

Charge Transfer across Liquid-Liquid Interfaces

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Although electrochemical studies of the interface between two immiscible electrolyte solutions (ITIES) started at the beginning of the century, this field of electrochemistry has remained in the background for a long time. The breakthrough came only in the early 1970s when Gavach and his colleagues in Montpellier (France) demonstrated that this type of interface could be polarized,¹ and that the Galvani potential difference between the two phases could be used as a driving force for charge transfer reactions. There are basically two types of reactions that can be driven electrochemically: (1) ion transfer and (2) electron transfer. Historically, most of the work was concerned with the study of ion transfer and facilitated ion transfer reactions, as those were readily amenable to experimental investigations. The principal obstacle to the study of electron transfer reactions has been the difficulty in identifying redox couples for which the products of the electron transfer reactions would not cross the interface, thereby generating ionic transfer currents that would impede the measurements.

At the beginning, when Gavach *et al.* [2-6] and later Koryta *et al.* [7-9] pioneered electrochemical studies of what is now often

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referred to as ITIES very little was known about the structure of the interface between two immiscible liquids and more importantly about the polarization distribution at this interface. Some theoretical calculations based on the idea that the interface between two immiscible electrolyte solutions could be represented as two back-to-back, diffuse Gouy–Chapman layers had been carried out by Verwey and Niessen as early as 1939,¹⁰ but had never been corroborated by experiments. Most of the results obtained by the French and Czech groups were at that time (1968–1980) analyzed using a direct transposition of the theories developed for metal–electrolytes systems. In this early period, most of the experimental work was based on applied current methodology, as it was only in 1979 that Samec *et al.*¹¹ introduced the concept of the 4-electrode potentiostat, enabling a potentiostatic control of the interfacial potential difference. This experimental approach opened the way to the modern studies of both the interfacial structure of the ITIES and of charge transfer reactions.

Until very recently, most of the publications in this area of electrochemistry reported mainly experimental results. However, in the last few years, theoreticians started to take interest in what must be a new green pasture for them, and as a result few models of interfacial structure or charge transfer processes have been proposed.

The purpose of this review is to give first a brief summary of the generally accepted models for the interfacial structure of the ITIES and to review more thoroughly the different types of charge transfer reactions, including those which are photoinduced.

The elementary thermodynamics of the polarized liquid–liquid interface have been largely covered in previous reviews [12–19] and will therefore not be repeated.

I. THE INTERFACE

The pioneering electrochemical investigation of the structure of the ITIES was carried out in 1977 by Gavach and co-workers.^{20,21} They studied first the interface between two solutions of tetraalkylammonium bromide partitioned between water and nitrobenzene. By varying the concentration of the salt and by

measuring the interfacial tension by the drop weight method, they were able to demonstrate the presence of specific adsorption, especially for the large tetraalkylammonium ions. Indeed, if we call $\Gamma_i^{\alpha,\beta}$ the surface excess of a species, i , with respect to the bulk of the adjoining phases, α and β , it is easy to show from the electroneutrality of the interphase,

$$\Gamma_{C^+}^{\alpha,\beta} = \Gamma_{A^-}^{\alpha,\beta} = \Gamma_{\text{Salt}}^{\alpha,\beta} \quad (1)$$

that the surface excess concentration of a salt C^+A^- , $\Gamma_{\text{Salt}}^{\alpha,\beta}$, is given by

$$\Gamma_{\text{Salt}}^{\alpha,\beta} = -\frac{1}{2RT} \left[\frac{\partial \gamma}{\partial (\ln a)} \right]_{T,P} \quad (2)$$

Similar surface tension results were reported by Boguslavsky,^{22,23} which confirmed the specific adsorption of hydrophobic ions at the interface. Gavach *et al.*²⁰ proposed that the observed specific adsorption was taking place by the formation of interfacial ion pairs. In their second paper²¹ they studied the interface between a solution of sodium bromide in water and tetraalkylammonium tetraphenylborate in nitrobenzene. They were able to control the Galvani potential difference across this polarizable interface by adding tiny amounts of tetraalkylammonium bromide to the aqueous side and were able in this way to construct, point by point, an electrocapillary curve for this system. This very interesting result, reproduced in Fig. 1, shows that the electrocapillary curves obtained were the same for the 3 tetraalkylammonium cations used (i.e., tetraethyl-, tetrapropyl-, and tetrabutylammonium) when centered on the potential of zero charge (PZC) but more importantly that this unique curve corresponded to that obtained from the integration of the charge, q , predicted by the Gouy-Chapman theory:

$$q = [8RT\epsilon^n C^n]^{1/2} \sinh \left[\frac{F}{2RT} (\Delta\phi - \phi_{2w} - \chi) \right] \quad (3)$$

where ϵ^n and C^n are the permittivity and the salt concentration in the nitrobenzene phase, respectively, where $\Delta\phi$ is the potential difference between the two phases, ϕ_{2w} is the potential drop in the

