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Analytical applications of electrified interfaces between two immiscible solutions

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Analytical applications of electrified interfaces between two immiscible solutions

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Abstract

Interfaces between two immiscible electrolyte solutions have some properties that can be investigated and utilized by methods of electrochemistry. This review compares electrochemistry on such interfaces with electrochemistry of metal electrodes immersed in solutions. It builds on knowledge of methods of electroanalysis and shows how it can be applied to the interfaces of immiscible liquids. A simple differential adapter that can convert any potentiostat to the 4–electrode potentiostat needed for the work is described. Experimental techniques involving potentiometry, polarography with dropping electrode, voltammetry and microinterfaces are outlined.

The interfaces between two immiscible electrolyte solutions (sometimes abbreviated ITIES) should be of interest to any practitioner in analytical chemistry. They can be used for understanding and development of practical electroanalytical processes and devices. The interfaces can be described in simple terms quite similar to many equations describing processes already well understood for metal electrodes.

Consider a system with an ITIES containing a salt AB in water and a salt CB in the oil phase. Assume further that the cations A^+ and C^+ are confined to their original phases, whereas anion B^- can partition between the two phases. The electrochemical potentials of ion B^- in either phase must be at equilibrium equal. This leads to a relationship that relates the ratio of the ion activities in the two phases to the interfacial potential, $\Delta^{\alpha}_{\beta}\varphi$ $(=\varphi(\alpha)-\varphi(\beta))$:

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^{\circ}_{B^-} + \frac{RT}{zF}\ln\frac{a^{\beta}_{B^-}}{a^{\alpha}_{B^-}} \qquad (1)$$

where $\Delta^{\alpha}_{\beta}\varphi^{\circ}_{B^-}$ is the standard potential of transfer of ion B^- from phase α to β, a_{B^-} is the activity of ion B^- in the designated solvent and z is the signed charge of the ion (−1 for B^-). Values of $\Delta^{\alpha}_{\beta}\varphi^{\circ}_{B^-}$ for individual ions can be determined from extraction data and some are listed in Table 1.

Because ITIES behave similarly to electrode/solution interfaces, many techniques of electrochemistry have been adopted to ITIES studies, e.g., polarography with an electrolyte dropping electrode[1], cyclic voltammetry, chronopotentiometry, polarography with current scan, impedance spectroscopy, electrocapillary techniques and utilization of a microinterfaces. Several in–depth reviews are available in the literature[2–7].

Voltammetry

The ITIES in most experimental situations consists of a free–standing horizontal boundary, which arises between two immiscible phases of different densities such as water and nitrobenzene. Figure 1 shows a schematic diagram of the voltammetric cell with two reference electrodes (RE_1 and RE_2) and two platinum counter electrodes (CE_1 and CE_2), connected to a four–electrode potentiostat. The reference electrodes sense the potential difference between the tips of the reference Luggin capillaries and the potentiostat adjusts the potential between the two Pt counter electrodes such that the potential difference between the tips of the reference electrodes is equal to an applied potential.

The solvents that can be used to setup these interfaces must be immiscible, but chemically compatible, their densities should differ so that a free–standing interface can be established, and they need to have high relative permittivity (ϵ) so that supporting electrolytes and analytes dissolved in these solvents dissociate. The most common solvents are water ($\epsilon = 78.58$), nitrobenzene ($\epsilon = 34.82$), nitroethane ($\epsilon = 30.3$), 1,2–dichloroethane ($\epsilon = 10.36$, all at 25 ^{0}C) and several other organic solvents. Typical supporting electrolytes are hydrophilic 0.1 mol/l LiCl in the aqueous phase and lipophilic tetrabutylammonium tetraphenylborate (TBATPB) of similar concentration in the nitrobenzene phase. An interface between two immiscible ionically conductive phases which can be polarized to a desired potential is established. A voltammogram obtained for typical supporting electrolytes[8] is shown in Figure 2.

The sign convention on ITIES is $U_{RE_1} - U_{RE_2}$ (Fig. 1) (RE_1 is always in the aqueous phase). Thus, the aqueous phase is most positive at the right hand side of the voltammogram in Fig. 2.

Consider first a scan from the middle of the potential window (about + 250 mV) to the right in Fig. 2. When the aqueous phase becomes sufficiently positive with respect to the nonaqueous phase, anions in nitrobenzene (TPB^-) will cross the interface to the water phase. Li^+ ions could also cross from water to nitrobenzene phase, but this process requires a potential 20 mV higher than that for TPB^- transport (c.f., Table 1). With increasing potential, TPB^- transport will become more pronounced, and will appear as an increasing electric current at the right.

Upon reversal of the scan, TPB^- will return to its original phases, causing a negative current peak near the extreme right. The height of the peak depends on the switching potential, which determines the amount of ions that have to be transported back to their original phase. Normally, it is not desirable to scan past the onset of the supporting electrolyte transport.

As the aqueous phase becomes even less positive, organic phase cations (TBA^+) will flow in the aqueous phase and negative current will be observed. Crossing of Cl^- from water to nitrobenzene would require 52 mV more negative potential that the TBA^+ transfer. Upon sweep reversal, positive current will be observed due to the return of TBA^+ to nitrobenzene.

Transport of ions that are less soluble in nitrobenzene than is TBATPB, but are also less soluble in water than is LiCl, can be observed and used for electroanalytical purposes. The range within which this transport can be studied is, with currently used supporting electrolytes, only about 500 mV wide.

