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Charge transfer processes on liquid/liquid interfaces:
The first hundred years

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ABSTRACT

Electrochemistry dealing with interfaces between two immiscible and ionically conductive solutions (ITIES) has been documented in literature already a hundred years ago. The work has only recently attracted a wider attention. The trends in experimental electrochemistry, optical studies of the interface and recently emerging theoretical work are reviewed. Currently about a 100 publications appear per year.

Systematic study of charge transport across immiscible interfaces and its implications to electrochemistry and electroanalysis as a separate discipline is relatively young. Its beginning could be placed approximately to middle 1970's. At first a research subject of only a few groups, it recently became a study project of quite a few individuals. To capture this interest, a symposium on this subject has

been organized jointly by the Physical Electrochemistry Division and the Sensor Group for the 182nd ECS meeting in Toronto. This review highlights recent developments and emphasizes non-traditional or unusual applications of liquid/liquid electrochemistry studies.

The original paper that spurred the present interest in the electrochemical behavior of an interface between two immiscible electrolyte solutions (ITIES) was that by Koryta et al.¹ from 1976. It pursued experimentally the idea that ITIES could serve as a model for a half of a simplified biological membrane. The similarity with a biological membrane surface has been noted however much earlier, in 1848 by Du Bois-Reymond,² who then suggested that the surfaces of biological systems have properties similar to those of an electrode of a galvanic cell.

Koryta's research¹ lead to the realization that description of transport across ITIES resembles in many ways description of redox processes on electrode surfaces. The parallelism of the ion transport through a liquid/liquid interface and an ion transport to an electrode surface is both advantage and disadvantage for understanding the concept of the ITIES. Experimental techniques, their principles and descriptive mathematics already known for redox studies are usually applicable to ITIES. However, although the processes on the interfaces are principally simple, they are not intuitively obvious and the ITIES studies do not enjoy a broad attention although the implications of its research are far reaching.

The work of Nernst³ and Planck⁴ from 1888–1890 mark the first important progress on transport in electrolyte solutions. The thermodynamics of the liquid/liquid interface at equilibrium leads to relationships that resemble the Nernst equation for electrodes in solutions. In a system of immiscible solutions (oil/water) in contact that contain such dissociated salts that both phases share

only a single ion i , the interfacial potential can be described by relationship:

$$\Delta\varphi_{oil}^{water} = \Delta\varphi_{oil}^{o\ water} + \frac{RT}{Fz} \ln \frac{a_i^{oil}}{a_i^{water}} \quad (1)$$

where $\Delta\varphi_{oil}^{o\ water}$ is the standard potential of transfer of ion i from water to an oil phase, a_i is the activity of the ion in the designated solvent, and z is signed charge of the ion.

The first original experiment on ITIES, polarization of water–phenol interface⁵, was performed 1902. In that experiment it was transport of iodide (in potassium iodide) that was observed. Until 1960's there were only a few papers related to but not directly addressing the topic of electrochemistry of ITIES. That has gradually changed until recent years, when the number of papers related to ITIES has reached almost hundred a year (Fig. 1). The counted publications include papers known to the author and deemed by him to be related to liquid/liquid electrochemistry. The fluctuations are caused by the fact that only several groups participate in the project and publication of new results is not a process evenly distributed in time. Not all publications with the date 1992 have yet appeared in print, which explains the decrease in number of publications for that year.

Systematic research on ITIES is limited to several groups throughout the world. The countries in which some work on liquid–liquid interfaces has been done are Argentina, China, The Czech Republic, Ethiopia, Finland, France, Germany, Holland, Italy, Japan, Poland, Portugal, Russia, Switzerland, United Kingdom and the USA. At current time Japan leads with about six groups actively involved in ITIES. The interest in ITIES in the USA is only recent and relatively small.

