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Electrified microscopic and conventional interfaces between two immiscible electrolyte solutions

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Electrified microscopic and conventional interfaces between two immiscible electrolyte solutions

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ABSTRACT

Transport studies on interfaces between immiscible phases bridges the field of heterogeneous electrode electrochemistry and that of homogeneous solution chemistry. Early work on liquid/liquid boundary was concerned with large area (order of a square centimeter) interfaces. Recent studies investigate phenomena on interfaces rendered in pores, capillaries and small holes. The behavior of such interfaces in the presence of dodecyl sulfate, forming micelles, is investigated. Voltammetry and amperometry on these small interfaces reveals that the accompanying voltammetric characteristics are similar to that of metal ultramicroelectrodes. Potentiometric studies of dodecyl sulfate on water/nitrobenzene and aqueous polymer immiscible interfaces allow determination of critical micelle concentration.

INTRODUCTION TO ELECTRIFIED LIQUID/LIQUID INTERFACES

Interfaces between two immiscible solutions containing ionic species are of interest to a wide range of scientific disciplines, reaching from theoretical physical electrochemistry, to analytical application in sensor design, to the use in interpretation of processes occurring on the biological membrane level and in biological systems.

The interface between two immiscible electrolyte solutions (ITIES) was studied for the first time at least 100 years ago, when Nernst performed the first experiments that provide the theoretical basis for today's potentiometric and voltammetric studies of interfaces (1). In 1963 Blank and Feig (2) suggested that an interface between two immiscible liquids could be used in an approximation as a model for one–half of a biological membrane. Later Koryta et al. (3) noted, that ITIES should have a behavior similar to that of an interface between an electronic conductor (i.e., an electrode) and a bathing ionic solution. Experiments that followed revealed that this predicted similarity is indeed real and the field of experimental electrochemistry on ITIES became open.

The similarities between ITIES and electrode electrochemistry make available a pool of electrochemical techniques that have been previously well tested in more common electroanalytical chemistry. To understand the similarities in the behavior, it is more useful to look at the differences first. The Faradaic current that flows through an electrochemical cell is associated with redox processes occurring on the electrode surface. The analog of an electrode surface in ITIES is the interface itself. In that case, however, the net current observed when the interface is polarized from an outside electric source is not a result of a redox process at the interface. It is, rather an effect, that is caused by transport of ions from one phase into the other through the interface. The overall macroscopic observable, current flow between two connecting electrodes, is the same in both cases. Once again, in liquid/liquid (L/L) electrochemistry, it is the interface itself that is responsible for the manifested voltammetric behavior; there are no metal electrode and a redox pair in the ITIES system that give a rise to voltammetric behavior. This becomes more clear when when the typical L/L voltammetric cell is considered (Fig. 1). The cell has provisions for connecting two reference electrodes, one on each side of the interface. This 2–reference electrode connection, that translates, in potentiostatic regime, to utilization of a 4–electrode potentiostat, is yet another difference between ITIES and electrode processes.

Total analysis of the closed circuit will of course reveal that redox processes occur in the system. But they take place on the two current supplying counter (or auxiliary) electrodes. As long as the potentiostat functions properly, polarization of these electrodes is inconsequential. Of course, care has to be taken to avoid any electrolysis products to enter the vicinity of the interface.

Common point between ITIES experiments and the studies of microdomains is in the experimentation with so called microinterfaces. The first liquid/liquid (L/L) microinterface was introduced by Taylor and Girault (4). In this experiment the L/L interface was supported on a capillary tip. The philosophy behind this approach is that diffusion to and from the small interface is governed by hemispheric, rather then linear symmetry. The same is observed with metallic ultramicrointerfaces, electrode discs with diameters below 10 μm. The advantage of the hemispheric diffusion is lower contribution of the *IR* drop and higher current densities at steady state in comparison with that of a large surface interface. The capillary support lacks the ideal geometry that would allow unhindered hemispheric diffusion on both sides of the interface. Inside the capillary the diffusion is cylindrical. To remedy this problem more work has been done on interfaces supported on a flat partitioning (5–8). The work on microinterfaces supported on a tip of a capillary continues to provide important kinetic results (9).

Study of microdomain systems benefits from another research field related closely to the work on microinterfaces. It is the area of microelectrodes, often referred to as ultramicroelectrodes. This field is some 10 years old (10) and already enjoys a degree of maturity and recognition. The aim of manufacturing ever smaller electrodes, already relevant to the microheterogeneous dimensions, resulted in constructing of a "nanoelectrode," (11) a metal electrode with almost atomic dimensions. Remarkable success in fabrication of minute size electrodes has been achieved by Martin (12) by growing miniature metal rods inside insulating tubules and by Potje–Kamloth et al. (13) by successful electrical insulation of a single carbon fiber by reliable electrical insulation via electropolymerization.

Because of the negligible contribution of *IR* drop on the small surfaces, these electrodes are suitable for kinetic measurements of fast rate processes requiring high voltammetric scan rates (14). Wightman (15) demonstrated practicality of scan rates up to 10^5 V s^{-1}. Baranski (16) gave theoretical foundation for optimization of AC voltammetric measurements on microelectrodes. Taylor et al. (17) presented results obtained for digital simulation of charge transfer on microelectrodes.

Micelles in liquid/liquid interface systems

To make the ITIES electrochemical experiment work, both the aqueous and the nonaqueous solutions must contain dissolved salts. These salts render the solutions conductive and in many cases have also the purpose of a supporting electrolyte that suppresses migration of the analyte ion. To dissolve a salt in a nonaqueous phase, the molecule has to be relatively large (hydrophobic). The salts for the aqueous phase have to be hydrophilic. Similarly, ions that produce signals on liquid/liquid interfaces are semihydrophobic species of intermediate Gibbs energy of transfer. Consequently, a number of molecules that are of interest to L/L work will have the properties of a surfactant.

Surfactant (surface active agent) molecules are molecules that possess both hydrophilic and hydrophobic moieties. They may aggregate under favorable conditions in water and form microscopic domains called micelles. The original description of these aggregates dates back to Hartley (18). The interest in this field has grown tremendously in the last several years. For example, in the period from 1980 to 1990 some 350 reviews (not primary articles) have been published on this subject (19). All fields of chemistry were touched by research of micelles. The most relevant to the studies done by us in liquid/liquid electrochemistry are the works on micelles in physical chemistry, analytical chemistry (20, 21) and, in particular, in electrochemistry. Recent review on analytical applications of micelles was given by McIntire (19) in 1990. The same author also presented a review on electrochemistry in micelles in 1986 (22). A monograph on the physical chemistry of micelles and microemulsions appeared recently (23). Electrochemistry remains an important tool of studying micellar systems. Polarography was used to measure micellar diffusion coefficients (24). Conductivity is used conveniently in studies of micelle formations (25), as well as, is voltammetry (26).

Micellar chemistry is important to the studies on L/L interfaces even in cases when micelles are not actively formed or pursued. The ITIES systems under study contain, by the necessity of dissolving lipophilic salts in organic solvent, amphiphilic species. Salts soluble in nonaqueous solvent, such as nitrobenzene, will be usually large (tetrabutylammonium, tetraphenylborate, cetyltrimethylammonium, dodecyl sulfate). The lipophilic moiety responsible for solubility in organic solvent can be well separated from the charged functionality responsible for salt dissociation, solution conductivity and electrochemical activity (cetyltrimethylammonium), or the charge can be localized inside bulky, symmetrical lipophilic structure (tetraphenylborate, tetraphenylarsonium, tetrabutylammonium). The first class of compounds will have the inherent tendency to form self–assembled aggregates or layers on the surface of interfaces with different hydrophilicities, whereas the second group, with higher symmetry, will be less prone to aggregation and surface adsorption. In the prevailing work on ITIES, it is not desirable to introduce a detergent (amphiphilic molecule) into the system. The typical experiment is based on charge transport studies across interface between two liquids. It is desirable to have this interface well defined. With a detergent present, there is always the danger that the interface will be perturbed and smeared out. However, in careful experiments where mechanical perturbation of the interface is absent, this rarely causes serious problem.

At low concentration of the surfactant in water, its molecules are simply dissolved and uniformly distributed throughout the solution. As the concentration is increased, the solution conductivity increases and the surface tension decreases. Upon reaching certain concentration of the surfactant, its molecules start to aggregate with the nonpolar tails of the molecule being packed together in the interior and the hydrophilic heads pointing outwards, forming roughly spherical objects. This aggregation occurs at a critical concentration, specific and different for each system and it is known as the critical micelle concentration (CMC). At concentrations above the CMC the concentration of unassociated surfactant remains virtually constant. Further addition of monomer causes increase in number of micelles. Thus surface tension remains virtually unchanged above the CMC. Similarly, the increase in conductance suddenly almost stops. It never levels off though, because the micelles, whose concentration keeps increasing, also contribute to the overall conductivity. Due to their large size (low mobility), the contribution of the micelles to overall conductivity of the solution is quite small. The size of the micelles depends on the nature of the surfactant, for example an SDS micelle aggregate has a weight of 17,000, which corresponds to 59 monomers in the unit (27). The typical size for most micelles is between 60 and 100 monomers, typical size 3 to 6 nm. Therefore, the macroscopic solution behaves as homogeneous, filtration does not separate micelles, and the solution does not exhibit light scattering. The micelle itself is not a static entity; there is a dynamic exchange between the micelle and the solvated monomer. Replacement of the whole micelle takes place in the course of milliseconds to seconds.