Figure 3 shows a voltammogram of the system in Fig. 2 with the addition of about 0.5 mmol/l of a semihydrophobic tetramethylammonium ($TMeA^+$) to the water phase. If the potential of the aqueous phase is increased by scanning to the right, transport of $TMeA^+$ into nitrobenzene will occur. However, as the aqueous phase becomes even more positive, $TMeA^+$ will be depleted in the vicinity of the interface resulting in gradual decrease of the current magnitude. Therefore a typical diffusion controlled peak will be observed. Upon reversing the scan, transport of $TMeA^+$ from nitrobenzene back to water, characterized by a negative diffusion controlled peak, will be observed.

The equations describing ion transport across the interface 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 kinetically reversible (rapid, relative to the scan rate used) process.

Potentiostat

A four–electrode potentiostat, i.e., a potentiostat with a *differential voltage* input, is required in order to compensate for the resistance of both phases. A commercial instrument that suits these needs is the Solartron 1286 Electrochemical Interface. Because this instrument is costly and its purchase may not be justified if only preliminary or occasional experiments are planned, adequate circuit may be constructed in the laboratory.[9–14] The most practical alternative is to build a differential input adapter and use it together with a commercial 3–electrode potentiostat.

A simple construction designed in our laboratory that requires only three active components, a bipolar ± 15 V power source and some hardware, is shown in Fig. 4. Two ultra–low offset voltage operational amplifiers, OP–07 (Precision Monolithics, Inc.), are used as voltage followers to increase the input impedance of the differential inputs. The outputs, also used to drive the shields of the input

BNC connectors, are connected to an AMP–03 precision unity gain differential amplifier (Precision Monolithics). Because of the choice of active components, no adjustments or other components are required. The circuit in Fig. 4 is connected to the electrochemical cell and a commercial potentiostat as shown.

EG&G 273 is also a suitable potentiostat that can be used for work with ITIES with only a minor modification. The differential electrometer of this instrument has one end connected to the ground by a jumper wire. By disconnecting this jumper and removing a resistor inside the electrometer box the instrument becomes a suitable 4–electrode potentiostat.

Reference electrodes

The differential potentiostat input requires two reference electrodes to sense the potential on the interface. The reference electrodes are placed in salt bridges inside Luggin–Haber capillaries, positioned in proximity of the interface. The most convenient electrode for the aqueous phase is a chloridized silver wire immersed in a lithium chloride supporting electrolyte. The potential of the nonaqueous phase with tetrabutylammonium tetraphenylborate supporting electrolyte is sensed by a capillary bridge which is in contact with aqueous solution of tetrabutylammonium chloride outside the cell. The water–nitrobenzene interface sharing the tetrabutylammonium cation of a fixed concentration between both phases has a constant potential. The constant concentration of TBA chloride in turn defines a constant potential of a Ag/AgCl electrode, which completes the circuit leading from the nonaqueous phase sensing Luggin capillary to the potentiostat input.

Analytical applications

Potentiometry

Potentiometric measurements on ITIES are related to the principle of ion selective electrodes (ISE). The contribution of ITIES to the study of ISEs is in its ability to isolate and study a single interface at a time. The interfacial potential produced by a single shared ion is described by equation (1). If more ions can take part in the equilibrium, the equation becomes considerably more complex:[15]

$$\sum_{i=1}^{j} z_i c_i^0 \Big/ \left\{1 + \frac{\gamma_i^\alpha}{\gamma_i^\beta} \exp\left[\frac{z_i F}{RT}\left(\Delta_\beta^\alpha \varphi - \Delta_\beta^\alpha \varphi_i^0\right)\right]\right\} = 0 \qquad (2)$$

This expression includes all ions, i (from 1 to j), involved in the equilibrium, with c_i^0 being the ion total concentration in both phases, z_i is the signed charge of the ion, γ is the ion activity coefficient in phase α or β, and $\Delta_\beta^\alpha \varphi_i^0$ is the standard potential of transfer of the ion involved. $\Delta_\beta^\alpha \varphi$, the interfacial potential, cannot be in general case separated in a closed form. Relationship (2) can still be simplified to expression (1) if only one ion dominates the equilibrium. If this ion is the analyte, the interface can be used for potentiometric determination.

Inorganic cations that can be determined directly by potentiometry are K^+, Rb^+ and Cs^+. It is possible to determine more ions indirectly if they can be made more hydrophobic by complexation with a suitable ligand. For example Pb^{2+} can be determined after complexation with polyethylene glycol.[16] Among inorganic anions that can be determined are SCN^-, ClO_4^-, BF_4^-, I^- and NO_3^-. A large number of organic cations and anions, which are more hydrophobic, can be determined. Examples are quaternary ammonium salts,[17] choline,[18] acetylcholine,[18] picrate[17] and laurylsulfate.[19] Many organic dyes that exist as cations can also be detected.[4,20] The response of a picrate ion sensitive interface[21] is shown in Fig. 5.

Cyclic voltammetry

Figure 3 is an example of the analytical applications of cyclic voltammetry. The position of the peaks is a function of the Gibbs energy of transfer (or the standard potential $\Delta_{\beta}^{\alpha}\varphi_{i}^{o}$) of the particular ion and it can be used for qualitative analysis. The quantity can be determined from the height of the peaks. The current measured at the peak (i_p) is given by

$$i_p = 269\ c^o\ n^{3/2}\ A\ D^{1/2}\ v^{1/2}. \tag{3}$$

The scan rate, v, is expressed in V/s, A is the interface area in cm^2, D is the diffusion coefficient in $cm^2 s^{-1}$, n is the charge of the ion and c^o is the analyte concentration in the bulk solution in mol/l.