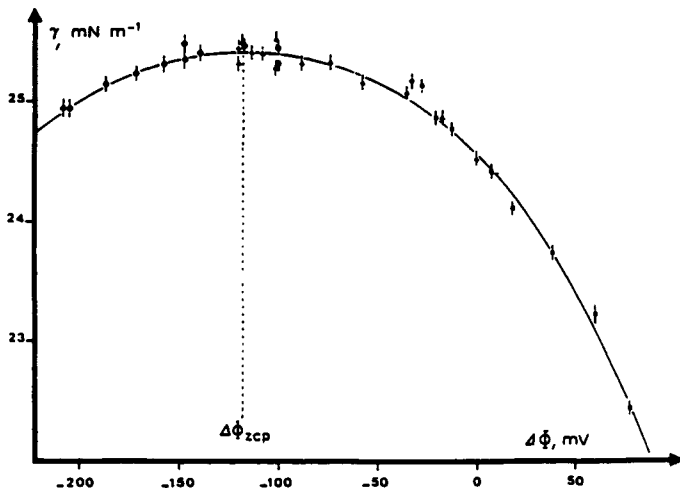


Figure 1. Electrocapillary curve: variation of the interfacial tension with the Galvani potential difference $\Delta\phi$. Filled circle, square, and triangle, experimental values and solid line, calculated values obtained by integration of charge derived from Gouy–Chapman theory. (Reprinted from Ref. 21 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

aqueous diffuse layer and χ the potential drop across the compact layer. The potential drop in the diffuse layer was in turn calculated from the Gouy–Chapman theory as being equal to

$$\phi_{2w} = \frac{RT}{F} \ln \left[\frac{(\epsilon^w C^w)^{1/2} + (\epsilon^n C^n)^{1/2} \exp[(F/2RT)(\Delta\phi - \chi)]}{(\epsilon^w C^w)^{1/2} + (\epsilon^n C^n)^{1/2} \exp[-(F/2RT)(\Delta\phi - \chi)]} \right] \quad (4)$$

This paper was a landmark not only from an experimental point of view but also because the authors proposed an interfacial model which pictures the interface as a “compact layer” of orientated dipole molecules separating the two diffuse layers. Nowadays, this model is often referred to as the modified Verwey–Niessen (MVN) model. Another very interesting conclusion of this work is that the potential drop across the compact layer was found to be negligible. A very similar experimental approach was followed by Buck *et al.*,²⁴ who obtained similar results for a tetraalkylammonium series ranging from tetramethyl- to tetrahexylammonium. In particular,

they confirmed that the potential drop across the compact layer was equal to zero within experimental error.

From Eq. (4), it is possible to calculate the Galvani potential profile across the space charged region by a conventional Gouy-Chapman derivation. Figure 2 illustrates the potential distribution for the interface between an aqueous solution of potassium chloride and a solution of tetrabutylammonium tetraphenylborate (TBATPB) in 1,2-dichloroethane.

Following the pioneering work of Gavach *et al.*,^{20,21} the early 1980s have seen the publications of three series of work dedicated to the study of N the water-nitrobenzene and the water-1,2-dichloroethane interfaces.

Using a drop time method for the determination of interfacial tension and a four-electrode potentiostat to polarize the interface, Kakiuchi and Senda^{26,27} measured electrocapillary curves for ideally polarized systems, in particular for the interface between an aqueous solution of lithium chloride and a solution in nitrobenzene of TBATPB. They showed that the surface charge density, Q , obtained by differentiation of the electrocapillary curve was equal to that calculated from the integration of the corresponding differential capacity versus potential curves. This demonstrated the validity of the Lippmann equation for the polarized ITIES:

$$Q = - \left(\frac{\partial \gamma}{\partial \Delta \phi} \right)_{\mu, T, P} \quad (5)$$

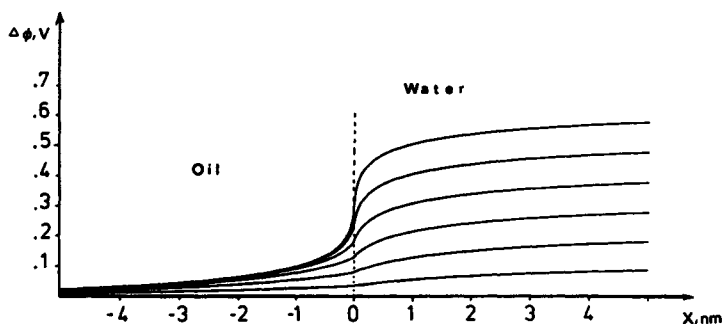


Figure 2. Potential distribution across the interface between 10 mM KCl in water and 1 mM TBATPB in 1,2-DCE for different applied interfacial potentials. (Reprinted from Ref. 25 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

They analyzed their results using a thermodynamic approach based on the Gibbs adsorption equation²⁸ and the main conclusion of their work was that relative surface excesses of the ionic species were well described by the Gouy–Chapman theory. They adopted the MVN model of the ideally polarized interface stating that the compact layer is an ion-free layer consisting of “laminated layers of water and nitrobenzene” sandwiched between two diffuse layers. The potential difference across this inner layer was estimated to be about 20 mV at the PZC but was found to vary with the surface charge density.

At the same period, Girault and Schiffrin using a video technique²⁹ to measure interfacial tension by the pendant drop method, studied the surface excess of water at the interface between pure organic solvents and aqueous electrolytes³⁰. They showed that in the case of polar solvents, contrarily to the air–electrolyte or metal–electrolyte systems, the surface excess of water was less than the equivalent of one monolayer. These results suggested that ions penetrate the interfacial region, leading these authors to conclude that the interface comprised a mixed solvent layer. They also studied another ideally polarized interface, namely that between an aqueous solution of potassium chloride and a solution of TBATPB in 1,2-dichloroethane.³¹ Again their results verified the Lippmann equation. However, they observed that the electrocapillary maximum did not coincide with the minimum of the measured capacitance curve but coincided with the PZC as measured by the streaming electrolyte method.³² They analyzed their results using a somewhat different thermodynamic approach based on the Guggenheim model of interfacial phase. The main difference with that proposed earlier by Kakiuchi and Senda²⁸ was that it clearly demonstrated how interfacial ion pairs, formed with an ion from each of the adjacent phases, contributed to the thermodynamic charge density, Q , defined as

$$\begin{aligned}
 Q &= -F \left(\frac{\partial \gamma}{\partial \Delta \phi} \right)_{\mu_{\text{KCl}}, \mu_{\text{TBATPB}}} \\
 &= F [(\Gamma_{\text{Cl}}^{o,w} - \Gamma_{\text{K}}^{o,w}) + (\Gamma_{\text{TBACl}}^{o,w} - \Gamma_{\text{KTPB}}^{o,w})] \quad (6)
 \end{aligned}$$

