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Interfacial tension studies of electrified liquid/liquid interfaces: Classical techniques for new data

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INTERFACIAL TENSION STUDIES OF ELECTRIFIED LIQUID/LIQUID INTERFACES: CLASSICAL TECHNIQUES FOR NEW DATA

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Several general methods used in measurement of interfacial tension are reviewed. Consideration is given to methods that can be used on interfaces with externally applied potential and current flow. A classical technique of interfacial tension measurement, the maximum bubble pressure method, is used to study an interface between two immiscible solutions of electrolytes. This work focuses on data interpretation of systems under interfacial ion transfer. A series of quaternary ammonium cations at a range of concentrations spanning several orders of magnitude are investigated. It is suggested how the data can be used to determine the Esin–Markov coefficient and to estimate interfacial ion adsorption and changes of the interface due to current flow.

Interfacial tension (IFT) measurements on interfaces between two immiscible electrolyte solutions (ITIES) pose a challenging experimental problem. Whereas many techniques for interfacial tension measurements between two immiscible liquids are reliable for work with liquids in equilibrium (1), few are suitable for situations where the liquids are either in a steady state or where an interfacial process is under way.

The most frequently used methods for determination of interfacial tension are the capillary rise method, a flow technique, several detachment methods, pendant and sessile drop methods and the method of a liquid bridge. Whenever two phases are brought in contact it has to be considered whether the phases are in equilibrium. In the case of immiscible liquids the concentration of analyte at the interface can be different from that in the bulk. Adsorption at the interface, orientation of molecules and changes in solvation also can take place. After contacting the two immiscible phases a period of time can lapse before equilibrium is achieved. That will be especially true in cases of immiscible liquids when dissolved analyte has to repartition. If the solution volumes are large and diffusion is the mass transport, it is often likely that a steady state, rather then equilibrium, will be reached.

In the case of interfaces between ionic phases the interface is also a site of electrical potential. Conversely, imposition of electric potential on the interface can be used to alter the interfacial concentrations to accommodate the new equilibrium. Therefore only those IFT methods, that allow interfacial potential measurement and current flow across the interface are of value. In particular when current is expected to flow through the system, provisions have to be made to allow for current flow without *IR* drop or without restrictions due to diffusion mass transport flow.

Capillary elevation technique, although the most exact method for surface tension (liquid–air), is usually not suitable for electrified interfaces where current flow is expected. The primary concern in this case would be the narrow capillary which would increase the circuit resistance. From this point of view the interfaces of larger areas are more desirable. Techniques that require a larger interface are the De Noüy ring and the Wilhelmy plate methods. The ring method is based on determination of the force needed to tear the ring, held at the interface by interfacial forces, off the interface. The ring, typically made from platinum wire, has to be coated by suitable insulating material such as paraffin, to prevent shorting of the interface (2). The Wilhelmy plate method is more suitable for the ITIES work because in this case a thin glass plate (electrically insulating) is pulled through the interface and the required force is recorded. This method was successfully employed by Higgins and Corn (3).

INTERFACIAL TENSION OF ITIES

The most prevalent method of interfacial measurement on ITIES is the drop weight (size) method. A practical procedure is described by Gavach, Seta and d'Epenoux (4). The size and shape of the drop can be used also for the purpose of this measurement. Digital imaging of the drop silhouette first used by Schiffrin (5) is now also commonly used (6). A new instrument was developed to measure accurately in automated way interfacial tension from the time elapsed for a known number of liquid droplets, formed under a constant flow rate, to detach from a submerged capillary orifice (7).

ITIES is a system in which two immiscible liquids, such as water and nitrobenzene with dissolved aqueous (e.g., LiCl) and nonaqueous (e.g., tetrabutylammonium tetraphenylborate) supporting electrolytes are in contact. An interface of such a makeup has the properties of an essentially ideally polarizable interface. Within a certain region (about 500 mV) the interface can be polarized without significant current flow through it. It is this current, however, caused by repartitioning of ions of the supporting electrolytes, that makes this interface a dynamic, rather then an equilibrium system.

Even greater complication arises in IFT measurements from the situation where a semihydrophobic ion is present in the system in addition to the supporting electrolytes. Such an ion can be transported from one phase to the other within the supporting electrolyte window. The recorded current *vs.* potential characteristics is the very basis for the electrochemistry on ITIES. However, because this transport is almost in all cases time dependent, interfacial tension measurements, unless they are made in a real time, will always be time averages.