Dropping electrolyte electrode

This technique is similar to polarography. The interface is formed at the surface of an electrolyte drop expelled into the second immiscible electrolyte. Voltage scan[1] or now more popular current scan[22,23] is used to polarize the interface. Figure 6 shows a current scan polarogram on the water–dichloroethane interface. Curve (*A*) is for the supporting electrolyte, while curve (*B*) is obtained in the presence of an analyte. The wave position is useful in quantitative analysis, whereas its height is a function of the concentration.

Microinterfaces between two immiscible electrolytes

The purpose of using a small orifice separating two immiscible electrolytes is the same as it the purpose of ultramicroelectrodes, i.e , to lower or eliminate the effect of *IR* drop in the solutions. Small interfaces have been used by Girault and coworkers[24–27] and by Senda et al.[28] The experiment is challenging in finding methods to restrict the area of the interface. One possibility is to work with a small blunt capillary tip. The inside of the capillary however increases the system resistance. To take full advantage of the hemispherical diffusion lowering the IR 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, while we have used a hole in a thin glass wall.[29]

Changes in interfacial tension that arise from polarization of the interface, uneven hydrostatic pressure, thermal expansion and vibrations in the laboratory cause movement of the interface that complicates the properties of the device. An alternative is to use one phase that is solidified by a gel, such as PVC, in the case of nonaqueous nitrobenzene solution.[30] This gel solidified microinterface was used successfully as an amperometric sensor. Figure 7 shows a voltammogram of picrate in water. The arrow indicates the potential at which the current, caused primarily by picrate transport, was used to construct a calibration curve. Since the diffusion towards a microinterface is hemispherical, the steady state current has a finite value and stirring of the solution is not required.

Future trends

In addition to analytical applications reviewed in this paper, the ITIES has recently attracted workers in fields allied to electroanalytical chemistry. Benjamin[31] used computer methods to model the structure of the liquid/liquid interface. Marcus[32] used experimental data of Geblewicz and Schiffrin[33] to derive relationships describing electron transport on ITIES. Higgins and Corn[34] used a method of second harmonic generation on surfaces to probe the structure of the polarized interface between water and 1,2–dichloroethane. They also observed electron transfer on such interface.[35]

ITIES electrochemistry became an established subdiscipline, which is steadily finding new applications. Applied electroanalytical interest is now complemented by efforts of researchers who are applying various methods to probe the structure of the interface.

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List of figures:

Fig. 1. Schematic diagram of the experimental cell and the 4–electrode apparatus used in voltammetric studies of ITIES. Reference electrodes RE_1 and RE_2 sense the potential across the interface. CE_1 and CE_2 supply via a potentiostat a current needed to maintain the program potential. Transport of tetraphenylborate of the supporting electrolyte from nitrobenzene to water results from an applied positive potential to the aqueous phase. (c.f., Fig. 2).

Fig. 2. Supporting electrolyte voltammogram[8]. Aqueous phase is 0.1 mol/l LiCl, nitrobenzene phase is 0.1 mol/l tetrabutylammonium tetraphenylborate. Scan rate 20 mV/s. The processes responsible for individual current features are indicated close to the feature.

Fig. 3. Transfer of tetramethylammonium between water and nitrobenzene[8]. $c(TMeA^+) = 4.7 \times 10^{-4}$ mol/l, supporting electrolyte the same as in Fig. 2. Scan rate 20 mV/s. Processes responsible for the rise of the peaks are indicated.

Fig. 4. Differential adapter for a 4–electrode potentiostat. The device outlined by the dashed rectangle can be used to convert many 3–electrode commercial potentiostats into a 4–electrode potentiostat. The outputs of OP–07 are also used to drive the shields of their inputs. The shown resistors are built in the AMP–03 package. The device is powered from a ± 15 V source.

Fig. 5. Picrate potentiometry[21] with gel solidified microinterface. 15 % PVC/nitrobenzene gel contains 0.02 mol/l tetrabutylammonium tetraphenylborate and 1 mmol/l (curves *A*) or 10 mmol/l (curves *B*) tetrabutylammonium picrate. Arrows show the hysteresis of the experiments.

Fig. 6. Current scan voltammogram on an ascending electrolyte drop. (*A*) Aqueous supporting electrolyte 1 mol/l Na_2SO_4, dichloroethane phase 0.01 tetrahexylammonium tetraphenylborate. (*B*) addition of 0.3 mmol/l 1–phenyl–3–methyl–4–trifluoroacetyl–5–pyrazolone anion in the aqueous phase. (Adapted with permission from reference 22. © 1987 American Chemical Society.)

Fig. 7. Amperometric detection of picrate ion in aqueous phase with 15% PVC–nitrobenzene gel microinterface. (*A*) Cyclic voltammogram of the sensor with 0.2 mmol/l tetrabutylammonium picrate in gel, 0.4 mmol/l picric acid in water. Scan rate 20 mV/s. The arrow indicates the potential used in amperometry. (*B*) Calibration curve of the microinterface for amperometric determination of picrate. (Adapted with permission from reference 30. © 1990 Academic Press)

Table I

Standard potentials of transfer $\Delta_\beta^\alpha\varphi^\circ$ for selected individual ions[2] from water (phase α) to nitrobenzene (β).