The third series of papers on the subject was published by Samec *et al.*^{33–36} who chose to measure capacitance data for dif-

ferent interfaces. The common conclusion of this series of 4 papers was that the Gouy-Chapman theory applied to the simplest MVN model of two back-to-back, diffuse layers could account for the experimental data. The results also confirmed that the interfacial potential drop across the mixed solvent layer was negligible in the vicinity of the PZC. Although Samec *et al.* keep on referring to the interfacial mixed solvent layer as the inner layer, which is an expression belonging to the vocabulary of the mercury-electrolyte interface and used to describe a layer of orientated dipole molecules, they clearly state that "the boundary between the space charge region and the inner layer is considered to be diffuse rather than sharp"³³ and that "ions are allowed to penetrate into the inner layer over some distance."³⁵ It appears therefore that the difference between the interfacial mixed solvent layer proposed by Girault and Schiffrin and the inner layer model supported by Samec *et al.* is only a matter of semantics as the physical pictures emerging from the two models are similar. It is also interesting to note that Samec *et al.*³³⁻³⁶ did not find any evidence for the specific adsorption of ions or ion pairs for the systems studied. The overall picture emerging from these 3 series of papers can be summarized as follows:

The interface can be described as a mixed solvent layer separating two diffuse layers.

Most of the charge is distributed between the two back-to-back, diffuse layers, hence the relatively good agreement with the Gouy-Chapman theory which when examined closely appears more qualitative than quantitative.

The potential drop across the interfacial mixed solvent layer is negligible near the PZC.

The third conclusion is quite important as it states that the Galvani potential difference at the PZC is equal to zero. This statement is in fact an extra thermodynamic assumption which fixes the zero of the scale of ionic Gibbs energy of transfer as proposed by Girault and Schiffrin.³⁷

The main discrepancy between the investigations described above concerns the presence or absence of specific adsorption at the ITIES. Both Kakiuchi and Senda²⁶⁻²⁸ and Samec *et al.*³³⁻³⁶

concluded the absence of adsorbed interfacial ion pairs. On the other hand, Girault and Schiffrin³¹ assigned the observed difference between the PZC, or electrocapillary maximum, and the minimum of the capacitance curve to the presence of specific adsorption. Such a difference was also observed by Koczorowski *et al.*^{38,39} for both the water–nitrobenzene + benzene and the water–1,2-dichloroethane interfaces. This important problem of specific adsorption has been recently addressed by Schiffrin *et al.*,⁴⁰ who used the Bjerrum theory of ion pair formation to calculate the contribution of specific adsorption to the interfacial capacitance. As illustrated in Fig. 3, the capacitance increases markedly in the positive potential range (water versus oil) in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, indicating that the cations are specifically adsorbed. The conclusion reached by the Liverpool group was that a mixed solvent layer, with penetration of the ion pairs

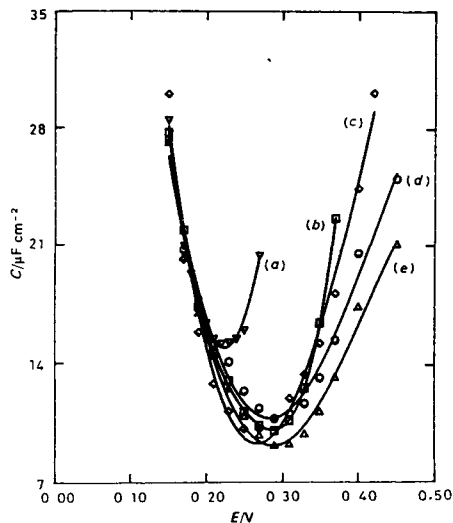


Figure 3. Potential–capacitance curves for the alkali–metal chlorides studied. The concentration of the electrolytes in both phases was 10^2 mol dm^3 (see cell I). (a) CsCl, (b) RbCl, (c) KCl, (d) NaCl, (e) LiCl (Reprinted from Ref. 40 with permission. Copyright The Royal Society of Chemistry, London.)

dependent on the ionic radii, best represented the structure of the ITIES.

All these experimental results have been recently complemented by a very useful theoretical study by Kharkats and Ulstrup,⁴¹ who calculated analytically the electrostatic Gibbs energy profile of an ion between two dielectric phases separated by a planar boundary, incorporating both the ionic finite size and the dielectric image interactions. The profile obtained, illustrated in Fig. 4, shows that there is no discontinuity as the ion traverses the boundary and that cation and anion concentration distribution will differ if they have different ionic radii, as they will penetrate the boundary to a different extent. This has important repercussions on the Poisson-Boltzman equation as the work term is not only the electrical energy, $zF(\phi - \phi^b)$, but also an electrostatic contribution to the Gibbs energy of solvation as the ion