The topics that are relevant to the study of ITIES and most of which are included in the data of Fig. 1 are: 1. single ion partition theory; 2. double layer

structures; 3. double layer potential profiles in relation to kinetics of single-ion transfer; 4. unusual diffusion properties in mixed layers of solvent between two immiscible phases; 5. charge transfer kinetics; 6. redox electron transfer across ITIES; 7. ionophore/charge carrier/complex induced or sustained ion transport; 8. ITIES related to transport in lipid bilayers and biological structures and physiological studies; 9. ITIES related to behavior of chemical microdomains; 10. electrolyte/ion-exchanger charge transport; 11. surface phenomena of ITIES; 12. design and construction of chemical sensors; 13. ion exchange chromatography; 14. power sources with nonaqueous electrolytes; 15. phase transfer catalysis and 16. instrumentation used or usable in ITIES studies.

Introduction to the technique

The concept of the ITIES experiments can be explained on cyclic voltammetry. The interface in most experimental situations consists a horizontal boundary, that arises between two immiscible phases of different densities such as water and nitrobenzene.

The diagram of the voltammetric cell is shown in Fig. 2. The cell is connected with two reference (RE_1 and RE_2) electrodes and two counter platinum electrodes (CE_1 and CE_2) to a special four-electrode potentiostat with differential reference electrode input. The potentiostat maintains desired potential between the tips of the reference electrodes, placed in the vicinity of the interface. It is possible to polarize the interface with a voltage program appropriate for voltammetry.

A voltammogram obtained for typical supporting electrolytes⁶ is shown in Fig. 3, curve A. The usual supporting electrolytes are LiCl solution in the aqueous

phase and tetrabutylammonium tetraphenylborate (TBATPB) in the nitrobenzene phase. Because LiCl is a hydrophilic salt Li^+ and Cl^- ions will remain confined mostly in the aqueous phase. Similarly, TBATPB dissociates in nitrobenzene, but its respective ions TBA^+ and TPB^- remain almost exclusively in the nitrobenzene phase. Thus, an interface between two ionically conductive but immiscible phases is formed. Such an interface, as long as it does not pass charge carriers, can be polarized to a desired potential value and behaves as an ideally polarizable interface. The sign convention on ITIES is such that the aqueous phase is most positive at the right extreme of the voltammogram. The currents limiting the supporting electrolyte working range are due to the supporting electrolyte ions transport into phases in which they are normally absent. The current of the right extreme is caused by crossing of tetraphenylborate from nitrobenzene to water, and Li^+ in the opposite direction. The left limit is caused by Cl^- flow from water into nitrobenzene and tetrabutylammonium flow in the reverse direction. In the middle of the potential window only a charging current is observed. The range of potentials in which no transport of supporting electrolytes takes place is suitable for studies of semihydrophobic ions.

Curve *B* in Fig. 3 results from addition of 0.47 mmol/l of tetramethylammonium (TMeA^+) in the aqueous phase. If the aqueous phase is made more positive by scanning to the right, a transport of the TMeA^+ cation into nitrobenzene will occur. Upon reversing the scan at the right extreme, the transport of TMeA^+ from nitrobenzene back to water is observed.

The transport across the interface is by all indications diffusion controlled and therefore the voltammetric curves and equations describing them are similar to those for transport of oxidizable species to an electrode and transport of the oxidized product away from the electrode. Therefore, the voltammograms for both

processes have similar features, e.g., a separation of the positive and negative peak potentials by $58/n$ mV for a reversible process.

The voltammetric curves can be used for analytical as well as mechanistic studies. The position of the peaks is a function of the Gibbs energy of transfer (or the standard potential of transfer ($\Delta\phi^{\circ}_{\text{oil}}^{\text{water}}$) of the particular ion and it can be used for qualitative analysis. Quantity can be determined from the height of the peaks. The current measured at the peak of the curve (i_p) is given by

$$i_p = 269 c^{\circ} n^{3/2} A D^{1/2} v^{1/2} \quad (2)$$

The current will be in amperes if the scan rate v is expressed in V/s, the interface area A in cm^2 , the diffusion coefficient D in cm^2s^{-1} and the bulk analyte concentration c° mol/l. The n is charge of the transported ion.