	$\Delta_\beta^\alpha\varphi^\circ$ [mV]
Li^+	395
Mg^{2+}	361
Na^+	354
K^+	242
Rb^+	201
Cs^+	159
choline	117
acetylcholine	49
$TMeA^+$	35
TBA^+	– 248
TPB^-	372
picrate	47
dodecylsulfate	– 43
ClO_4^-	– 83
Cl^-	– 324

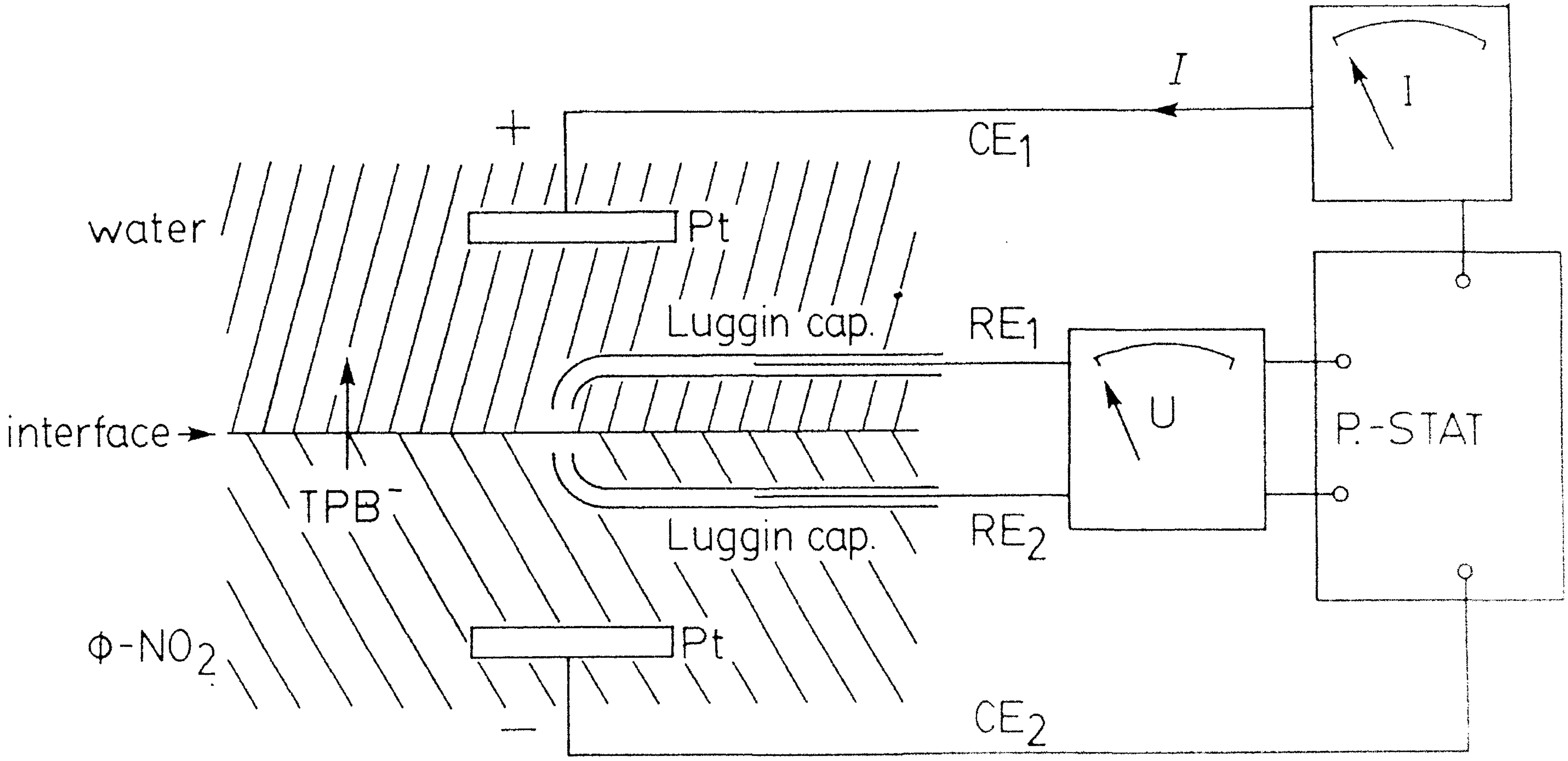
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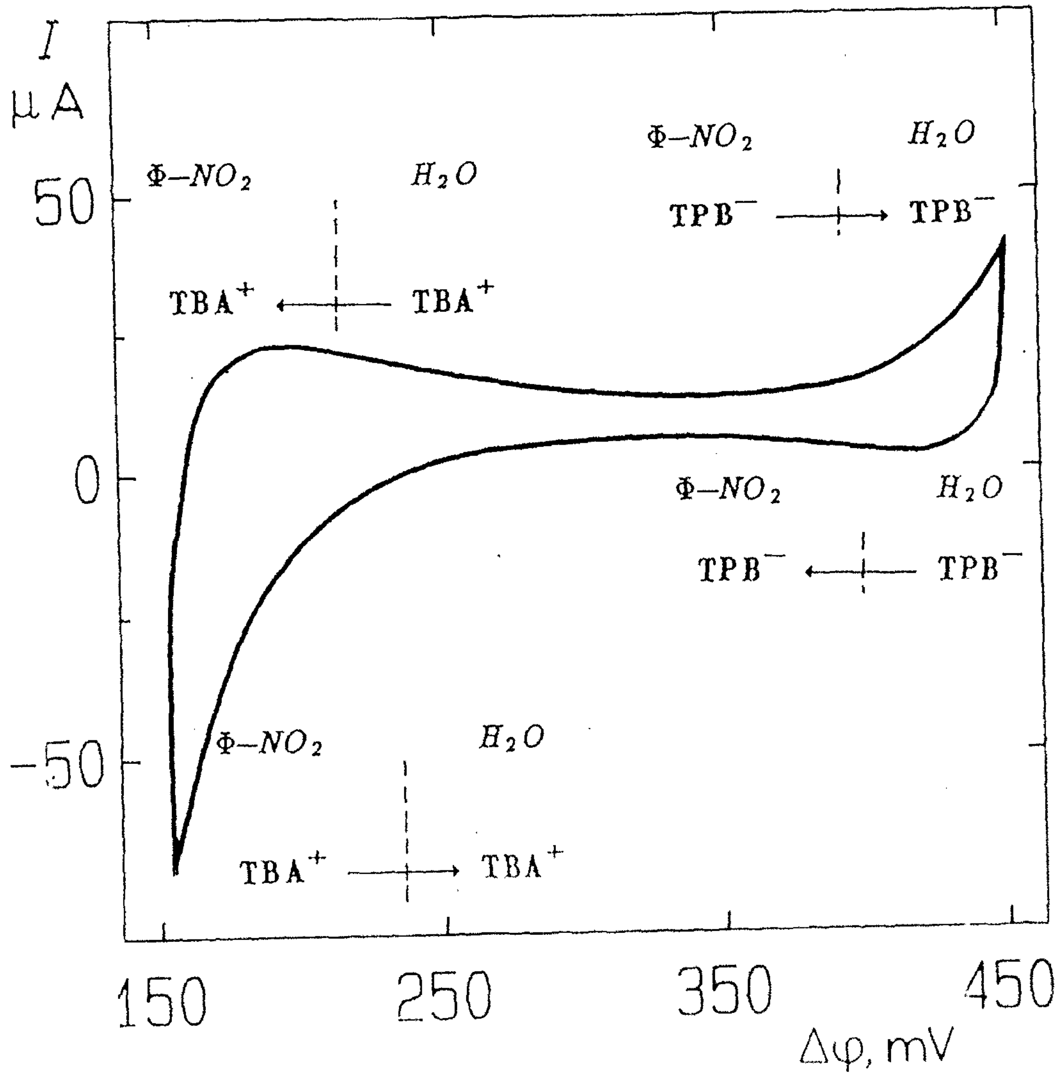
Figure 1