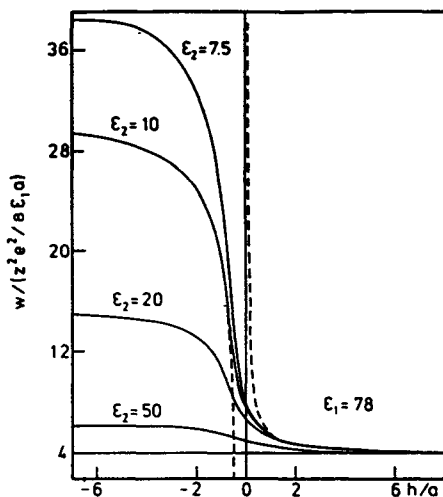


Figure 4. Electrostatic Gibbs energy profiles for ion transfer across the ITIES boundary. Solid lines: finite-size ion profiles in units of $(ze)^2/\epsilon_1 a$, $\epsilon_1 = 78$ and different values of ϵ_2 . Dashed lines: profile for the point charge model in the same units, $\epsilon_1 = 78$, $\epsilon_2 = 10$. (Reprinted from Ref. 41 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

approaches the interface and starts to feel the image forces. The additional work term obtained by Kharkats and Ulstrup is

$$W = \frac{(ze)^2}{8\varepsilon_1 a} \left\{ 4 + \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) \frac{2}{h/a} + \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^2 \left(\frac{2}{1 - (h/a)^2} + \frac{1}{2h/a} \ln \left[\frac{2h/a + 1}{2h/a - 1} \right] \right) \right\} \quad (7)$$

in the region $h > a$, where h is the distance between the boundary and the center of the ion and a is the ionic radius. The first term of Eq. (7) represents the Born solvation energy, the second is the interaction of the ion with its image (independent of ionic radius), and the third stems from the consideration of the finite size of the ion. When $0 < h < a$, we have

$$W = \frac{(ze)^2}{8\varepsilon_1 a} \left\{ \left(2 + \frac{2h}{a} \right) + \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) \left(4 - \frac{2h}{a} \right) + \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^2 \left(\frac{(1 + h/a)(1 - h/a)}{1 + 2h/a} + \frac{1}{2h/a} \ln \left[1 + \frac{2h}{a} \right] \right) \right\} + \frac{(ze)^2}{4\varepsilon_2 a} \left(\frac{2\varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) \left(1 - \frac{h}{a} \right) \quad (8)$$

The limiting form when the ionic center is located on the boundary (i.e., when $h = 0$) is simply

$$W = \frac{(ze)^2}{a(\varepsilon_1 + \varepsilon_2)} \quad (9)$$

The Gibbs electrostatic energy at the boundary depends symmetrically on the two dielectric permittivities, but is not equal to the average of the two Born solvation energies.

As mentioned by Kharkats and Ulstrup,⁴¹ simple dielectric considerations show that excess surface charges are expected on the side of the ITIES with a low dielectric constant, i.e., the organic phase accompanied by a surface charge depletion on the aqueous side. This very simple argument leads to the conclusion that hydrophobic ions in the organic phase are likely to be specifically adsorbed. The experimental results of Schiffrin *et al.*,⁴⁰ which show that the interfacial capacitance depends on the nature of the aqueous counterion demonstrate that this specific adsorption occurs via the formation of interfacial ion pairs.

The work of Kharkats and Ulstrup⁴¹ has also an interesting bearing on the applicability of the Gouy-Chapman theory to analyze capacitance data. Indeed at low concentrations of electrolytes in the adjacent phases, the image contribution is important and the classical Gouy-Chapman capacitance is lower than that calculated taking into account the image effects. At high concentrations of electrolytes, the image contribution is decreased by screening.

The applicability of the Gouy-Chapman theory to describe the charge distribution at an ITIES has been thoroughly discussed by Torrie and Valleau,⁴² who used Monte Carlo simulation to highlight the shortcomings of the theory. The first point mentioned by these authors is the general inadequacy of the theory in solvents with a low dielectric constant, as the inherent mean field approximation neglects the ion-ion spatial correlations within the organic diffuse layer. The effect of those correlations is to allow a thinner organic diffuse layer and consequently a smaller potential drop within it, for a given charge density. The second point raised by Torrie and Valleau⁴² is the ion-ion correlation between counterions from the two sides, resulting in an overall attractive force between the layers which in turn should result in thinner diffuse layers on both sides together with smaller potential drop. This argument violates the basic concept of Verwey and Niessen,¹⁰ which considers the adjacent diffuse layers as independently reflecting only the surface density of the other. However, the authors of Ref. 42 pointed out that this "between-layer" correlation is small when water is used as one of the solvents, because of its high dielectric constant.

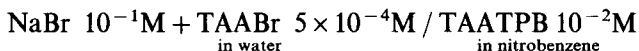
II. ION TRANSFER

1. Experimental Results

The first major observation of ionic current across the interface between two immiscible solutions was reported by Nernst and Riesenfeld,⁴³ who in 1902, studied the transport of colored electrolytes across water-phenol-water concentration cells. However, it was only in 1974 that Gavach *et al.*^{2,3} applied what we could call

modern electrochemical methodology and studied the transfer of tetrabutylammonium from an aqueous solution of tetrabutylammonium bromide (TBABr), in the presence of sodium bromide as supporting electrolyte, to a solution of TBATBP in nitrobenzene. Having measured the partition coefficient of TBABr to be equal to 0.25 (activity in nitrobenzene/activity in H₂O) and having established that the Gibbs energy of transfer of TBA⁺ from water to nitrobenzene was less than that of bromide from nitrobenzene to water, they showed² that the passage of a constant current from water to nitrobenzene was carried by the diffusion-controlled transfer of TBA⁺ from the aqueous to the nonaqueous electrolyte. This pioneering experiment demonstrated that ion transfer across a liquid-liquid interface was a rather fast process, and consequently that all the electrochemical methodology based on the solution of the differential equations for diffusion with different boundary conditions was applicable. In their case, they applied the conventional analysis of chronopotentiometric data and showed that the experimental chronopotentiograms obeyed the Sand equation and found the diffusion coefficient of TBA⁺ in water to be equal to $5.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25°C. The reversibility test, consisting of plotting the potential versus $\log[(\tau^{1/2} - t^{1/2})/t^{1/2}]$, was verified for current densities less than $10 \mu\text{A cm}^{-2}$.