New developments

Early works on ITIES have drawn from the experience of polarography and have lead to the construction of an electrolyte dropping electrode with voltage scan. Current scan is now more popular.^{7,8} Further studies utilize cyclic voltammetry and chronopotentiometry. Many new techniques of electrode electrochemistry have been adopted for ITIES studies, with such examples as impedance spectroscopy, electrocapillary techniques and most recently, in parallel with ultramicroelectrodes, the utilization of a microinterface between two immiscible liquids.

The purpose of using a small orifice separating two immiscible electrolytes is the same as is the purpose of ultramicroelectrodes; to lower or eliminate the effect of IR drop in the solutions. This is made possible because the diffusion towards the interface is hemispherical rather than semilinear. Small interfaces have

been used by Girault and coworkers⁹⁻¹² and by Senda.¹³ One complication that makes the experiment challenging is restricting the area of the interface. Some of the work was done on a small blunt capillary tip. To take full advantage of the hemispherical diffusion in both solutions, the microinterface has to be made in a thin flat separator. Girault used on one occasion a plastic film with specially etched hole, others used a hole in a thin glass wall.¹⁴ An alternative that makes the interface more rigid is to solidify one phase by a gel, such as PVC in the case of nonaqueous nitrobenzene solution.¹⁵

Three schools of thought regarding the structure of the interfacial double layer are represented by H. H. Girault, T. Kakiuchi and Th. Wandlowski.¹⁶ The main differences and concerns, that still need to be resolved, are the appearance of the boundary, in particular whether the boundary can be perceived as a sharp border or whether it is smeared out, over several molecular lengths.

The ITIES has also caught attention of some theorists and workers in fields allied to electrochemistry using some combined techniques. Light is used to detect movement of the interface,¹⁷ concentration gradient changes,¹⁸ fluorescence quenching upon dye transport from one phase to another¹⁹ and it is also directly used to investigate photoelectric effects on ITIES.²⁰⁻²⁴ Higgins and Corn²⁵ used their method of second harmonic generation on surfaces to learn about molecules adsorbed at a polarized interface between water and 1,2-dichloroethane.

Information about interfacial structure of ITIES is also important in theoretical work in ITIES. Marcus²⁶ derived relationship for electron transfer across ITIES. He used the experimental data of Geblewicz and Schiffrin²⁷ to derive relationships describing electron transport on ITIES. This work fills a gap between theoretical prediction and an experiment. To decide between two models

proposed by Marcus, more experimental data on electron transfer across ITIES, which are so far quite rare, are needed.

Recent years attracted theorists to apply their skills to ITIES. Molecular dynamics calculations on ITIES were done as well as was performed modeling of surfactant absorption on liquid/liquid interfaces. Benjamin^{28,29} used computer methods to model ion transfer across the liquid/liquid interface. Smit^{30,31} used computer simulation to model a water/oil interface in presence of micelles. In the past year a work from several new groups has appeared, for example in Finland,³² at Chiba University, Japan,³³ and Hebei University, China.³⁴