I
µA
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250
350
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Δφ, mV
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H_2O
TBA^+ ← TBA^+
$\Phi-NO_2$
H_2O
TPB^- → TPB^-
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H_2O
TPB^- ← TPB^-
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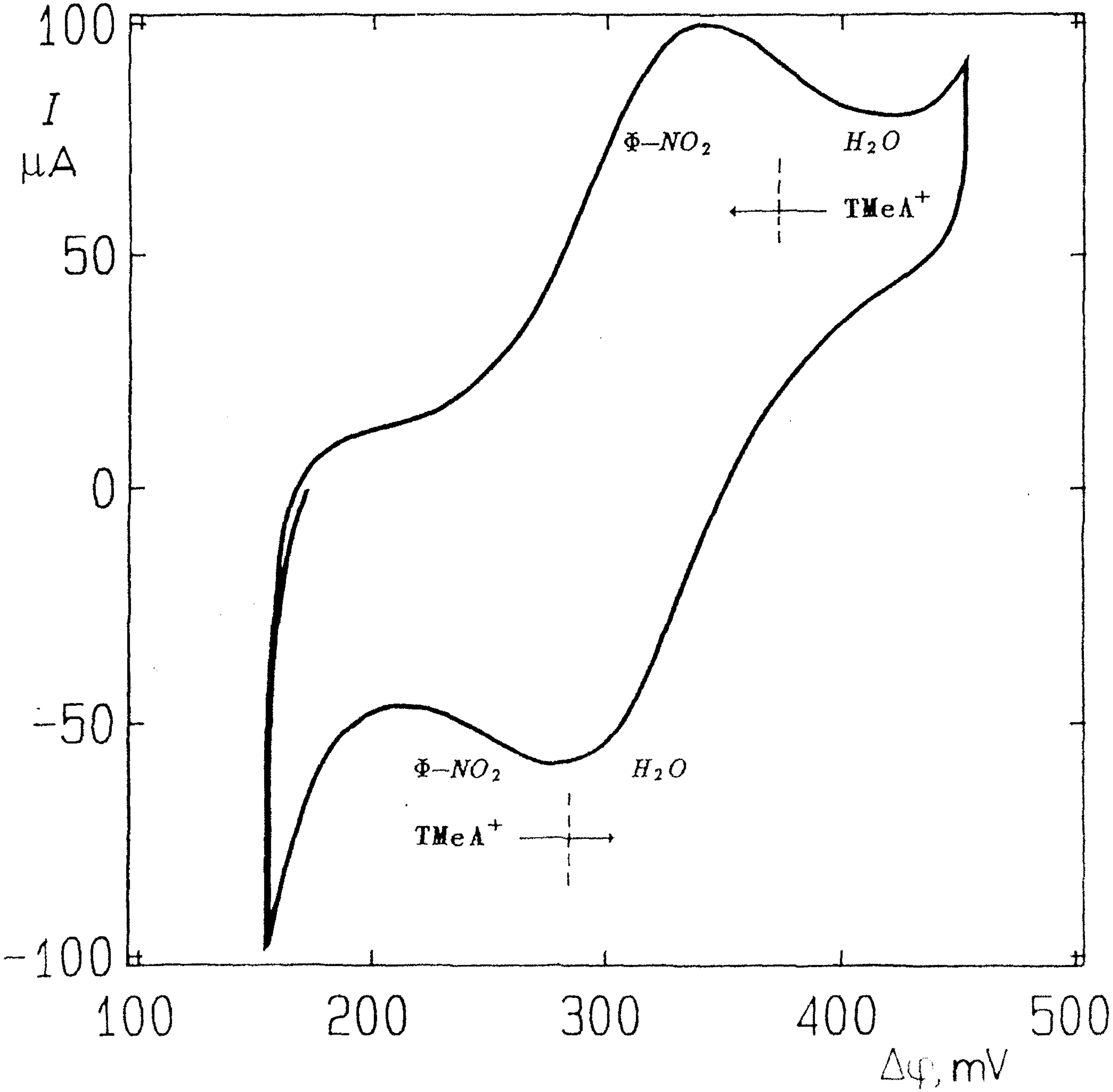
H_2O
TBA^+ → TBA^+