Having realized how much information could be gained by applying electrochemical techniques to the study of ion transfer reactions, Gavach *et al.*⁴ went on investigating the transfer of a series of tetraalkylammonium ions (TAA⁺) for the following systems:



Working with higher current densities, ranging from $10 \mu\text{A cm}^{-2}$ to $100 \mu\text{A cm}^{-2}$, they studied the kinetics of the transfer reactions. Assuming that the concentration of the transferring ion in the organic phase was constant, and assuming that the current versus voltage relationship obeys a Butler-Volmer law:

$$\frac{i}{F} = k_f^\circ C_{\text{TAA}}^w \exp\left[\frac{\alpha F \Delta\phi}{RT}\right] - k_b^\circ C_{\text{TAA}}^n \exp\left[\frac{-(1-\alpha)F \Delta\phi}{RT}\right] \quad (10)$$

they derived the following equation for the overpotential ($\eta = \Delta\phi - \Delta\phi_{\text{eq}}$):

$$\eta = \frac{RT}{F} \ln \left[1 - \left(\frac{t}{\tau} \right)^{1/2} \right]^{-1} + \frac{RT}{F} \times \ln \left[1 + \frac{(i/i_0) \exp(1 - \alpha) F\eta}{RT} \right] \quad (11)$$

where i_0 represents the exchange current density, defined for example as

$$i_0 = Fk_f^\circ C_{\text{TAA}}^w \exp \left[\frac{\alpha F \Delta\phi_{\text{eq}}}{RT} \right] \quad (12)$$

The experimental results obtained appeared to validate the Butler-Volmer assumption, and the standard rate constants, k° , can be recalculated from the published data of k_f° , and k_b° , and α as being equal to 0.0022, 0.0023, and 0.0048 cm s^{-1} for tetraethyl-, tetrapropyl-, and tetrabutylammonium, respectively, knowing that

$$k^\circ = k_f^\circ \exp \left[-\frac{\alpha F \Delta\phi^{\circ'}}{RT} \right] = k_b^\circ \exp \left[\frac{-(1 - \alpha) \Delta\phi^{\circ'}}{RT} \right] \quad (13)$$

where $\Delta\phi^{\circ'}$ is the formal transfer potential.

Using the MVN model of interface they proposed in 1978,^{20,21} they reinvestigated the transfer of tetraalkylammonium ions from water to nitrobenzene,⁵ taking into consideration that the surface concentrations, C^σ , of the transferring ion differed from the bulk concentration, C^b , according to a Poisson-Boltzman distribution:

$$C^\sigma = C^b \exp \left[-\frac{F(\phi^\sigma - \phi^b)}{RT} \right] \quad (14)$$

An interesting conclusion of this work was a graph showing that the Gibbs activation for the transfer of TAA^+ from water to nitrobenzene was proportional to the length of the alkyl chain in TAA^+ , the slope being 2.9 kJ mol^{-1} per CH_2 group. The values of standard rate constants obtained in this later work have been criticized for being too low,⁴⁴ and it has been proposed that these data were not corrected enough for iR drop. However, the error

caused by residual iR loss was estimated by Gavach *et al.* to be negligible, and that the values of standard Gibbs energy of transfer recalculated from the published data of k_f° and k_b° using Eq. (13) compare very well with values obtained by calorimetry (e.g., Ref. 18). Perhaps, the main criticism of this work is the injudicious choice of the aqueous anion. Indeed, the tetralkylammonium bromide salts partition to the organic phase, and the transfer back to water of the bromide anion dissolved in nitrobenzene, upon passage of the current, would impede any quantitative analysis. However, note, as illustrated in Fig. 5, the existence of a linear relationship between the activation energy, as calculated by Gavach *et al.*, and these recalculated values of the Gibbs energy of transfer (*vide infra* for the physical meaning of this graph).

The comment that could be made regarding the use of chronopotentiometry to study the systems investigated by Gavach *et al.*²⁻⁵ concerns the transition time. Indeed, in the case of redox reactions—say an oxidation—the transition time corresponds to the depletion of the reduced species at the interface. At this point

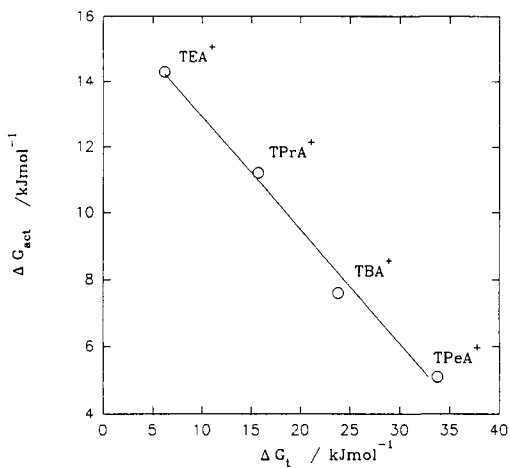


Figure 5. Variation of the Gibbs energy of activation for tetralkylammonium transfer (obtained from Fig. 6 of Ref. 5) as a function of the Gibbs transfer energy calculated from the values of k_f° and k_b° (given in Table I of Ref. 5) using the relation $\Delta G_t = RT \ln(k_f^\circ/k_b^\circ)$.