Upon polarization of ITIES a change in the interfacial tension occurs. This behavior of ITIES follows well the existing Gouy–Chapman theory and its later modifications (8). Understanding of changes in interfacial tension is essential for a thorough study of double–layers arising on ITIES. To understand the relationship between interfacial tension and electrical parameters of the interface, it is possible to invoke the formalism of the metal interface thermodynamics and apply it to ITIES.

The dependence of interfacial tension (γ) on the interfacial electrical potential can be described by the Gibbs–Lippmann equation:

$$d\,\gamma = -\,q\,d\varphi_w^o - \Sigma\,\Gamma_i\,d\mu_i\,. \qquad [1]$$

Here q is the interfacial charge density, φ_w^o is the water/oil interfacial potential, Γ_i is the surface excess (surface concentration) of ion *i* at the interface and μ_i it the chemical potential of the involved ion.

The first derivative of equation [1] is equal to the surface charge density

$$-\left[\frac{\partial\,\gamma}{\partial\,\varphi_w^o}\right]_{p,\,T,\,\mu_i} = q \qquad , \qquad [2]$$

The second derivative is the differential capacitance of the interface

$$\left[\frac{\partial^2\gamma}{\partial\,{\varphi_w^o}^2}\right]_{p,\,T,\,\mu_i} = \left[\frac{\partial\,q}{\partial\varphi_w^o}\right]_{p,\,T,\,\mu_i} = C_d \qquad [3]$$

This quantity is in general a function of the interfacial capacitance whose derivation for metal electrode follows from the Gouy–Chapman theory. In its approximate validity it also holds for the ITIES.

$$C_d = \left[\frac{2z^2F^2\epsilon\epsilon_0 c}{RT}\right]^{1/2}\cosh\left[\frac{zF\varphi_w^o}{2\,RT}\right] \qquad [4]$$

where z is the charge of the considered ions, F is the Faraday constant, R is the gas constant, T is absolute temperature, c is concentration, ϵ_0 is the permittivity of vacuum and ϵ is the relative permittivity of the interfacial region.

It is certainly easier with contemporary instrumentation to acquire impedance spectra than perform mechanical measurements of IFT. However, assignment of interfacial capacitance from impedance data is not always easy and it can be equivocal. Therefore IFT measurements are a valuable complement to impedance data.

INSTRUMENTATION

The interfacial tension technique and instrumentation used in our work are the same as used previously by Reid, Melroy and Buck (9). Its principle is based on the maximum bubble pressure method. The advantage of this technique in the non–equilibrium systems is that a fresh interface is formed before each measurement and thus hysteresis and long–time effects of ion repartitioning are eliminated. The key part of the system is a sensitive pressure controller connected to the inner atmosphere of the reservoir holding the nonaqueous phase. It allows to vary with high precision the gas pressure exerted on the liquid in the bulb. The liquid from the reservoir is expelled through a calibrated capillary into a thermostated bath of the aqueous phase. The pressure p needed for expulsion of the nonaqueous solution from the capillary is used to determine the interfacial tension γ through a relationship

$$p = h\, g\, \Delta\, \rho + 2\, \gamma / r, \qquad [5]$$

where h is the depth of the capillary immersion, g is the gravitational constant, $\Delta\ \rho$ is the density of the liquid (water) above the capillary and r is the radius of the capillary. The available precision of the method is primarily determined by the ability to control and measure the depth of immersion and the solutions heights.

The glass cell used in the measurement is show in Fig. 1. Because interfacial tension is temperature dependent, the container holding the aqueous phase is equipped with a hollow jacket allowing flow of thermostated liquid. All measurements reported here were done at 25 °C. The bulb containing the nonaqueous liquid is obviously maintained at the same temperature. It is filled with known volume of appropriate nonaqueous solution and connected with a hose at the point of the arrow to a precision pressure controller RUSKA DDR 600 (Houston, TX).