Figure 2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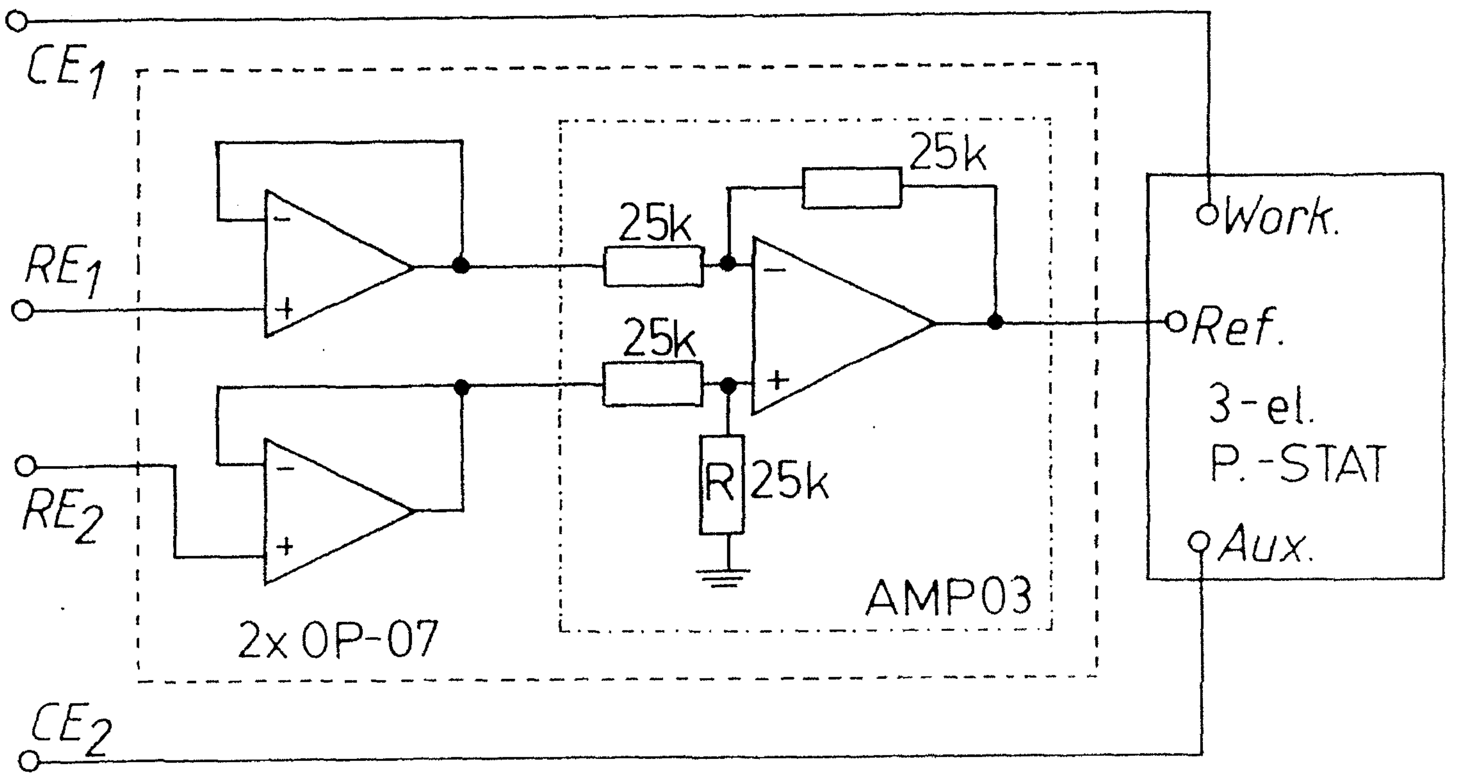
TMeA⁺