there is a large variation of potential due to the fact that the current flows via another oxidation process occurring at more anodic potentials, and it is assumed that the two processes do not interfere. This assumption may not always be realized at liquid-liquid interfaces; especially for the systems studied by Gavach *et al.*²⁻⁵ for which the transition time corresponds to the depletion of tetraalkylammonium on the aqueous side of the interface and for which the current continues to flow via either the transfer of sodium from water to nitrobenzene or the transfer in the opposite direction of TPB⁻ from nitrobenzene to water. According to Gibbs energy of transfer data (e.g., Ref. 18), the former is more likely than the latter, but either process will occur with a strong formation of interfacial ion pairs (NaTPB) which will certainly hinder the determination of the transition time. A comprehensive analysis of the use of chronopotentiometry to investigate ion transfer reactions across liquid-liquid interfaces was published by Buck *et al.*⁴⁴⁻⁴⁶

After this pioneering investigation, which opened the way to modern studies of ion transfer reactions, Gavach *et al.* unfortunately had to stop their research in this area. By that time, Prague became the new center for research in the electrochemistry of liquid-liquid interfaces. Koryta *et al.*^{7,9} started by adapting the principle of polarography to the study of charge transfer reactions across an ITIES and developed the electrolyte dropping electrode. Using the 4-electrode potentiostat designed by Samec *et al.*,¹¹ the electrolyte dropping electrode produced polarograms similar to those obtained on mercury.⁴⁷ This pioneering work opened the way to the application of other amperometric techniques to charge transfer reactions across liquid-liquid interfaces. Because of its ubiquity, cyclic voltammetry^{48,49} was then applied to study caesium and picrate transfer across water-nitrobenzene interfaces at mechanical equilibrium.

The systematic application of modern electrochemical methodology proved in a first instance to be a very useful tool to gather thermodynamic information, as Gibbs energies of transfer from half-wave potential measurements. Then, in 1981, Samec *et al.* used convolution linear sweep voltammetry to address experimentally the fundamental aspects of ion transfer reactions.⁵⁰ The main advantage of this technique when studying charge trans-

fer kinetics is that it does not require any assumption on the potential dependence of the rate constants. They used this technique to study first the transfer of choline and acetylcholine⁵¹ and then of the tetraalkylammonium series⁵² across the water–nitrobenzene interface. The gist of this work is the proposition that there exists a Brønsted-type relationship between the activation energy for transfer and the driving force, i.e., the Gibbs transfer energy. To demonstrate the validity of this proposition, Samec *et al.*^{50–52} followed basically the same theoretical approach as that utilized earlier by Gavach *et al.*⁵ In order to clarify the terminology, these authors called the apparent standard rate constant that defined by Eq. (13) and called the true rate constant, k_t , that defined after correction for the difference between surface and bulk concentrations (see Eq. (14))

$$k_f = k_{f_t} \exp \left[- \frac{F(\phi^s - \phi^b)}{RT} \right] \quad (15)$$

Similarly, they called the apparent charge transfer coefficient that defined by

$$\alpha_{\text{app}} = \frac{RT}{zF} \left(\frac{\partial \ln k_f}{\partial \Delta\phi} \right) \quad (16)$$

and the true charge transfer coefficient that defined by

$$\alpha_t = - \frac{RT}{zF} \frac{\partial \ln k_{f_t}}{\partial (\Delta\phi^s - \Delta\phi^i)} \quad (17)$$

where $\Delta\phi^s$ is the standard transfer potential given by $\Delta\phi^s = -\Delta G_t^s / zF$, where ΔG_t^s is the standard Gibbs energy of transfer and $\Delta\phi^i$ is the potential drop across the “inner layer,” assumed for all purposes to be negligible.

Samec *et al.* calculated the potential drop in the diffuse layers, using Eq. (3) together with charge density data obtained by integration from the PZC of the measured interfacial capacitance values.^{34,35} In this way, they obtained what they called the true rate constants and observed that the true charge transfer coefficient α_t was constant and equal to 0.5, as illustrated in Fig. 6. This observation led them to conclude that the ion must overcome

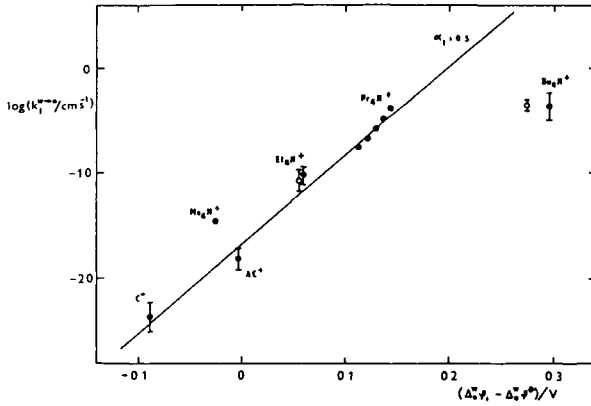


Figure 6. Correlation of the true rate constant, $k_T^{w \rightarrow o}$, with the corrected Gibbs energy, $\Delta G_{rp} = -zF (\Delta_o^\beta \phi_i - \Delta_o^\beta \phi^o)$, for the ion transfer from the OHP in water to that in nitrobenzene. Symbols: choline (C^+) [4], acetylcholine (AC^+) [4], tetramethylammonium (Me_4N^+) [1], tetraethylammonium (Et_4N^+), tetrapropylammonium (Pr_4N^+), and tetrabutylammonium (Bu_4N^+). (Reprinted from Ref. 52 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

a symmetrical potential energy barrier when crossing the interface. The data of Gavach *et al.* (reproduced in Fig. 5) did show, in a hidden manner, a similar behavior with a true charge transfer coefficient value of 0.34.