Most often, micelles are formed within aqueous solutions, thus the hydrophilic moiety of the surfactant points outward. These micelles are called normal. In a mirror image situation, surfactants can also aggregate in nonpolar media, forming reverse or inverse micelles (28, 29) (Fig. 2). The hydrophobic moiety extends to the bulk of the nonpolar solution, while the polar ends of the surfactant molecules are drawn together to form the hydrophilic core of the inverted micelle. Very often any water present in the system will tend to be included inside the reverse micelle aggregates. In liquid/liquid electrochemical experiments on a free standing interface there is a possibility of micelle formation in the presence of a surfactant in both the aqueous and the nonaqueous (less polar) phase. In many cases formation of micelles in studies of well behaved ITIES systems is however undesirable.

Low concentrations of surfactants (below the CMC) have long been used in polarography to suppress maxima. These maxima are exaltations of current above the values expected from diffusion controlled behavior. They arise from whirling motion of the mercury drop electrode which can be effectively suppressed by addition of surfactant. Concentrations above the CMC have been used only sparingly. The possibility of the use of micelles in electrochemistry can be divided into several categories, that include electrochemical masking, electrocatalysis and the provision of a low—cost and nontoxic alternative to nonaqueous solvents (19, 22). In the studies in L/L electrochemistry, micelles become a species of interest due to the fact that they are carriers of a charge in the solution.

Electrochemists tend to discount nonelectrochemically active substances as unimportant (21). In L/L electrochemistry the concept of "electroactive species" is different from the one in electrode studies. In L/L the species have to have a charge and be able to be transported across the interface to be noted on voltammetric curve. Electron transfer is not taking place. Thus, one can detect chemically quite nonreactive species such as the tetramethylammonium cation.

Even if the substance is not transportable across the L/L interface, its adsorptive behavior can be of great importance. Vanýsek and Sun (30) studied transport of probe ion (Cs^+) in the presence of bovine serum albumin, and the capacitive behavior of the interface in response to protein concentration, pH and temperature.

Equilibrium thermodynamics of liquid/liquid interfaces is based on several simple principles. Hung (31) first presented an implicit equation that is based on the equality of the electrochemical potentials of each participating species between the two solvents in contact and on the general requirement of electroneutrality.

$$\sum_{i=1}^{j} z_i c_i^0 / \left\{ 1 + \frac{\gamma_i^{a}}{\gamma_i^{\beta}} \exp\left[\frac{z_i F}{RT} (\Delta\varphi - \Delta\varphi_i^0) \right] \right\} = 0 \tag{1}$$

$\Delta\varphi$ is the interfacial equilibrium potential, $\Delta\varphi_i^0$ is the standard potential of transfer for ion *i*, z_i is the ion charge, c_i is the total analytical concentration of *i* in both phases and γ is the activity coefficient in phase *a* and β.

Although the thermodynamic principle of this equilibrium is simple, the implications are not immediately obvious. Buck and Vanýsek (32, 33) used the concept of equilibria and the Gibbs energy of transfer for calculating a series of equations for various interfacial systems, including L/L equilibria. In many instances, micellar systems can be regarded as related to L/L systems. Caselli and Maestro (34) used the concept of Gibbs energy change between water and lipophile to calculate equilibrium micellar radius of reverse micelles as a function of saline solution concentration in aqueous phase. This concept is quite far–reaching, e.g., it has been applied to interaction of oil dispersion in photographic developer systems (35).

Water/nitrobenzene experiments

Typical studies of ion transport between two immiscible electrolytes involve the interface between water and nitrobenzene (8). Nitrobenzene is used since it is essentially immiscible with water. Because of its relatively large relative permittivity (ϵ - 35) salts soluble in nitrobenzene dissociate, thus rendering a conductive, nonaqueous, water–immiscible medium.

For an ion transfer experiment between water and nitrobenzene, two suitable supporting electrolytes are chosen such that one of these salts in not soluble in one phase, the second electrolyte is insoluble in the other phase. Typically, the salt used in water is very hydrophilic, LiCl, whereas the salt suitable for the nonaqueous phase can be a lipophilic tetrabutylammonium tetraphenylborate (TBATPB). In such a configuration, the supporting electrolytes are preferentially contained in their original solvent phases and application of a potential on the interface from an external source will cause only a small degree of salt transport into the opposite phase. Thus, one obtains an interface on which an arbitrary potential within a certain range can be applied, without causing significant current flow. Such an interface is called an ideally polarizable interface in parallel with electrode electrochemistry terminology.

Addition of a semihydrophobic ion into either phase provides the L/L system with a charged species that can be driven across the interface from one phase into another, as a function of the applied potential on the polarizable interface. The transport of the charged species is manifested in the external electric circuit as current. Experimental voltamperometric characteristics of the L/L system exhibits a current–voltage dependence similar to that of a voltammogram of a reversibly reducible species. Figure 3 illustrates an example of the transfer of the semihydrophobic anion, picrate, between water and nitrobenzene. Unlike in electrode electrochemistry, where the peaks correspond to reduction and subsequent oxidation of a species, here the peaks correspond to the transport of picrate anion from nitrobenzene to water (top, right) and the peak on the reverse sweep is caused by transport of picrate from water to nitrobenzene. Since the transport of the anion across the interface in the presence of high concentration of supporting electrolytes is governed by the same principles of diffusion, the L/L voltammetric curves are very similar to those obtained for redox processes on metal electrodes.

The ionic species (both cations and anions) whose transport can be followed voltammetrically on the described interface, must be less hydrophilic that the supporting electrolyte in water and at the same time they must be less lipophilic than the supporting electrolyte in the nonaqueous phase. Since the potential window of the ideally polarizable interface is fairly narrow (approximately 500 mV for the described system), only a few ions can be directly observed. They include quaternary ammonium cations shorter than butyl, choline, acetylcholine, picrate, iodode, perchlorate, thiocyanate, Rb^+, Cs^+ and several others. From our interest, it is important that dodecyl sulfate, which forms micelles at certain concentrations, also can be transported within this potential window.

Water and nonaqueous solvent is not the only immiscible solution system, that can be used for ITIES studies. There are a number of aqueous two phase systems that show, at least, a promise in ITIES electrochemistry applications. A two phase aqueous system can arise when two polymers (e.g., polyethylene glycol and dextran) are dissolved in water, with one polymer predominating in each phase (36, 37). Such systems are being used for physical separation of a wide range of biomolecules (38). The advantages quoted for these separations are primarily biocompatibility (contents of water is 75–90%). For the most part, the work that involved two phase aqueous systems was mostly centered on extraction and separation techniques, although potentiometric work has been also reported (39).

In our work we are reporting potentiometric results on several systems including dodecyl sulfate. Voltammetric studies on these interfaces were also performed. Because the Gibbs energy of transport of ionic species between the two phases is quite low, we were not able to establish a system with appropriate supporting electrolytes that would provide a potential window sufficiently wide for any kind of meaningful voltammetric measurement.

MATERIALS AND METHODS

Voltammetric studies of laurylsulfate (sodium salt of dodecyl sulfate, SDS) on a water/nitrobenzene interface were done on a microinterface (6). The cell used in this work is shown in Fig. 4. It was made from two pieces of a No. 9 O–ring Pyrex glass joint. An opening in one of the arms was filled with thinly blown glass in which a small hole was introduced by Tesla coil discharge. The diameter of the hole for the results reported in this paper was determined to be ~ 130 μm. An alternative reliable way of realization of small interface is in Fig. 5. The tubular probe device was made from a 7–mm poly(tetrafluoroethylene) rod, drilled out with a 5–mm flat bottom drill so that only about 0.3 mm thick poly(tetrafluoroethylene) bottom remained. An opening of 0.1 mm was drilled in the bottom. Due to the nature of poly(tetrafluoroethylene), the hole closed somewhat after smoothing on the lathe. The typical opening in both the glass and the poly(tetrafluoroethylene) wall were ~ 50 μm. Although this diameter does not accomplish entirely the prerequisite for hemispheric diffusion, the contribution of *IR* drop is negligible and a 2–electrode system for polarization can be used. More suitable techniques for manufacturing small partitioning were recently described by Girault (40, 41).

The electrical circuit requires only a 2–electrode connection, but care has to be exercised in sufficient amplification of the small currents and in shielding to prevent electrical noise. Keithley 470 current amplifier was used for the current to voltage conversion at a typical setting 10^7 V/A. The circuit diagram used for the low current voltammetric experiments is schematically shown in Fig. 6.

For the aqueous/aqueous interface the experiment was potentiometric. Figure 7 shows the schematics of the apparatus used to measure the potential difference between the two aqueous phases. The reference electrodes were Ag/AgCl wires immersed in 0.1 mol l^{-1} KCl, placed in a salt bridge separated from the polymer gel solutions by a vycor porous glass plug. The potential difference between the two reference electrodes was measured with a pH meter set on the millivolt scale.

A constant potential reference electrode for nonaqueous solution requires additional water/organic interface with a common ion. The shorthand notation of the water/organic voltammetric cell is given in the following diagram:

$$\begin{array}{c|c|c||c|c|c|c} \text{Ag} & \text{AgCl} & \text{LiCl (+ SDS)} & \text{TBATPB} & \text{TBACl} & \text{AgCl} & \text{Ag} \\ \text{(s)} & \text{(s)} & \text{(aqueous)} & \text{(nitrobenzene)} & \text{(aqueous)} & \text{(s)} & \text{(s)} \end{array} \quad (2)$$

The interface on which the transfer of ions of interest takes place is marked by the two vertical lines. The potential on this interface and its variation produces the analytical signal. All other interfaces have known and constant potential. The function of the tetrabutylammonium chloride (TBACl) bathing the right hand reference Ag/AgCl electrode is to establish constant potential on the water/nitrobenzene interface by virtue of sharing common TBA^+ ion. As long as the activity of the TBA^+ in both phases remains constant, the interfacial potential will be also constant and its value will be given by the Nernst–Donnan equation:

$$\Delta\varphi = \Delta\varphi_i^{\mathrm{o}} + \frac{\mathrm{RT}}{\mathrm{nF}} \ln \frac{\mathrm{a_i}(\alpha)}{\mathrm{a_i}(\beta)}, \qquad (3)$$

where $\Delta\varphi_i^{\mathrm{o}}$ is the standard potential of transfer of a common ion i from phase α to phase β. For equal concentrations of the tetrabutylammonium cation for water/nitrobenzene this potential difference is -248 mV. The sign denotes the polarity of the aqueous phase.