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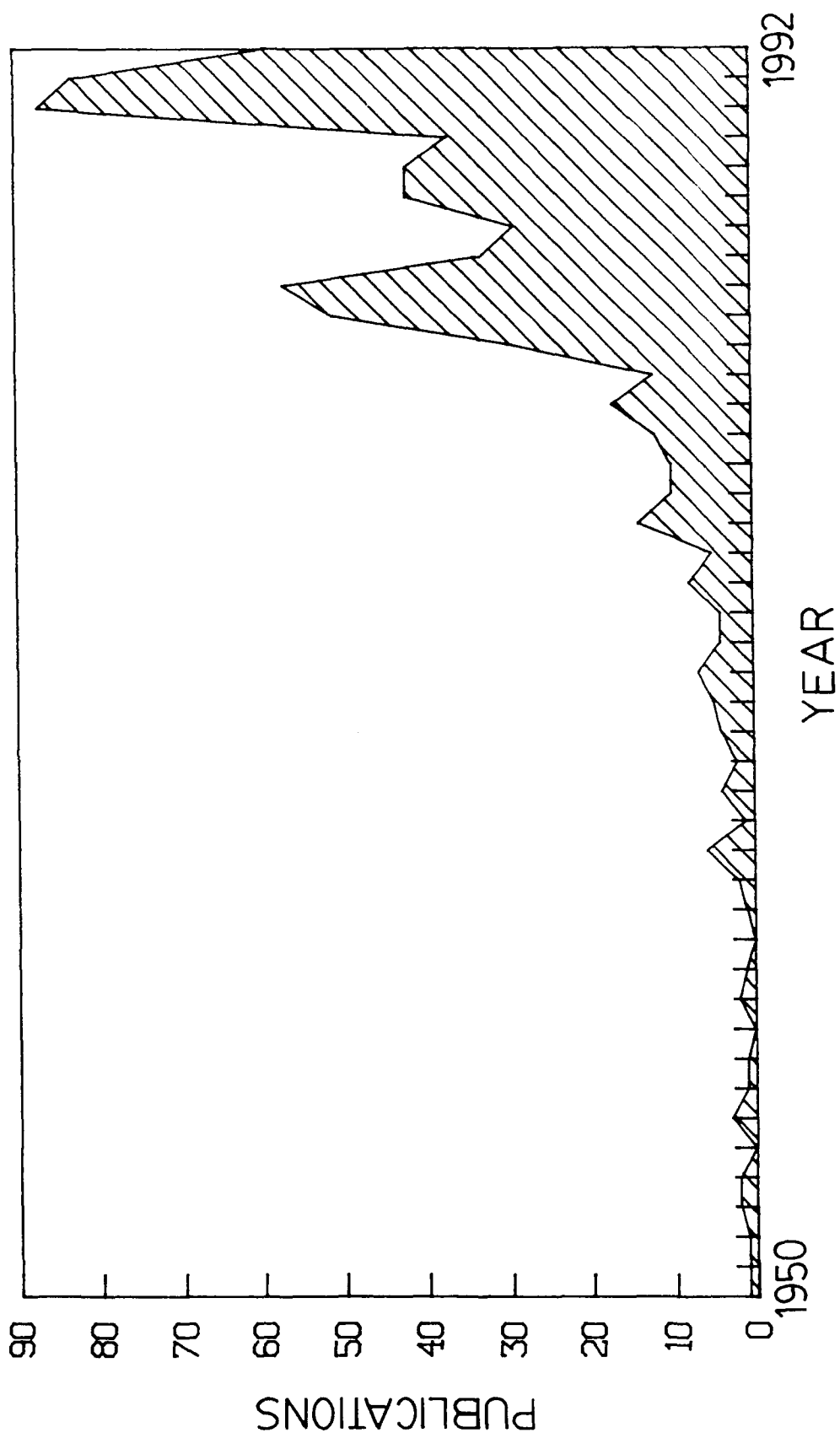
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List of figures:

- Fig. 1 Number of publications written on the ITIES subject that appeared each year during period 1950 – 1992.
- Fig. 2 A diagram of the experimental arrangement for voltammetry on ITIES, between water and nitrobenzene. Reference electrodes RE_1 and RE_2 sense the potential on the interface, CE_1 and CE_2 supply via a 4-electrode potentiostat the current required to maintain the program potential between the reference electrodes.
- Fig. 3 Voltammetry on ITIES.⁶ *A* – Supporting electrolyte voltammogram, aqueous phase 0.1 mol/l LiCl, nitrobenzene phase 0.1 mol/l tetrabutylammonium tetraphenylborate. Scan rate 20 mV/s. *B* – transfer of tetramethylammonium ($c = 4.7 \times 10^{-4}$ mol/l) added to the aqueous phase. The $TMeA^+$ transport responsible for the rise of the peaks is indicated.