The operation of the pressure controller is manual. For the measurement a pressure inside the bulb is gradually increased and the orifice of the capillary is observed. The pressure inside a drop is inversely proportional to it diameter. Therefore the pressure inside the drop is the highest before it begins to for. Thus, one this critical pressure is reached, the drop starts to form without any further restriction and steady flow of drops will be observed. the pressure at which this occurs is then recorded used for calculation of the IFT. It should be possible to calculate from the know parameters of equation [5] the absolute IFT values. In practice the least certain value is the radius of the drop that is equated to the diameter of the capillary. The diameter of the used capillary was determined to be 0.4 mm. The work with know liquids suggests a larger diameter, about 0.42 mm. Therefore, for a practical measurement the calculated data are standardized against liquids or gases of know IFT.

The cell design allows to polarize the interface at the position of the forming drop. Because some of the studied interfaces pass electric current upon polarization, compensation of *IR* drop associated with current flow through long capillaries needs to be compensated. Therefore a four–electrode potentiostat (Solartron 1286) was used in this work. The four electrode connections of the potentiostat are made to two reference and two auxiliary electrodes, as shown in Fig. 1. Figure 2 shows in detail the reference electrode for the nonaqueous phase. Its upper part contains aqueous tetrabutylammonium chloride bathing a Ag/AgCl electrode. The bottom part contains a nitrobenzene solution of tetrabutylammonium tetraphenylborate. Thus, a chain of interfaces with constant potentials is established.

Nonaqueous phase inside the bulb contained typically only a hydrophobic supporting electrolyte at a constant concentration. The nonaqueous solvent in this work was nitrobenzene. The makeup of the aqueous phase was varied and a series of progressively more hydrophobic cations (tetramethyl–, tetraethyl–, tetrapropyl– and tetrabutylammonium) at concentrations spanning several orders of magnitude were measured. The point–by–point interfacial pressure data were recorded at a sequence of applied interfacial potentials. Since the interfacial tension is a measure of the state of the interface, even at nonequilibrium state, it is used to investigate the properties of the interface under current flow conditions. It was also used in an attempt to determine the Esin–Markov coefficient to estimate interfacial adsorption as a function of concentration and length of the quaternary ammonium ions.

Interfacial tension and capacitance are closely related. Our study complements capacitance results and compares the data obtained with the maximum pressure method to those calculated from impedance spectroscopy data. The comparison is a useful tool in analysis of impedance spectroscopy data. Although capacitance measurement is at current state of technology a simpler and more automated task then the bubble pressure approach, the correct assignment of impedance data to the interfacial capacitance and to other circuit components, such as charge transfer resistance in the system with current flow, is not a straightforward task. Therefore independently obtained data from interfacial tension measurements allow correct interpretation of individual components in an impedance spectroscopy model.

RESULTS

As is with every experimental technique, main concern is reproducibility and repeatability of the measurements. Figure 3 shows interfacial tension of aqueous phase (with LiCl) and nitrobenzene phase (with tetrabutylammonium tetraphenylborate) as a function of applied interfacial potential. The hysteresis observed on the curve is a repeatable phenomenon. It has to do with repartitioning of ions at the interface as a result of applied interfacial potential. The rate of this repartitioning is governed by diffusion and is therefore fairly slow. The repartitioning alters the chemical makeup of the immediate interface environment and contributes to the hysteresis. Other factor is the fate of the repartitioned ions. In some cases the ions transported into the opposite phase combine with a counter–ion to form an insoluble salt. This material will adsorb on the interface, altering ultimately IFT.

Using of the drop has the inherent potential to lower the hysteresis. Renewing interface by dislodging contaminated drops makes this possible, although it appears that residual contaminants remain at the neck of the newly formed drop and the hysteresis is never eliminated fully.

The above example in Fig. 3 is for an interface that is in principle ideally polarizable and thus passes only limited amount of ions upon its polarization. A liquid/liquid system with a common ion in both phases will experience much greater extend of repartitioning. The progress of repartitioning can be followed potentiometrically as the concentration ratio at the interface changes the interfacial potential. Figure 4 shows the change in potential at water/nitrobenzene interface as a result of concentration step [10]. This time–dependent process is responsible for a uncertainty in voltammetric studies of fresh (non–equilibrated) L/L interfaces as well as IFT data.

Figure 5 is an example of a data set obtained for IFT measured in a system with ion flow across interface. Tetramethylammonium originally present in in aqueous phase can be transported by applied potential to nitrobenzene. The charge flow across the interface influences the measured apparent interfacial tension. It still remains a point of discussion to what extent the Guy–Chapman curves can be used for nonequilibrium systems. There are maxima in γ observed for each concentration which correspond to normal electrocapillary curves. The maxima observed on metal electrodes are usually associated with the potential of zero charge. Correspondingly, on liquid interfaces the maximum appears when the interface has to lowest surface excess concentration of ions combined for both phases.