The polymers used for the two–phase aqueous system experiments were polyethylene glycol (PEG), average m.w. 3 350 (Sigma, No. P–3640) and dextran, average m.w. 67 900 (Sigma, No. D–1390). Sodium dodecyl sulfate was supplied by Aldrich. Water doubly distilled from glass was used throughout. All experiments were done at 25 $^{\mathrm{o}}$C.

RESULTS

Figure 8 shows the voltammetric response of an interface between two liquids created in a thin glass window. The diameter of the opening was ~ 130 μm. Voltammetric curve *1* shows the response of the system containing only the supporting electrolytes, 0.02 mol $\mathrm{l^{-1}}$ LiCl in water and 0.02 mol $\mathrm{l^{-1}}$ TBATPB in nitrobenzene. Only negligible current flows in the central potential range known as the potential window. Subsequent curves *2 – 5* show voltammograms obtained with the supporting electrolyte system upon addition of 0.4 mmol $\mathrm{l^{-1}}$ dodecyl sulfate (sodium salt) into the aqueous phase. The response at several scan rates is shown. At lower scan rates the voltammogram does not display a peak; a current plateau is formed instead. As mentioned earlier, this small interface is expected to display similar behavior as do ultramicroelectrodes. At slower scan rates the diffusion towards the interface has hemispheric symmetry. The ions are approaching the interface from the volume of a hemisphere. Thus, a constant, steady state current is observed. At higher scan rates the symmetry becomes semilinear with the ions approaching the interface from one direction only. The voltammetric curves reach a maximum after which diffusion continues to deplete the amount of ions available for interfacial transport.

Because the L/L interface can be formally treated in the same way as an electrode/electrolyte interface, the equation describing the limiting current under conditions of hemispheric diffusion can be written for an ion *i* in the following form (4):

$$I = 4\ FD_ic_ir, \tag{4}$$

where F is the Faraday constant, D_i and c_i are the diffusion coefficient and the bulk concentration of ion i and r is the radius of the interface (6). Similarly, an approximate equation can be derived from the spherical term of the voltammetric curve derived by Nicholson and Shain (42) in the limit of the radius of the electrode tending to zero:

$$I_{r\to 0}^{(approx)} = 2\ \pi nFDcr. \tag{5}$$

We have published this equation in (6) and (7), but with the factor 2 inadvertently omitted.

At higher scan rates, when the mass transport is controlled by linear diffusion, the voltammetric curves display peaks on both the positive and negative scans. Since the transport of SDS is reversible (i.e., transport can proceed unhindered across the interface in both directions), the separation of peaks for this univalent ion is about 58 mV on repetitive cycling. In agreement with diffusion theory, the peak current is directly proportional to the square root of the scan rate (Fig. 9).

It has also been shown that in accordance with expected behavior, the peak current at a given scan rate is proportional to the concentration of the transported ion. Figure 10 gives the dependence for picrate, tetramethylammonium, and choline. The results for dodecyl sulfate, which was also investigated (43), were erratic at higher concentrations in comparison with the other ions. The probable cause was twofold. SDS acts as a detergent, which can solubilize nitrobenzene in water or water in nitrobenzene. This problem was apparent especially in mechanically perturbed systems such as those where ITIES is realized in the form of a dropping electrode. The critical micellar concentration for SDS is 8 mmol l^{-1} (27). Above that concentration, the concentration of solubilized SDS remains essentially constant. That is not to say, that the transport of SDS must level off at the CMC. Instead, the micelles contribute to the total amount of SDS available for interfacial transport. But the contribution is further complicated by the rate of aggregation/disaggregation and also by the fact that the concentration of the analyte is nearing that of the supporting electrolytes (20 mmol l^{-1}) and the transport description is further complicated by migration component.

Unusual phenomena on L/L interface were observed in the presence of colloids, such as denatured proteins (insulin, ovalbumin) and even dispersed colloidal particles of polystyrene (44). It was observed in the presence of these agents that current across the interface increases and the potential window of the supporting electrolytes narrows. This phenomenon has been explained in a qualitative way by availability of charged colloidal particles for interfacial transport.

Potentiometric experiments on nitrobenzene/water interface were performed in a similar setup as is the one for potentiometric measurements on the two-phase aqueous systems (c.f., Fig. 7). Heavier nitrobenzene was placed on the bottom of the cell, nonaqueous reference electrode was immersed next and the nitrobenzene phase was topped with the aqueous phase. Then the second reference electrode was placed in the aqueous phase. The aqueous phase reference electrode was an Ag/AgCl wire immersed in 0.01 mol l^{-1} LiCl. The reference electrode used in nitrobenzene was an Ag/AgCl wire immersed in aqueous 0.01 mol l^{-1} tetrabutylammonium chloride. Since the nitrobenzene layer contains 0.1 mol l^{-1} tetrabutylammonium tetraphenylborate, the TBA^+ ion common to both phases establishes the constant reference potential (c.f., cell diagram 2).

In ITIES voltammetric experiments it is usual practice to allow about 10 minutes to equilibrate the system after setting it up. We have followed the protocol, but as we were able to monitor the interfacial potential from the very beginning of setting up the cell, lot of variation between systems was observed. Figure 11 shows that with the SDS experiments, the steady state values were reached almost immediately.

Figure 12 shows the interfacial potential dependence as the function of sodium dodecyl sulfate concentration in the aqueous phase. The dependence shows sharp decrease in the potential of the aqueous phase (relative to the nitrobenzene solution) in the concentration range from 0.1 to 1 mmol l^{-1}. This behavior is in sharp contrast to the potentiometric curves obtained for example for picrate, where the dependence is essentially linear through several orders of concentrations. Above 10 mmol l^{-1} SDS the potential is no more dependent on the analytical concentration of SDS. This agrees with the micellar concept; the concentration of free SDS above CMC remains virtually constant.

The two–phase aqueous system was prepared by preparing separately 30% dextran and 30% polyethylene glycol solutions in water or appropriate aqueous supporting electrolyte (0.1 mol l^{-1} LiCl). For the experiment, a layer of the heavier phase (dextran) was placed on the bottom first, then the lower phase reference electrode was immersed, after which the top layer of polyethylene glycol solution was injected carefully with a syringe. Finally, the second reference electrode was placed in the top layer. The established interface was allowed to equilibrate. The time necessary for the equilibration was determined from diminishing drift of the potential difference. The required waiting varied widely with used systems. For the SDS experiments, the steady potential value was reached almost immediately and variation with time was minimal.

Figure 13 is a concentration dependence of the two–phase aqueous interfacial potential as a function of concentration of dodecyl sulfate. In contrast with the results obtained at the water/nitrobenzene interface, the PEG/dextran system does not display any leveling off at the highest measured concentrations. The CMC is a constant only for given environment. It varies greatly with ionic strength and solvent medium. The steady change of interfacial potential with increasing SDS concentration is indicative of lack of micellar formation in the aqueous polymers system at the attained concentrations. It is difficult to prepare higher concentrations of SDS since the 30% polymer phase is quite poor solvent.

The 2–phase aqueous polymer system is interesting candidate for further L/L and ITIES studies. The fact that the principal solvent in each phase is water allows otherwise impossible studies of Gibbs energies related to various degrees of solvation in single solvent. On the down side, these systems do not appear to be good candidates for ITIES electroanalytical chemistry. The difference of Gibbs energies of transfer between the two aqueous polymer phases is inevitably too small to provide a potential window sufficiently wide for voltammetric studies.

Experimentation on electrified immiscible interfaces has been applied in this chapter to problems that relate to the studies in microheterogeneous systems. Although the aim of ITIES electrochemistry is mostly towards aspects of large size heterogeneous systems (interfaces), microheterogeneity is occasionally investigated as well. Miniaturization of the liquid/liquid interfaces is one such case. With proper techniques the interfaces can be rendered sufficiently small to alter the diffusion to the interface from linear to hemispheric symmetry. Second aspect of microheterogeneity discussed here was formation of micelles in L/L systems. Case of dodecyl sulfate micelle formation in water/nitrobenzene has been documented. An interface between two aqueous polymer solutions, so far rarely studied in the electrochemical context, was also presented. In this polymer media, different from bulk water, micelle formation of sodium dodecyl sulfate below concentration 0.1 mol l^{-1} was not observed.