Figure 3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Ref.
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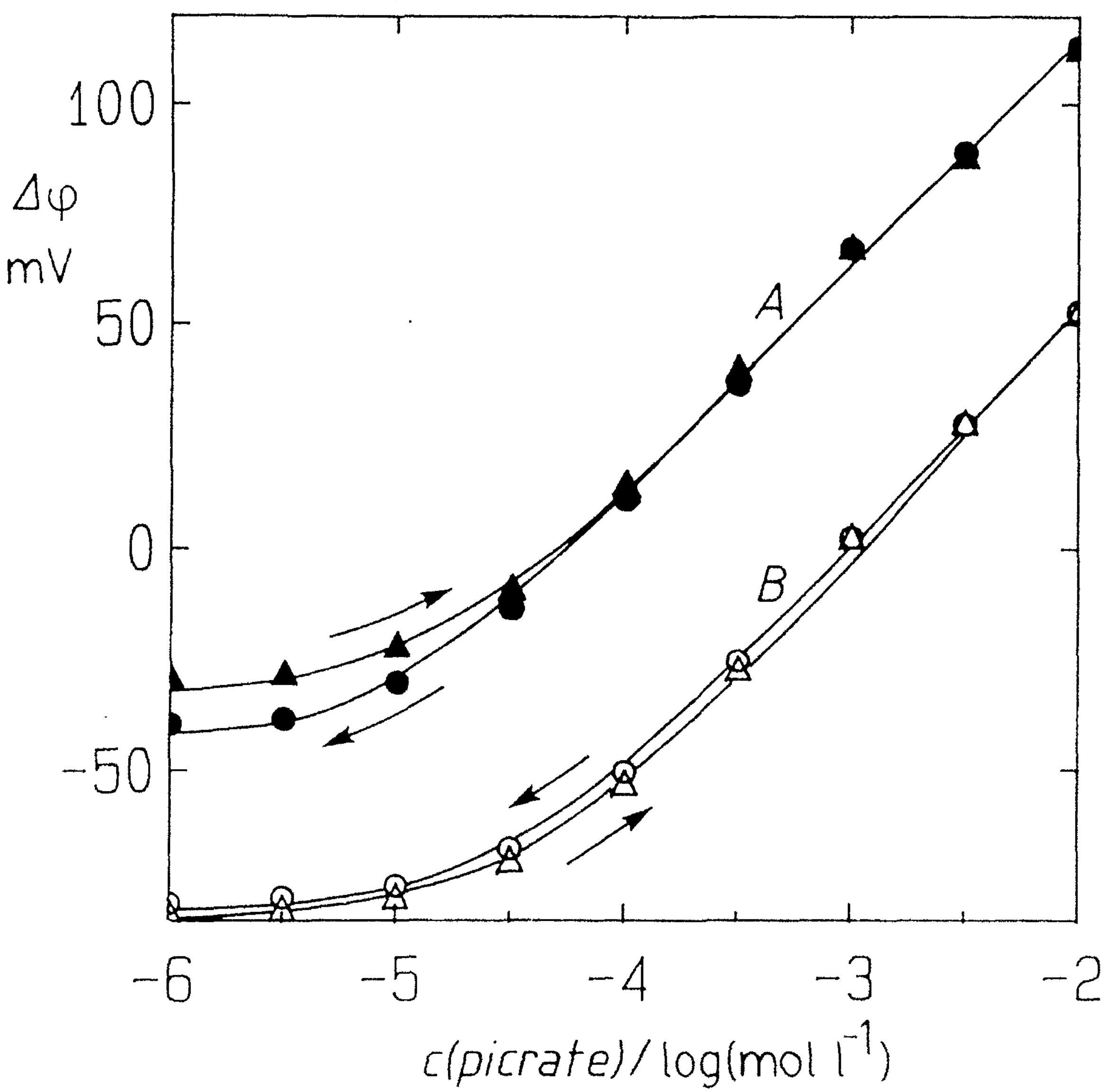
Figure 4



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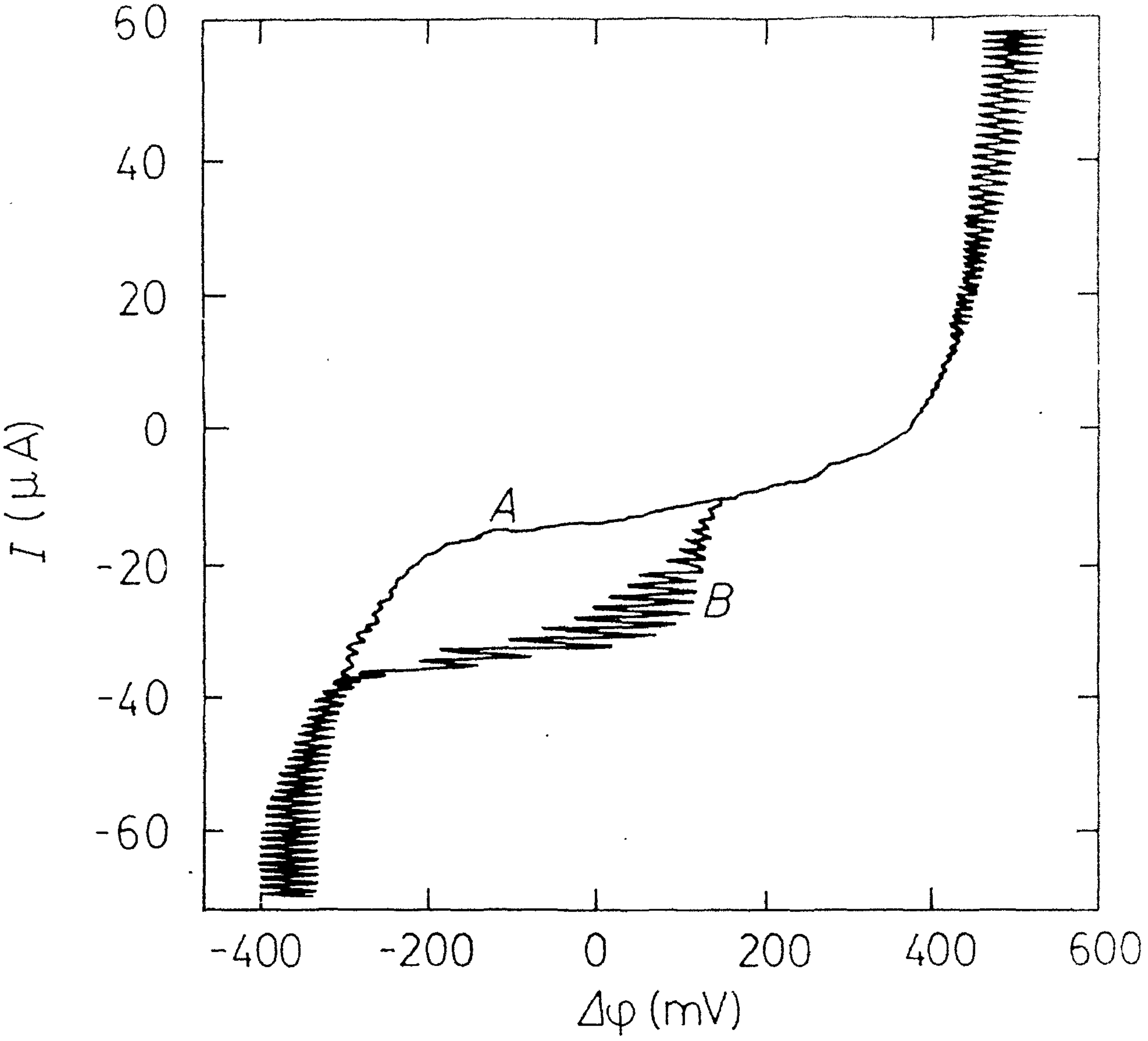