An attempt was made to determine whether the potential of the observed maxima depends on species concentration. Using Esin–Markov theory it would be possible to obtain data on specific adsorption. The uncertainly of the potential of maximum is so far too large and does not allow a quantitative evaluation.

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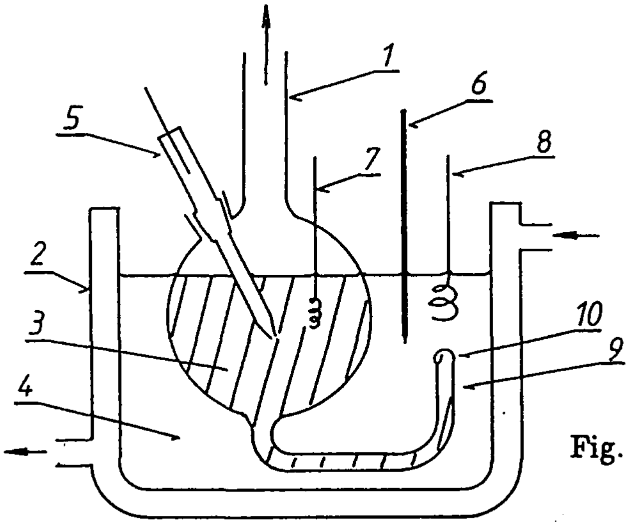

Fig. 1

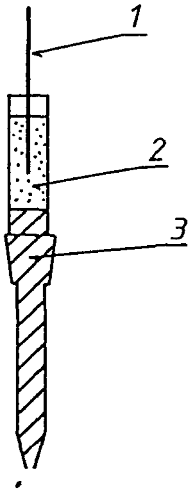

Fig. 2

Fig. 1 Diagram of the cell with expulsion capillary used for the interfacial tension measurements. *1* – body of the cell with outlet (arrow) to the pressure controller, *2* – aqueous phase vessel with jacket and outlet to a thermostat (arrows), *3* – nonaqueous phase, *4* – aqueous phase, *5* – nonaqueous reference electrode, *6* – aqueous reference electrode, *7* – nonaqueous auxiliary electrode, *8* – aqueous auxiliary electrode, *9* – expulsion capillary, *10* – formation of the drop.

Fig. 2 Detail of the nonaqueous reference electrode (*5* in Fig. 1). *1* – Ag/AgCl, *2* – aqueous phase with tetrabutylammonium chloride, *3* – nonaqueous phase with tetrabutylammonium tetraphenylborate.

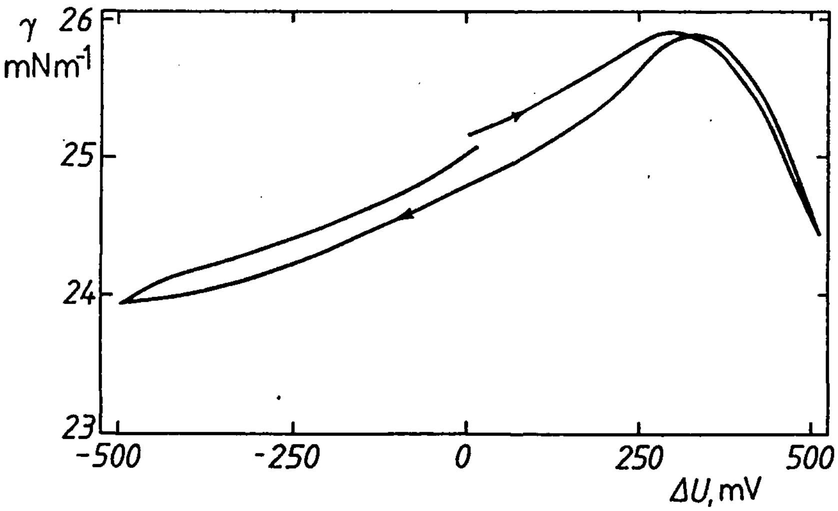

Fig. 3 Interfacial tension of an ideally polarizable interface as a function of applied potential. Water phase – 0.01 mol/l LiCl, nitrobenzene phase – 0.01 mol/l tetrabutylammonium tetraphenylborate.