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Legend for figures

Fig. 1	Voltammetric cell for 4–electrode ITIES work. The cell with 1 cm^2 area interface is approximately 14 cm high.
Fig. 2	Schematic representation of organized structures of surfactants in different media.
Fig. 3	Transport of picrate anion across water/nitrobenzene interface. 0.8 mmol l^{-1} tetrabutylammonium picrate in nitrobenzene; supporting electrolytes 0.02 mol l^{-1} LiCl in water and 0.02 mol l^{-1} tetrabutylammonium tetraphenylborate in nitrobenzene. Interfacial area 0.20 cm^2. Scan rate 40 mV s^{-1}. Potential relative to the TBA^+ electrode.
Fig. 4	Electrochemical cell used for μITIES studies on glass partitioning. (1) Ag/AgCl reference electrodes, (2) Aqueous investigated solution, (3) Aqueous "reference" solution c.f., cell diagram 2, (4) Nitrobenzene investigated solution, (5) Glass joints with an o–ring seal, held together by a screw clamp, (6) Glass wall with miniature hole.
Fig. 5	Compartment for μITIES work realized in a poly(tetrafluoroethylene) tube. (1) Ag/AgCl reference electrodes, (2) Aqueous investigated solution, (3) Aqueous "reference" solution, c f., cell diagram 2, (4) Nitrobenzene investigated solution, (5) Poly(tetrafluoroethylene) body, approx. 7 mm dia., (6) Poly(tetrafluoroethylene) thin wall with miniature hole.
Fig. 6	Diagram for measurement of low current signals.

Fig. 7 Schematic of the apparatus for L/L potentiometric measurements. Temperature is maintained by thermostated circulated water. The beaker diameter is 24 mm.

Fig. 8 Cyclic voltammograms of SDS–transfer (0.4 mmol l^{-1}) for several scan rates (in mV s^{-1}): (1) supporting electrolytes only, at 25 mV s^{-1}, (2) 10, (3) 50, (4), 200, (5) 1000. Supporting electrolytes, 0.02 mol l^{-1} LiCl in H_2O and 0.02 mol l^{-1} TBATPB in nitrobenzene. Interface diameter 130 μm. Potential relative to the TBA^+ electrode.

Fig. 9 Peak currents (for forward scan) as a function of the square root of scan rate. Concentration of the studied ions 0.4 mmol l^{-1}. Supporting electrolytes, 0.02 mol l^{-1} LiCl in H_2O and 0.02 mol l^{-1} TBATPB in nitrobenzene. (□) $TMeA^+$, (△) picrate, (◇) choline and (○) dodecyl sulfate.

Fig. 10 Plot of peak current (forward scan) versus concentration. (□) choline, (△) picrate and (○) $TMeA^+$. Scan rate 25 mV s^{-1}. Supporting electrolytes, 0.02 mol l^{-1} LiCl in H_2O and 0.02 mol l^{-1} TBATPB in nitrobenzene.

Fig. 11 Time dependence of potential on a water/nitrobenzene interface. The different SDS concentration in water shown in graph. Time begins at contact of the freshly prepared phases. Supporting electrolytes 0.02 mol l^{-1} LiCl in H_2O and 0.02 mol l^{-1} TBATPB in nitrobenzene.

Fig. 12 Potentiometry of sodium dodecyl sulfate in water/nitrobenzene system. The graph gives the initial analytical concentration of SDS in water. Supporting electrolytes 0.02 mol l^{-1} LiCl in H_2O and 0.02 mol l^{-1} TBATPB in nitrobenzene.

Fig. 13 Potentiometry of sodium dodecyl sulfate SDS in aqueous poly(ethylene) glycol/dextran system. The graph gives the initial SDS concentration in the (poly)ethylene glycol layer. Polymer solutions: lighter phase 30% (poly)ethylene glycol in 0.01 mol l^{-1} aqueous LiCl, denser phase, 30% dextran in 0.01 mol l^{-1} aqueous LiCl.

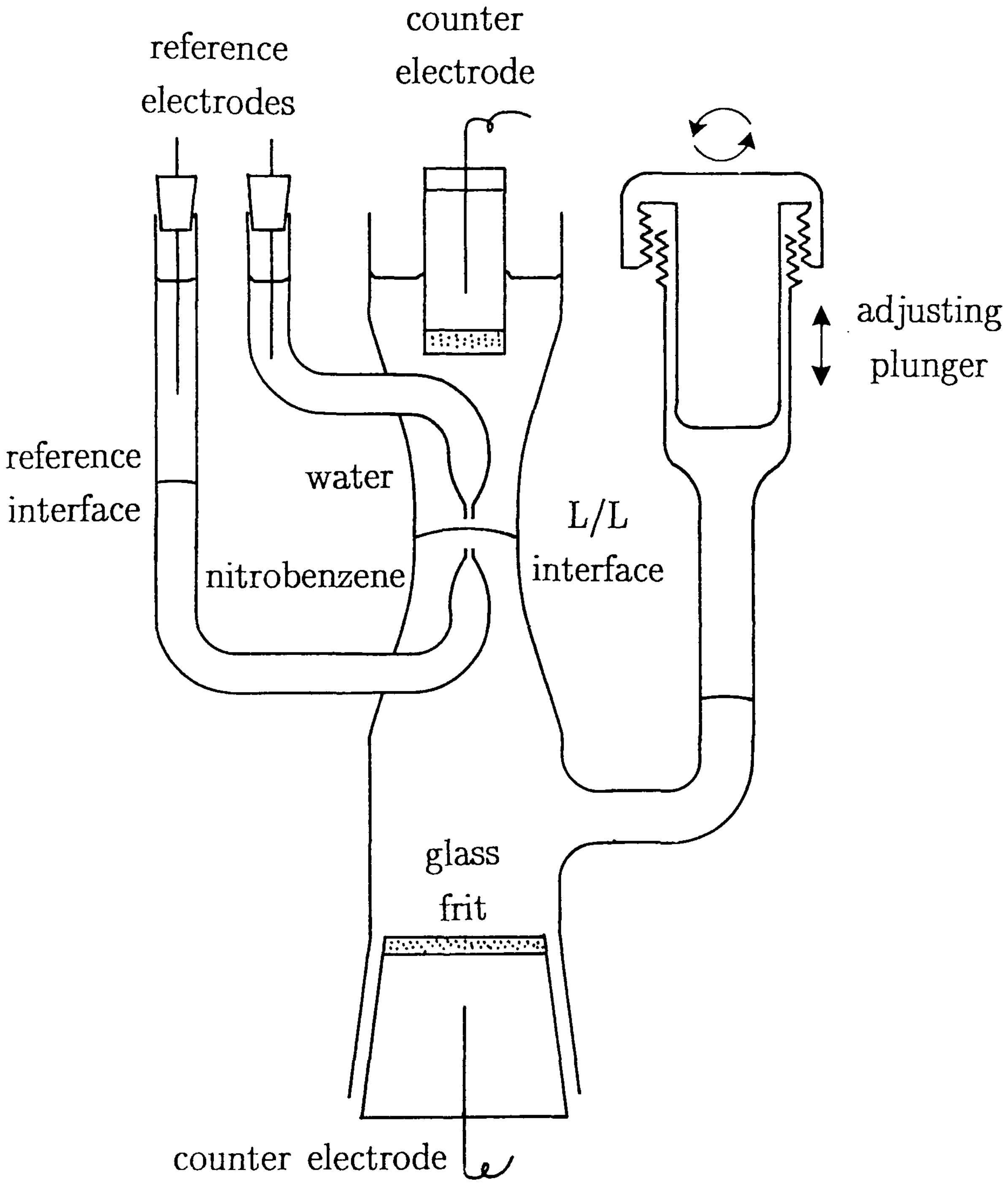
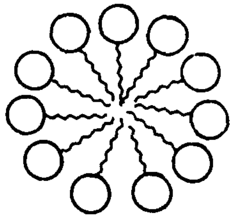
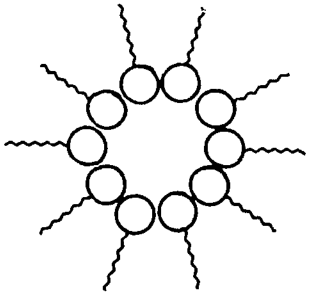

counter
electrode
reference
electrodes
adjusting
plunger
reference
interface
water
L/L
interface
nitrobenzene
glass
frit
counter electrode