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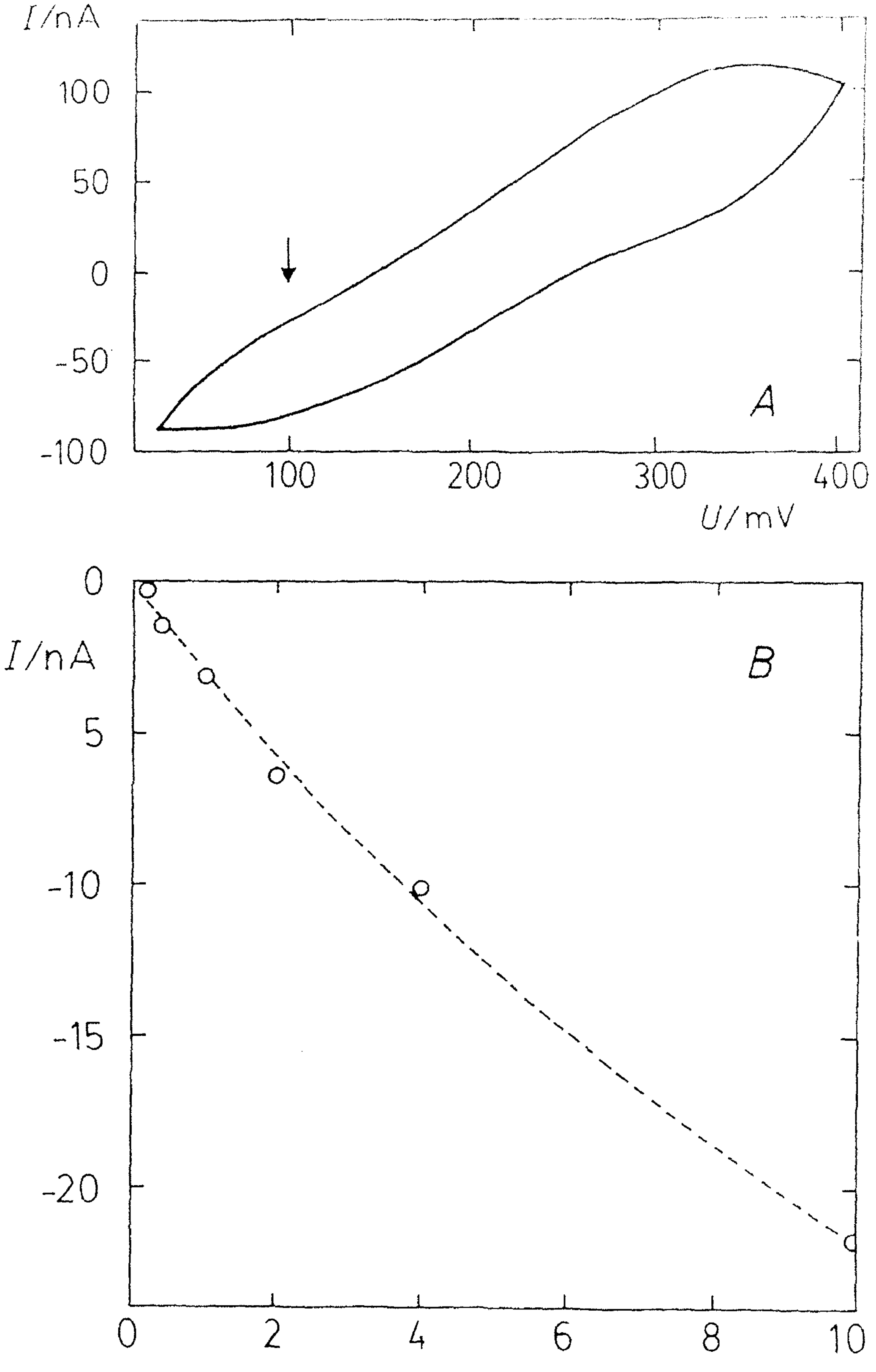
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10
c(Pi)/mmol l^{-1}
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Figure 7

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