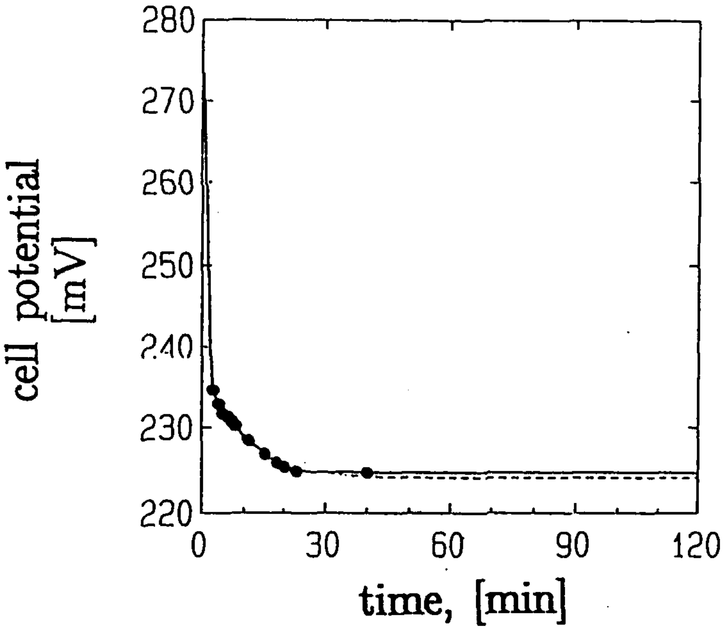

Fig. 4. Time dependence of a L/L interfacial potential after a concentration jump of tetrabutylammonium chloride from 0.01 mol/l to 0.001 mol/l. Solid line with points – recorded values, dashed line – exponential fit to the experimental points. (after reference (10)).

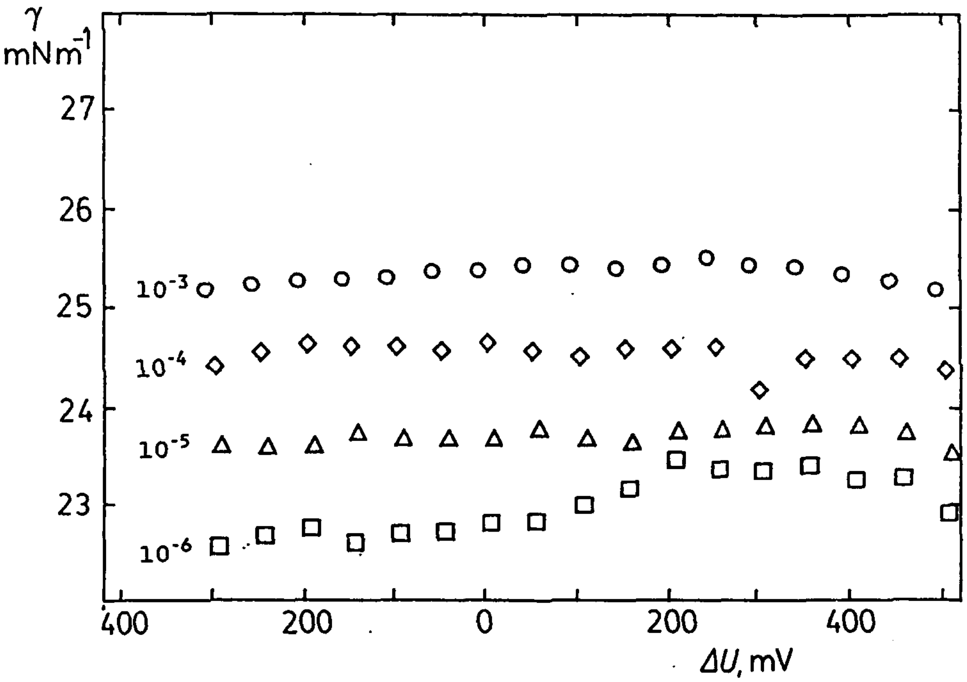

Fig. 5. Interfacial tension of an interface in the presence of tetramethylammonium as a function of applied potential. Nitrobenzene phase – 0.01 mol/l tetrabutylammonium tetraphenylborate, water – tetramethylammonium at concentrations marked (in mol/l) in the graph.

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