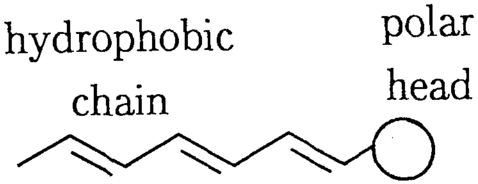
Fig. 1



spherical
micelle

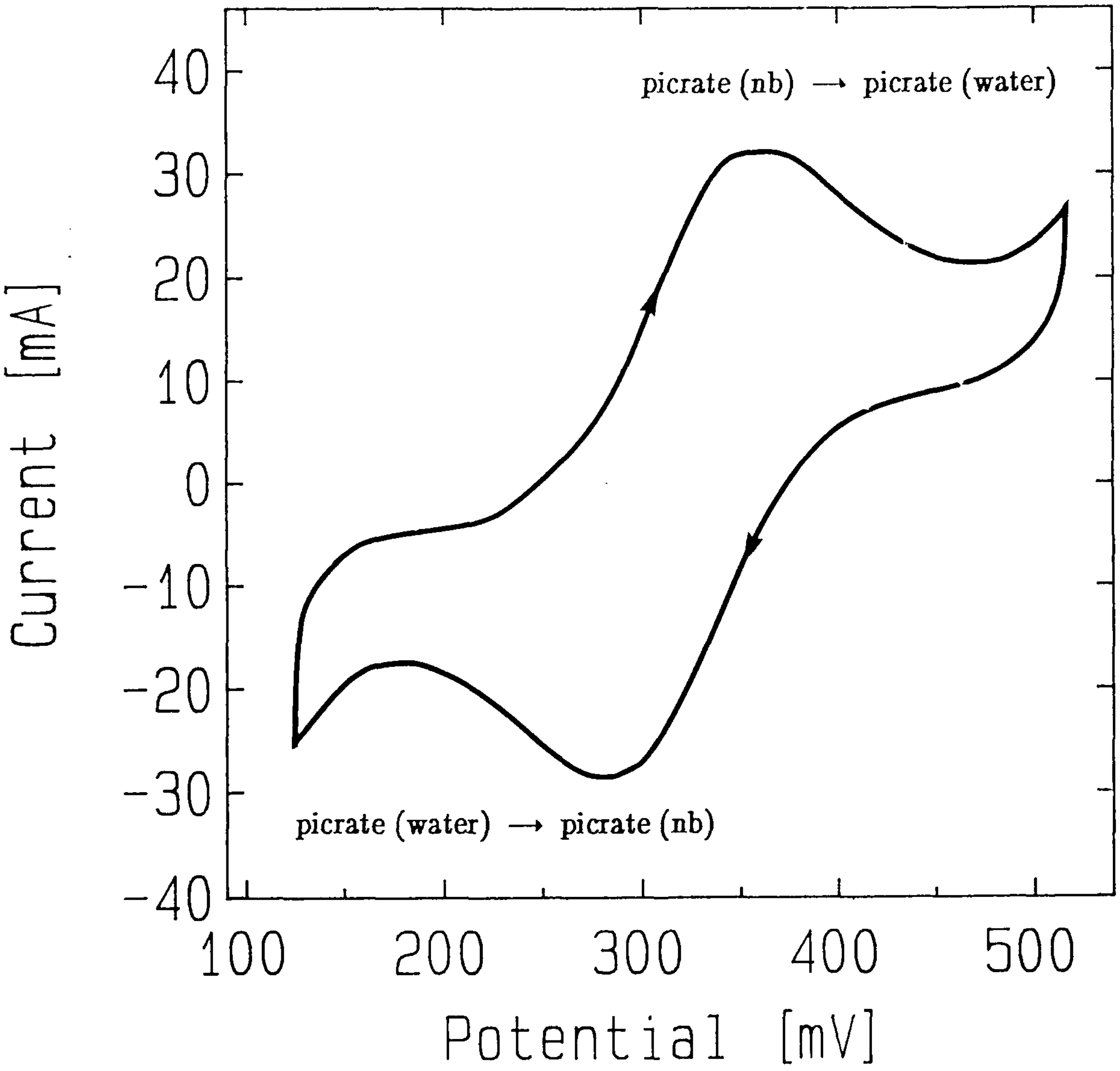


reverse
micelle

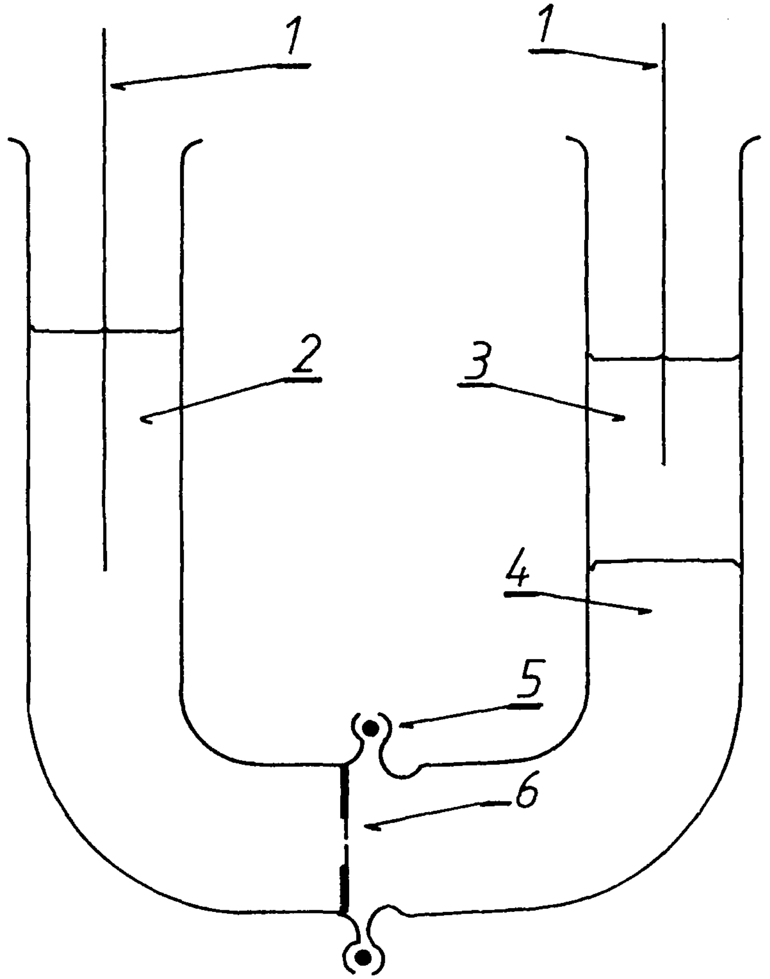


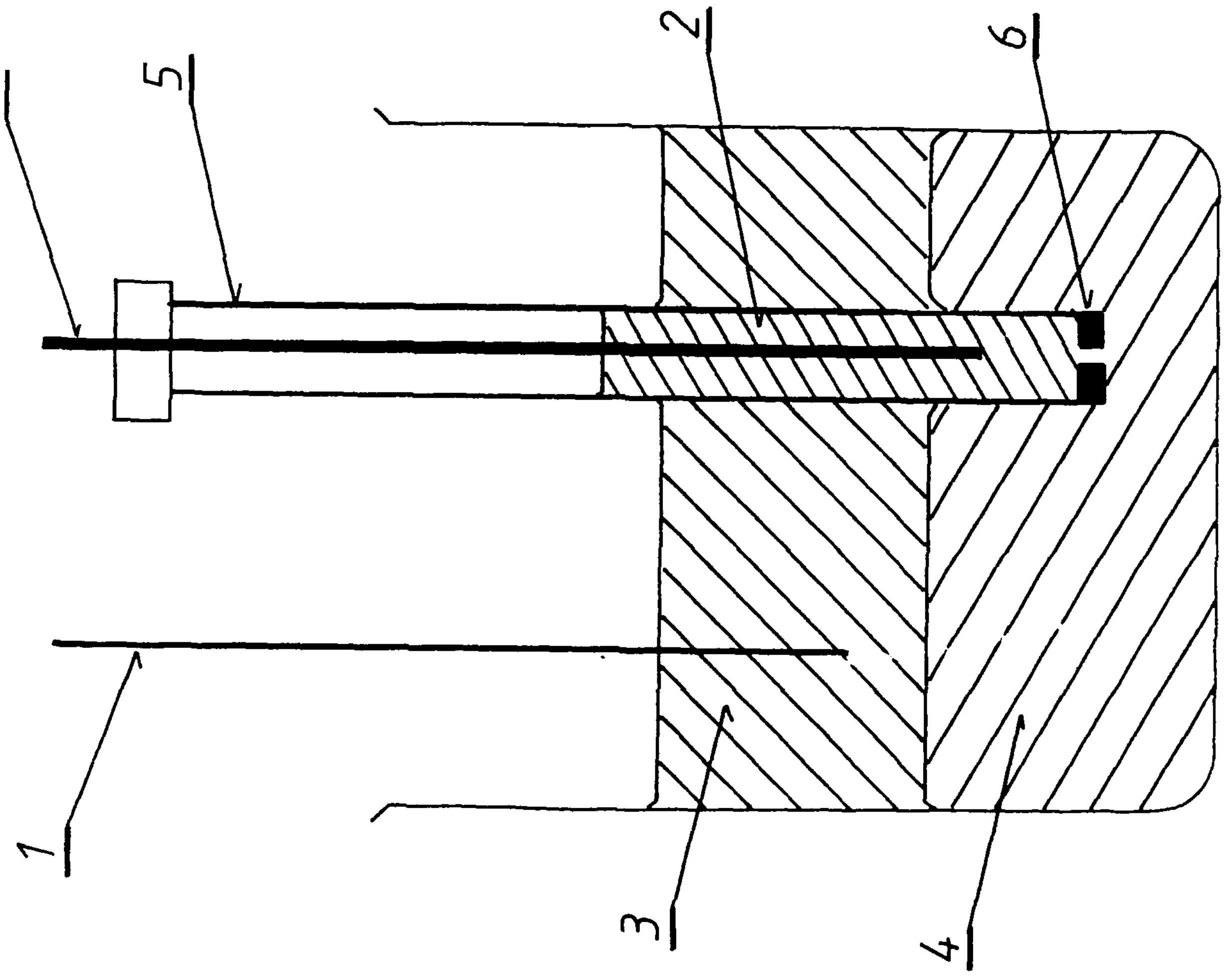
surfactant molecule