Fig. 1



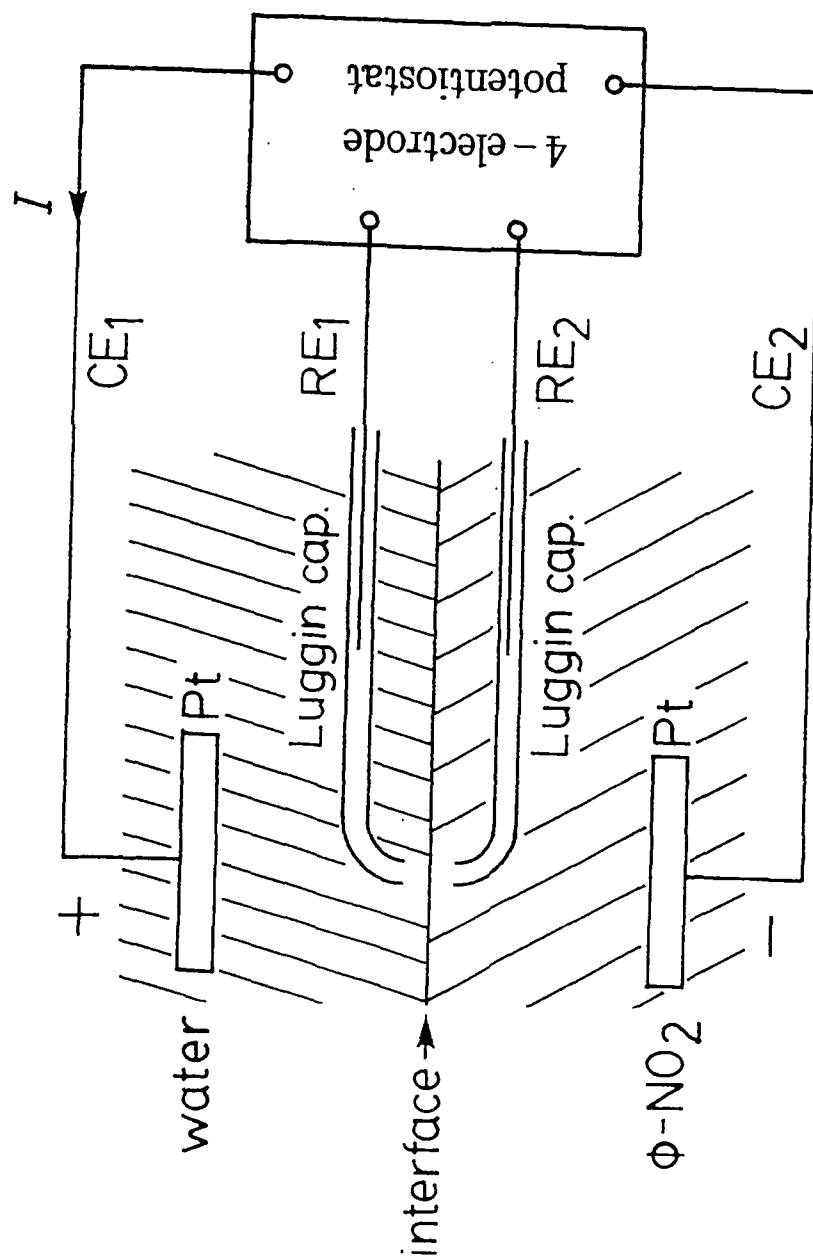


Fig. 2

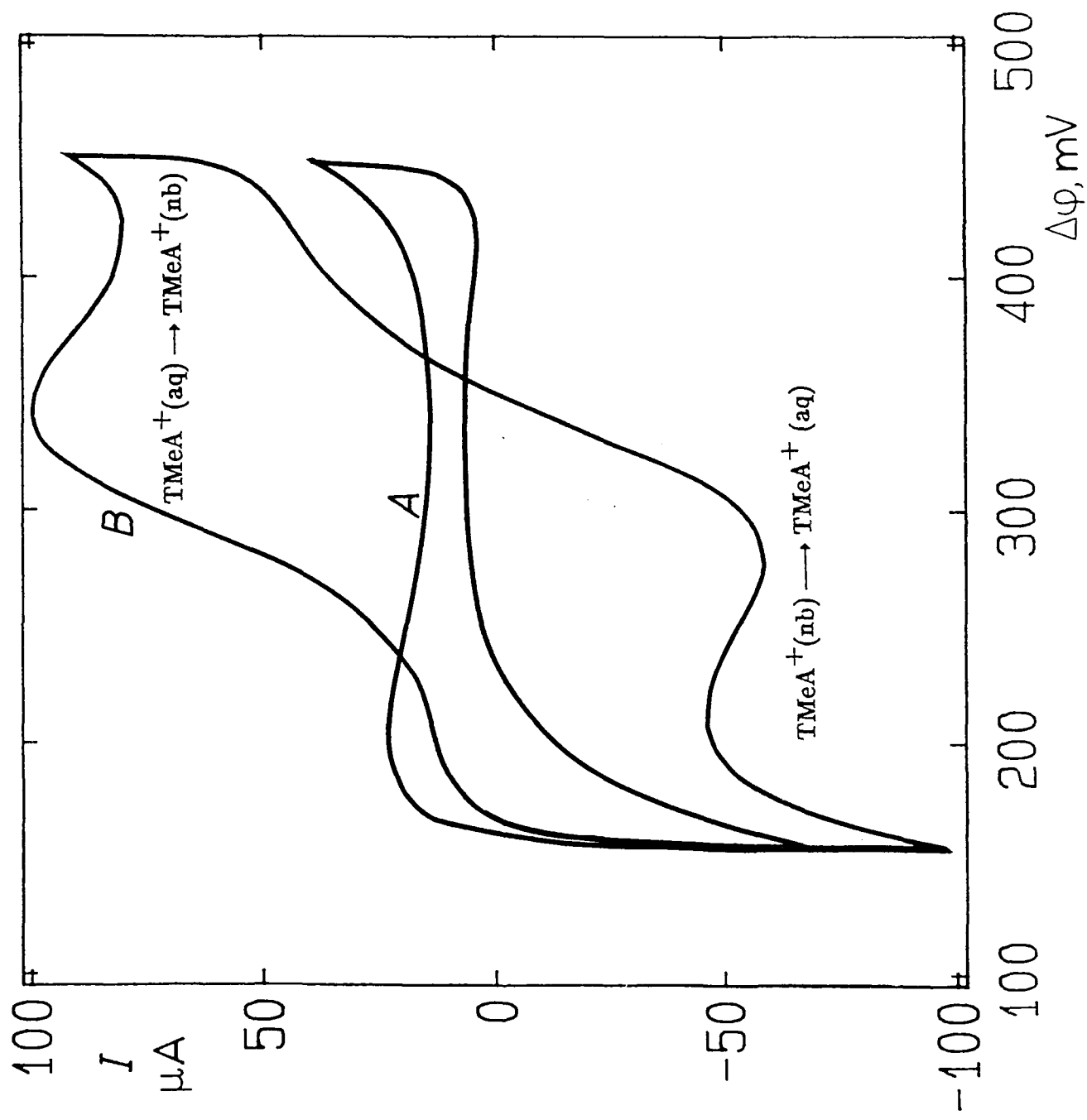


Fig 3

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