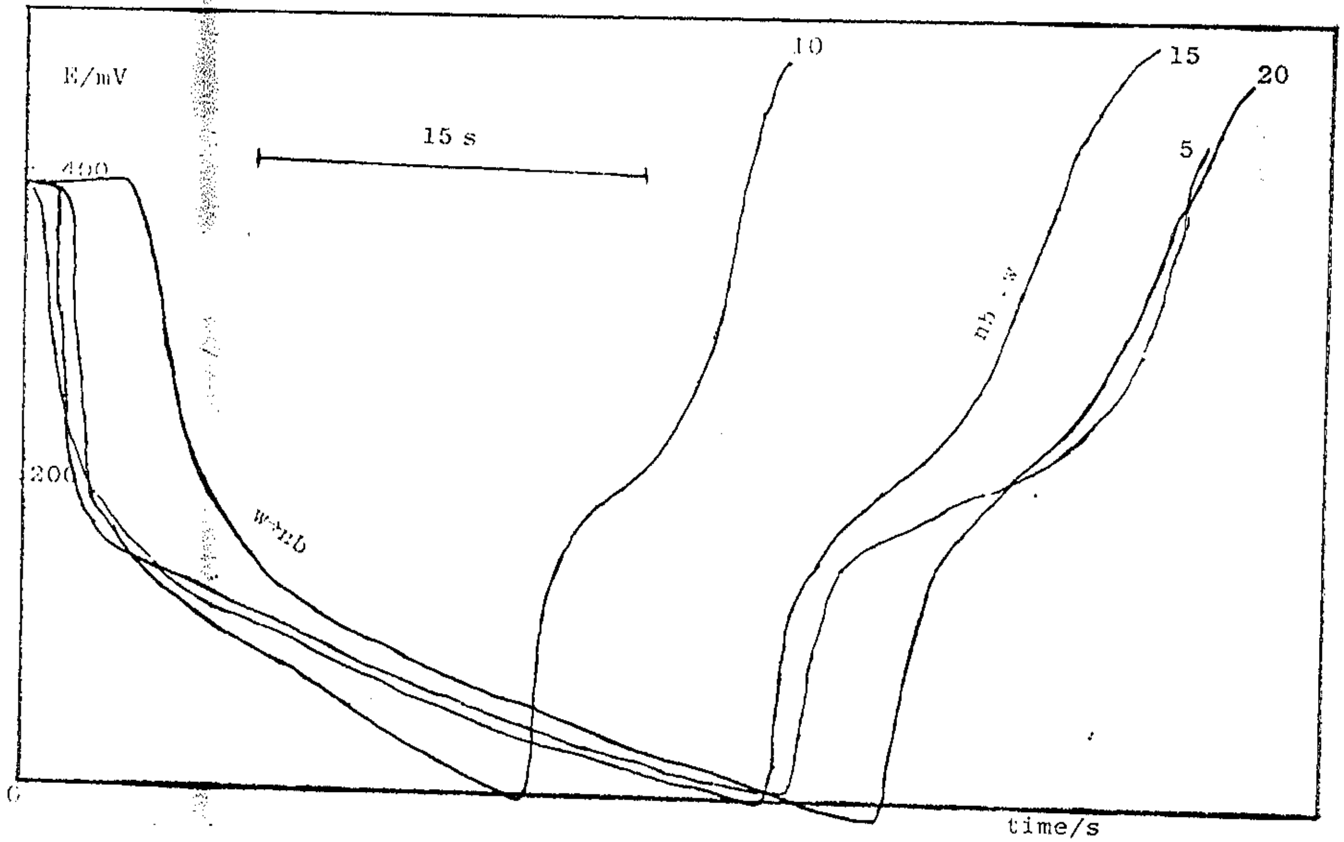

Fig. 9: **Potential-time curves of current reversal stripping of $5x10^{-5}$ M KSCN, The numbers indicated on the curves are current densities in μA, Aqueous phase: 10 mM M_gSO_4 and organic phase; 10 mM CVTPB in the PVC-nb gel.**

5. CONCLUSION

The ac voltammogram in Fig. 2 clearly shows the transfer of crystal violet across the PVC-nb gel/water interface. However, the whole ideal potential window at the negative side is limited by the transfer of sulfate ion from water to organic phase which appears at about 350 mV more negative than CV^+ ion transfer. The potential range at the positive direction was limited by the transfer of either TPB^- or Mg^{2+} ion across the interface. Note that the potential range was cut off by the transfer of the PNP^+ ion rather than by SO_4^{2-} ion transfer when CVTPB was replaced by PNPDCC in the PVC-nb gel.

Cyclic voltammetry has shown that there is a linear dependence of peak current on the square root of the sweep rates. From these linear dependences it was possible to calculate the diffusion coefficient of ions in both phases or the area of the interface for a given concentration. In the present work, the area of the interface calculated from the slope of the plot of peak current versus square root of sweep rate was almost identical to that obtained from the measurement of the internal diameter of the PTFE tube.

Generally, from this preliminary study of PSA across the liquid-liquid interface the technique is quite applicable provided that one can successfully prepare and construct a thin film of polymer gel electrode for this purpose. The linear dependence of transition time on deposition time indicated the applicability of PSA across the PVC-nb gel/water interface.

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