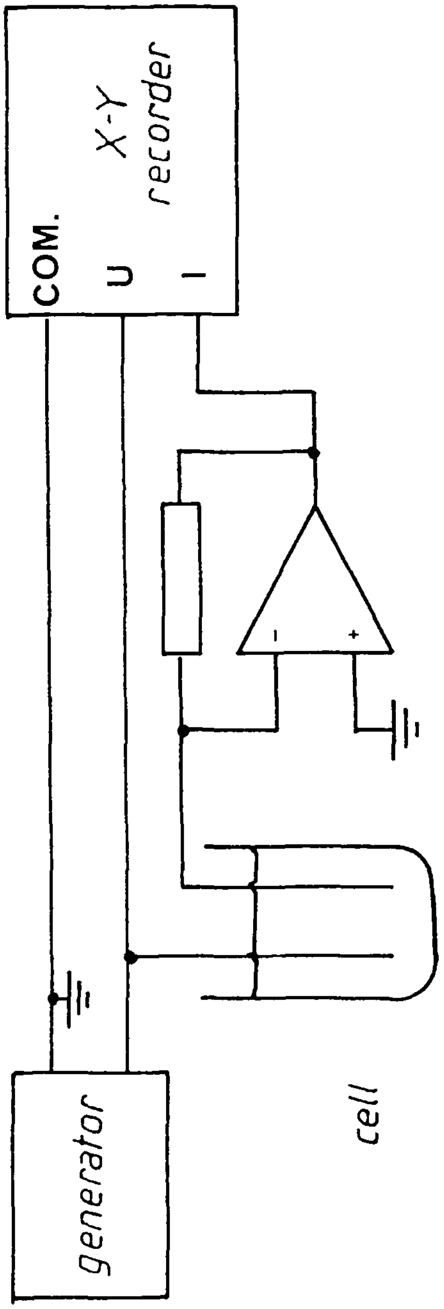
2

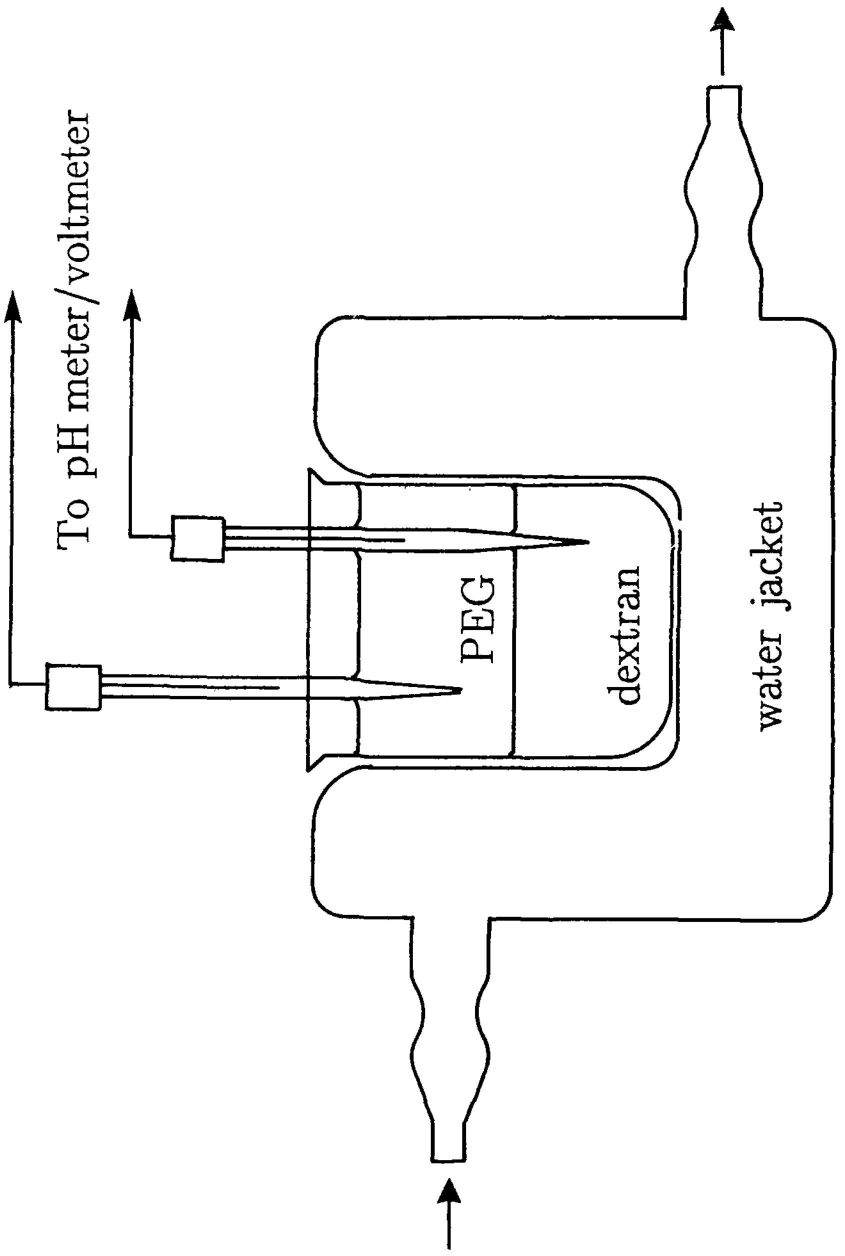

picrate (nb) → picrate (water)
picrate (water) → picrate (nb)
Current [mA]
40
30
20
10
0
−10
−20
−30
−40
100
200
300
400
500
Potential [mV]

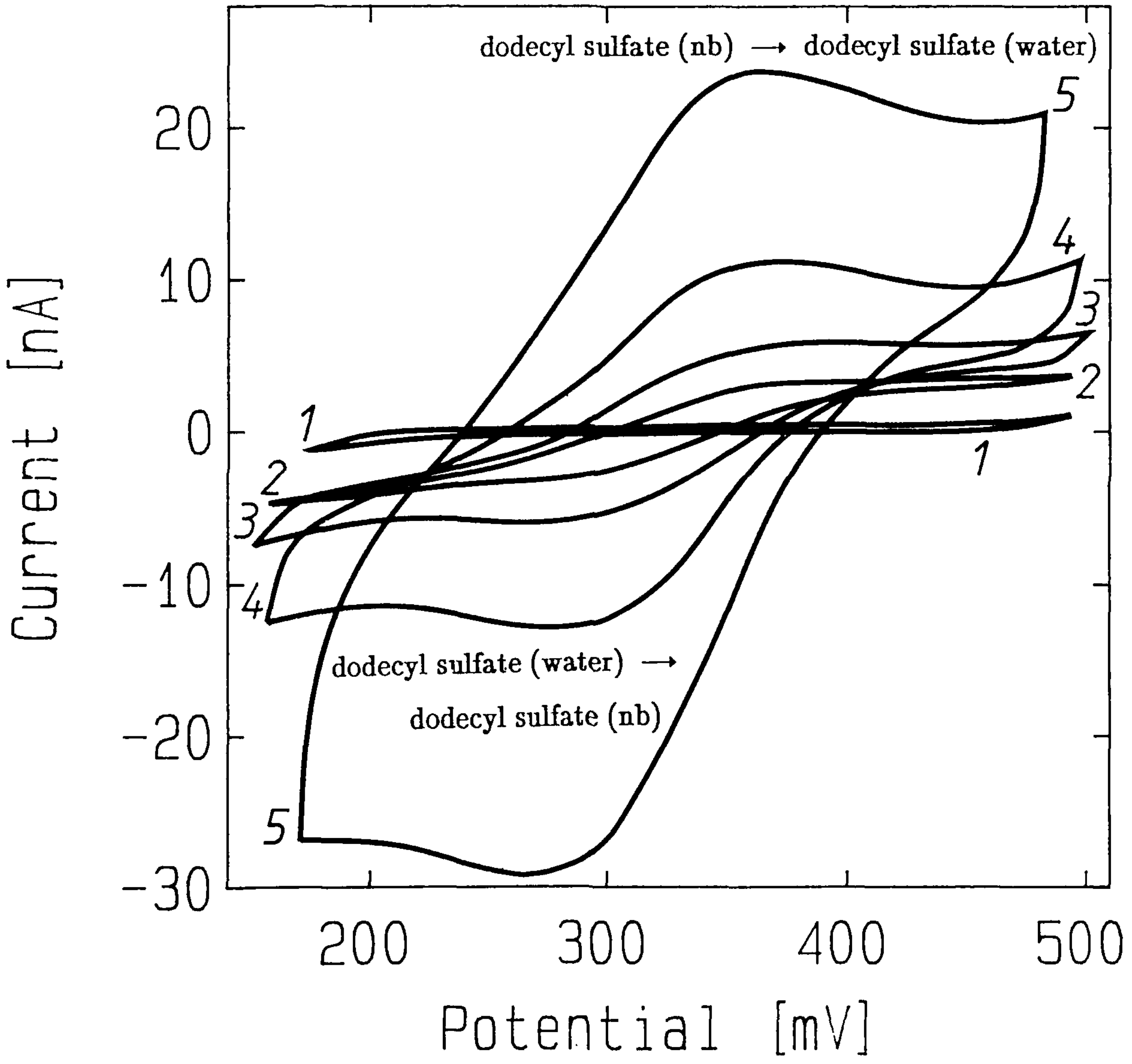
3


1
1
2
3
4
5
6

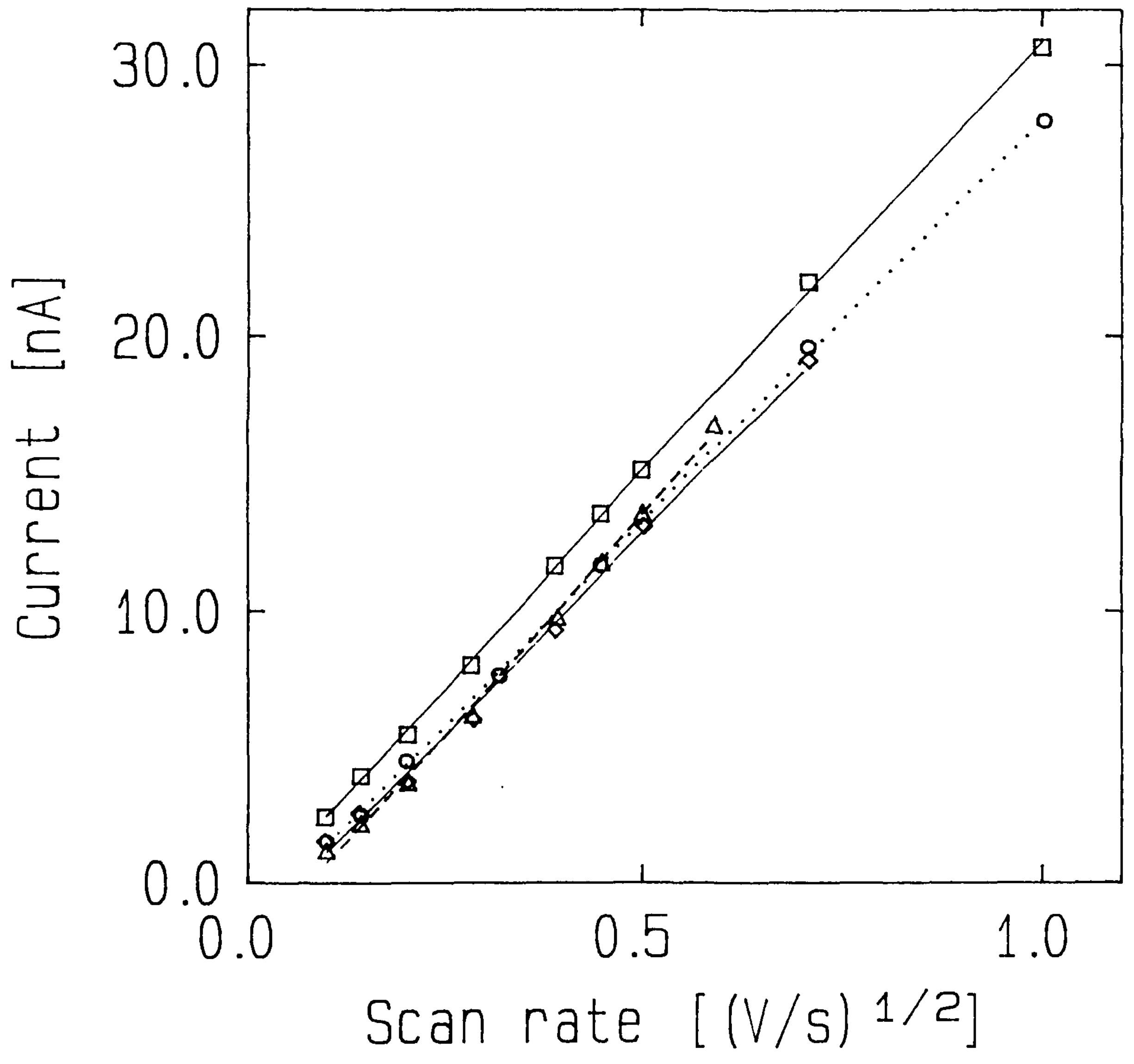

1
5
2
6
1
3
4


COM.
U
I
X-Y
recorder
-
+
generator
cell

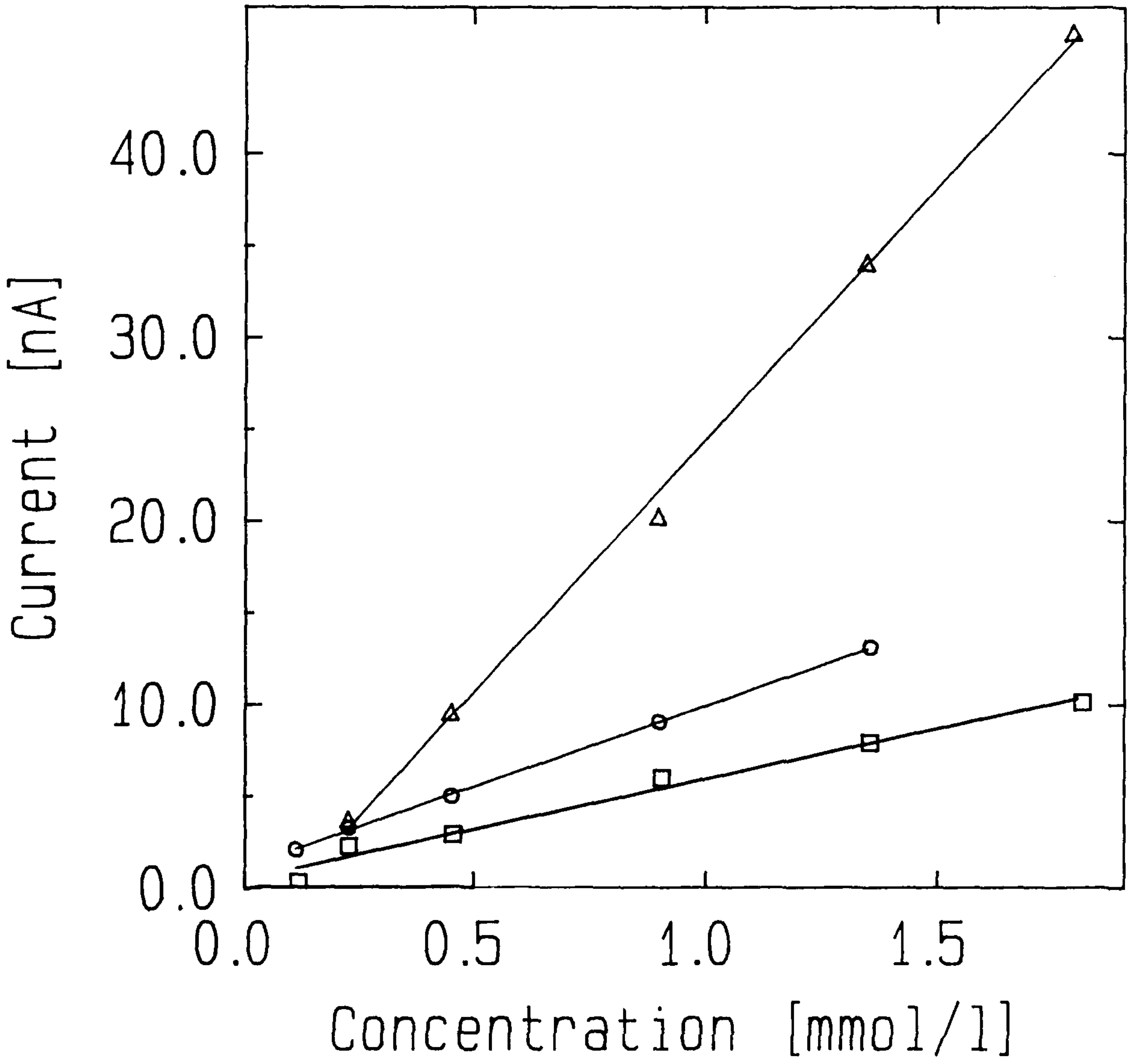

To pH meter/voltmeter
PEG
dextran
water jacket

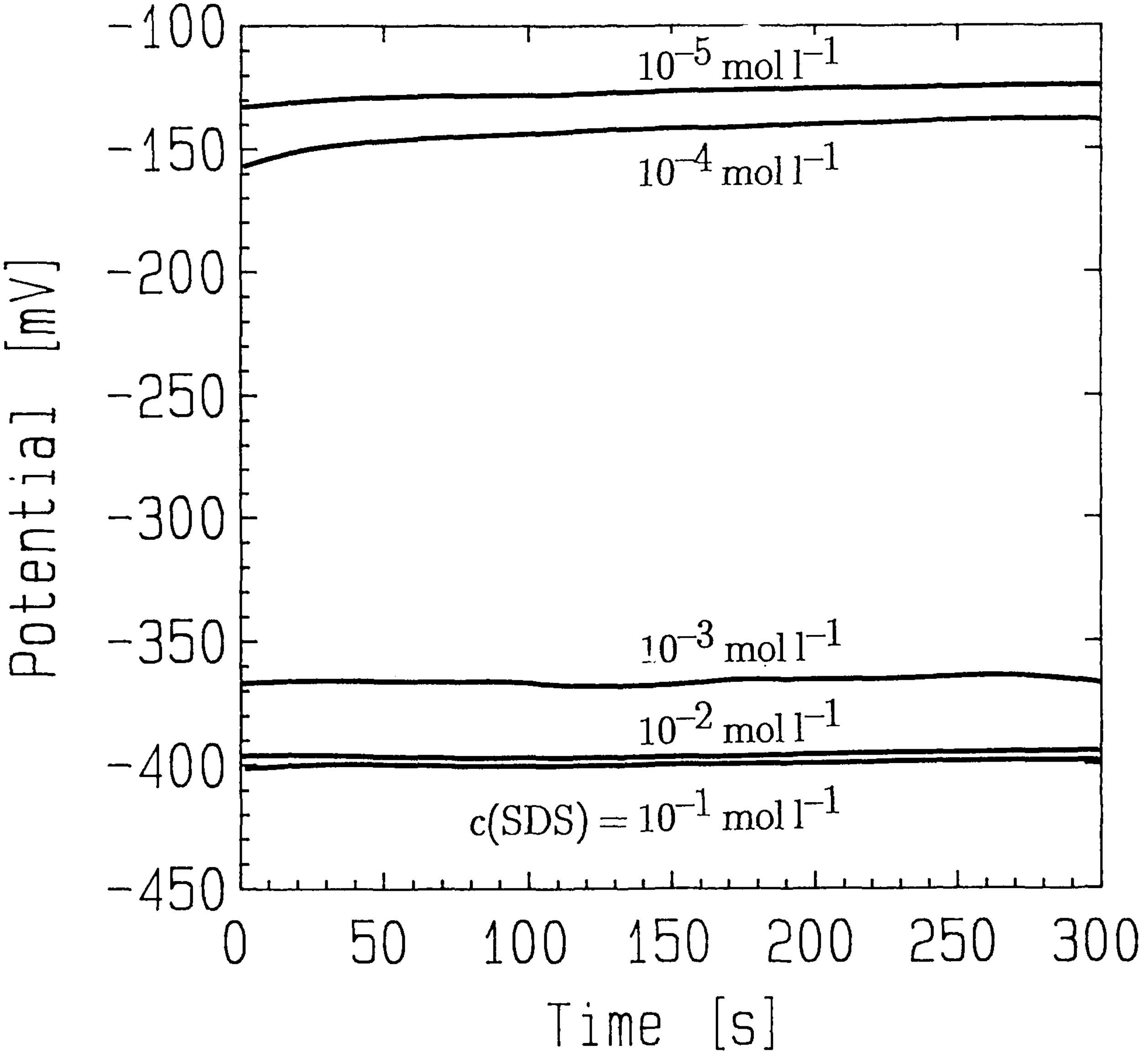

dodecyl sulfate (nb) ⟶ dodecyl sulfate (water)
dodecyl sulfate (water) ⟶
dodecyl sulfate (nb)
1
2
3
4
5
20
10
0
−10
−20
−30
200
300
400
500
Current [nA]
Potential [mV]

8

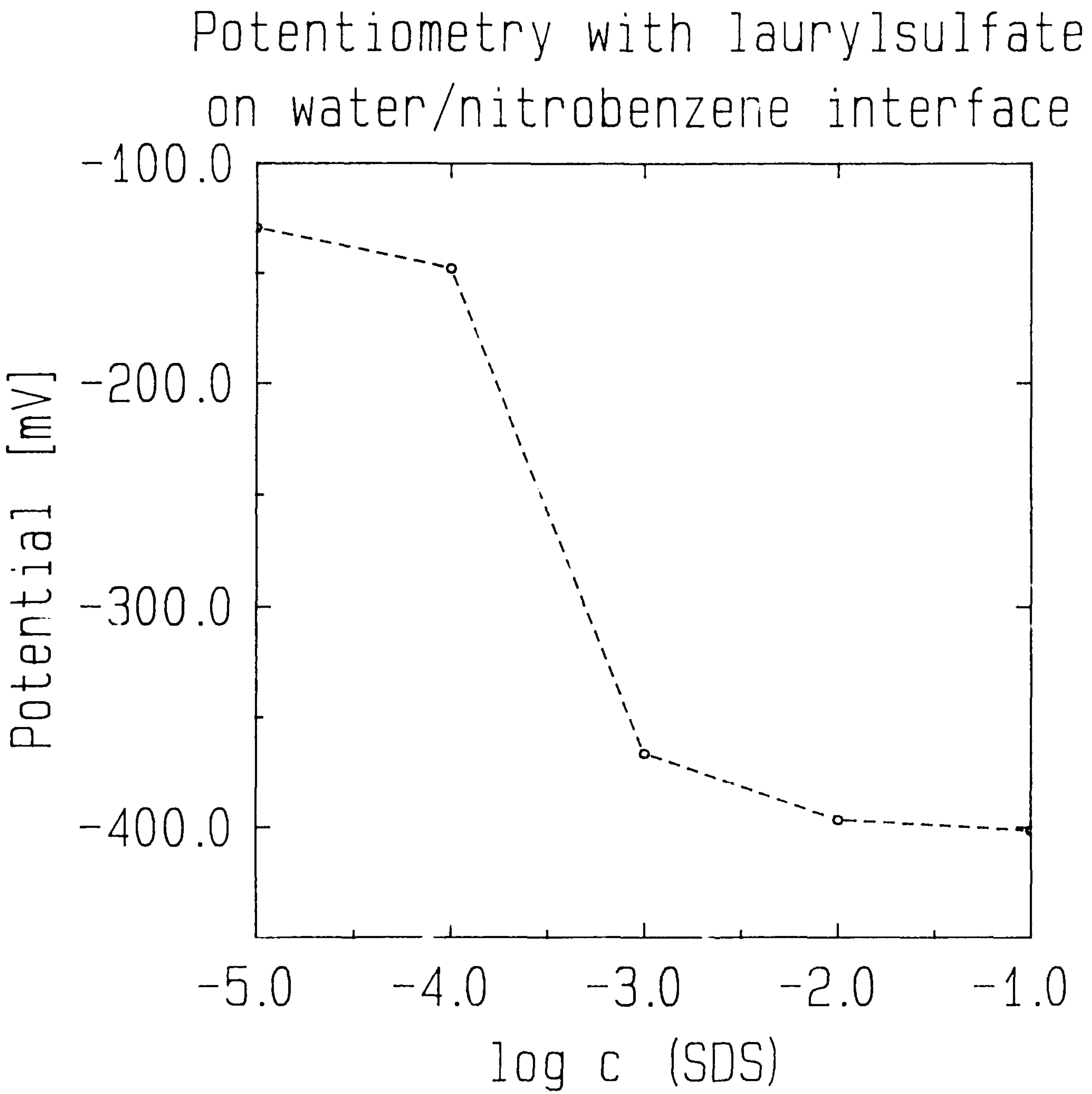


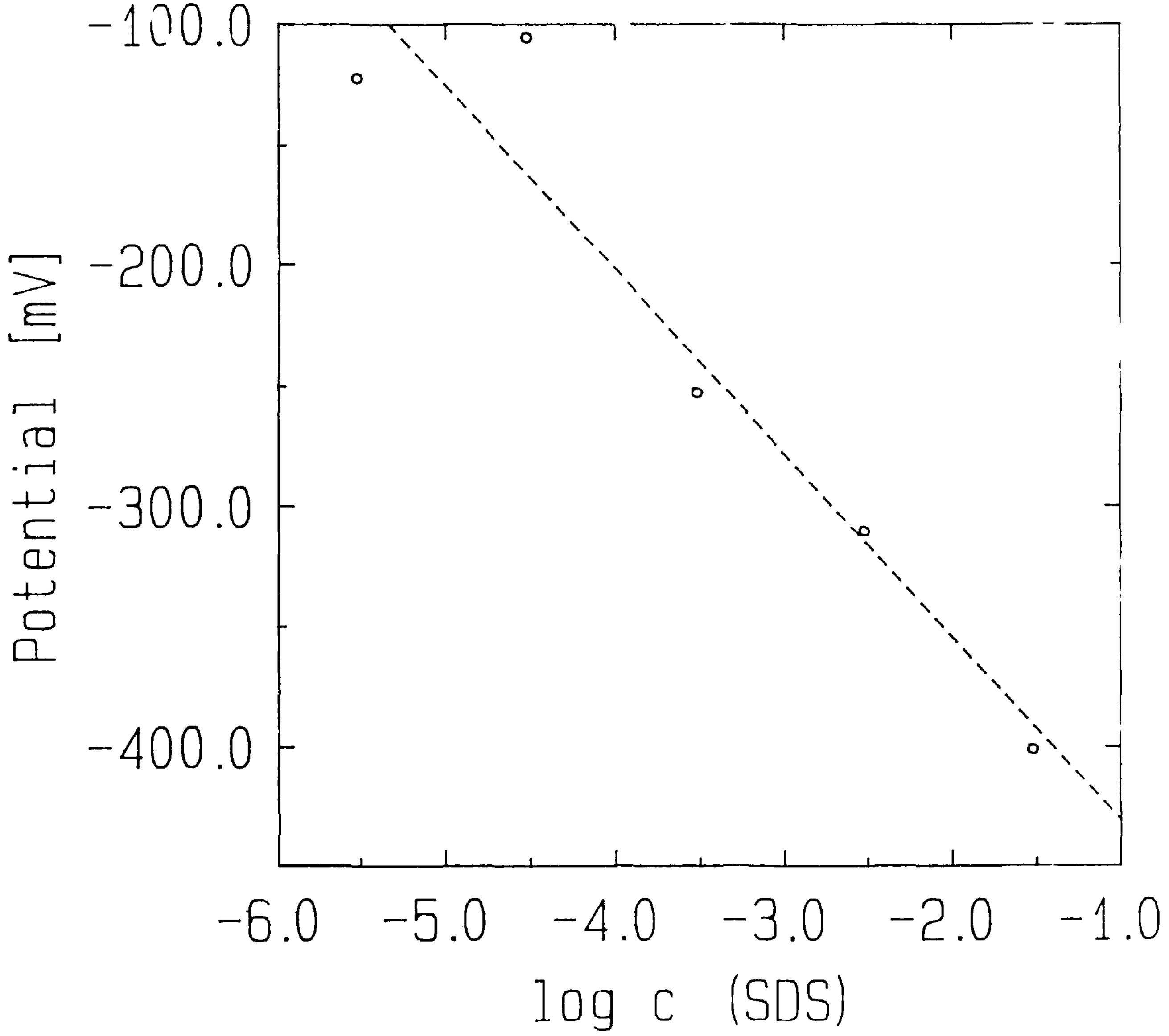
9


Current [nA]
40.0
30.0
20.0
10.0
0.0
0.0
0.5
1.0
1.5
Concentration [mmol/l]


-100
-150
-200
-250
-300
-350
-400
-450
Potential [mV]
0
50
100
150
200
250
300
Time [s]
10^{-5} mol l^{-1}
10^{-4} mol l^{-1}
10^{-3} mol l^{-1}
10^{-2} mol l^{-1}
$c(SDS) = 10^{-1}$ mol l^{-1}

//


Potentiometry with laurylsulfate
on water/nitrobenzene interface
Potential [mV]
-100.0
-200.0
-300.0
-400.0
-5.0
-4.0
-3.0
-2.0
-1.0
log c (SDS)


Potentiometry with laurylsulfate on PEG/dextran interface