Samec *et al.*^{53,54} published two papers on the kinetics of ion transfer across the water-nitrobenzene interface, using ac impedance measurements at the equilibrium potentials. The latter were determined by the Nernst equation for ionic equilibria, where the concentration ratio of the crossing ion in both phases was varied:

$$\Delta_\alpha^\beta \phi_{eq} = \Delta_\alpha^\beta \phi^{o'} + \frac{RT}{zF} \ln \left(\frac{C^\alpha}{C^\beta} \right) \quad (18)$$

Although the rate constants obtained are much faster than those obtained by techniques where a current is flowing (by about 1 order of magnitude), the analysis protocol led to similar conclusions. In particular, the true charge transfer coefficient, α_i , was also

found to be constant and equal to 0.5. Despite all the evidence reported in the first chapter of this review that there is no compact layer at the interface, Samec *et al.*⁵⁴ still concluded, in 1989, that "ion transfer across a rigid layer of solvent molecules at the phase boundary was the rate determining step" and that this rigid layer represented a potential barrier of 14–17 kJ mol⁻¹. This conclusion obviously ignored a decade of work (including their own) dedicated to the understanding of the interfacial structure.

The concept of ac measurements for the kinetic study of ion transfer had been applied previously by Senda *et al.*, who studied the transfer of tetramethylammonium,⁵⁵ picrate;⁵⁶ and the tetraalkylammonium series⁵⁷ by ac polarography. The study of picrate transfer⁵⁶ was interesting because it showed that the measured rate constants were independent of the supporting electrolyte concentration and because it casted some serious reservations the validity of the use of the Frumkin correction as practiced by Samec *et al.* (*vide supra*). Their results indicated that the observed potential dependence of the rate constants, obtained in moderately concentrated electrolyte solutions, may reflect the real potential dependence of the rate constants. The study of the series of tetraalkylammonium ions⁵⁷ comprising tetramethylammonium to tetrapropylammonium, for which the true rate constants should not differ a lot from the measured apparent values, did not seem to corroborate the Brønsted relationship.

In the mid-1980s, Koryta followed another approach to the determination of ion transfer kinetics based on the measurement of salt extraction kinetics.^{58–60} The basis of this approach is that when a salt is extracted from one phase to another, then the flux of the cation must be equal to the flux of the anion to maintain the electroneutrality of the phases. The extraction rate is followed potentiometrically, and the measured Galvani potential difference can be related to kinetic parameters via the assumption of a model of interfacial structure. However, when the interfacial extraction rate is rapid, as in the case for salt extraction at liquid–liquid interfaces, the overall extraction is influenced by the rates of mass transport on either on the interface. Therefore, this approach is not accurate enough to be a valuable tool for the measurement of ion transfer kinetics.

Until 1990, the experimental investigations of ion transfer

reactions were limited to measuring the transfer rate constants of series of ions for a given solvent pair, e.g., water-nitrobenzene or water-1,2-dichloroethane. The conclusion of all this work based on the same experimental approach could be summarized as follows:

Ion transfer reactions are relatively fast and difficult to measure.

The potential dependence of the apparent rate constant appears to follow a Butler-Volmer relationship, with a constant apparent charge transfer coefficient as described by Eq. (16).

The true charge transfer coefficient, as defined by Eq. (17), is constant for series of analogous ions^{52,54} showing that the "true standard activation energy," to employ Samec's terminology, is proportional to the standard Gibbs energy of transfer.

Rate constants obtained by ac impedance analysis are much higher than those obtained by techniques based on the passage of a direct current through the interface.

In 1990, Shao and Girault started a series of investigations based on the kinetic study of the transfer of acetylcholine $\{\text{Ac}^+ = \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\}$ in which the physical properties of one of the solvents were varied.⁶¹⁻⁶³ The experimental approach for the measurement of the kinetic parameters was chronocoulometry, a technique which, like convolution linear sweep voltammetry, does not impose any prerequisites on the potential dependence of the rate constants. To verify the suitability of the experimental method, they studied the potential dependence of the rate constant for Ac^+ transfer from water to oil and from oil to water. As illustrated in Fig. 7, the results obtained show that the apparent rate constants obey the Butler-Volmer relationship, expressed by Eq. 10. Note that Fig. 7 has been obtained from two independent experiments. In the first experiment, acetylcholine was only present in the aqueous phase as a chloride salt and forced to cross to the organic phase, whereas in the second, acetylcholine was only present in the organic phase as a tetraphenylborate salt and forced to transfer to the aqueous phase.

The first modification of solvent property carried out was the variation of the viscosity of the aqueous phase by addition of sucrose⁶¹. The advantage of this approach is that it is possible to

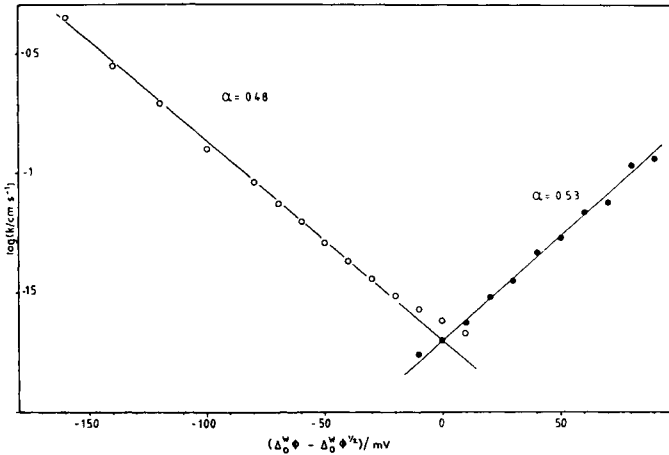


Figure 7. Tafel plots for ion transfer (●) from aqueous to DCE; (○) from DCE to aqueous phases. (Reprinted from Ref. 61 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

vary the viscosity by a factor of 5 without affecting the dielectric constant significantly. Upon addition of sucrose, 3 experimental variables could be measured:

The diffusion coefficient, using the sweep rate dependence of the peak current by cyclic voltammetry

The standard transfer potential and, consequently, the standard Gibbs energy of transfer, by measurement of the half-wave potential by cyclic voltammetry

The standard apparent rate constant, by chronocoulometry

The results obtained can be summarized as follows:

1. The diffusion coefficient in the aqueous phase is proportional to the fluidity (inverse of the viscosity) and obeys the Stokes–Einstein equation ($D = kT/6\pi r\eta$), where η is the viscosity and r is the Stokes radius.

2. The apparent standard rate constant, k^0 , is also proportional to the fluidity of the aqueous phase. This is interesting, as it shows in the present circumstances that the diffusion coefficient is

proportional to the apparent standard rate constant. This behavior is not, however, a general feature, as will be shown later.

3. $\ln D$ and $\ln k^o$ are proportional to the measured standard Gibbs energy of transfer, reflecting the change of the Gibbs hydration energy with addition of sucrose to the aqueous phase. In other words, it means that there is a linear Gibbs energy relationship between the activation energy for diffusion in the aqueous phase and the hydration energy, and also between the activation energy for transfer and either the Gibbs transfer energy or the Gibbs hydration energy. The first possibility would corroborate the proposition by Samec *et al.*⁵²⁻⁵⁴ of a Brønsted relationship.

The linear Gibbs energy relationship for diffusion is worth discussing at this stage as it might shed some light on ion transfer processes. Since the variation of Gibbs hydration energy is obtained with very small changes of dielectric constant, we can assume that the electrostatic part of the hydration energy (given by the Born equation [$\Delta G_{\text{Born}} = (ze)^2 (\epsilon^{-1} - 1)/8\pi\epsilon_0 r$]) remains constant. Consequently, the variation of hydration energy can be fully attributed to the variation of the neutral part of the hydration energy with viscosity. The latter includes the work for cavity formation and all the short-range interactions. The experimental results showed that the ratio $\partial \Delta G_{\text{act}}/\partial \Delta G_{\text{hydration}}$ equals 1.35, indicating that the cavity formation work term for transport in aqueous solution is 1.35 times that for hydrating the same species.

The second modification of the physical property of the system was the study of the water-nitrobenzene + tetrachloromethane mixture,⁶² for which the aim was to study the variation of the dielectric constant of the organic phase on the ion transfer itself. The slight disadvantage of the choice of organic solvents was that the decrease of dielectric constant of the mixture upon addition of tetrachloromethane (TCM) to the nitrobenzene was also accompanied by a diminution of the viscosity. As before, the results obtained can be summarized as follows:

The diffusion coefficient increased upon addition of TCM, following the Stokes-Einstein equation.

The apparent standard rate constant decreased upon addition of TCM.

The standard Gibbs energy of transfer from water to oil increased, showing that the solvation energy in the solvent mixture increased (as expected from the Born equation).

$\ln D$ and $\ln k$ are proportional to the measured variation of Gibbs energy of transfer.

First of all, this shows that the diffusion coefficient and the standard rate constant are not always proportional, as the former increased while the latter decreased. Second, these results negate the concept of the Brønsted relationship. Indeed, the standard rate constant decreased with increasing Gibbs energy of transfer, which is the opposite of what was observed by Samec *et al.*⁵² for an analogous series of ions, and of what was observed by Shao and Girault.⁶¹

The third work of modification of the solvent properties consisted of studying different organic solvents having the same dielectric constant but different viscosities.⁶³ The solvents studied were dichloromethane, 1,2-dichloroethane, and 1,2-dichlorobenzene. Again the results obtained can be summarized as follows:

The diffusion coefficient of acetylcholine in the organic phase obeys the Stokes–Einstein equation.

The standard rate constant is proportional to the fluidity of the organic phase, showing again that in this case the standard rate constant is proportional to the diffusion coefficient.

2. Discussion

Many theories for ion transfer reactions have been published^{5,25,64–68} since the first experimental work of Gavach.² However, since not a single theory has emerged as being able to account for all the experimental results described above, we shall not review all the theories proposed. Instead, we shall try to review the pertinent questions that should be asked and attempt to answer them using some of the arguments put forward by the different groups.

The first question to ask is purely experimental: Why are rate constants for ion transfer difficult to measure, and why is there such a difference between ac impedance data and faradaic data?

The second question one may ask is: If the potential drop across the mixed solvent layer is very small, why do we observe a Butler-Volmer relationship for the potential dependence of the apparent rate constant?

Another question which arises from the results described above is: What is the origin of the activation energy of transfer, and what is the relationship between this energy and the Gibbs transfer energy?

Finally, we may ask: Why do we sometimes observe a direct proportionality between the diffusion coefficient and the standard rate constant?

(i) *Experimental Techniques*

The answer to the first question is partly contained in two papers by Milner and Weaver⁶⁹ and by VanderNoot.⁷⁰ The former reports a digital simulation analysis, on the effects of the solution resistance on the evaluation of the standard rate constant, indicating that the measured value is generally smaller than the true value. In the case of liquid-liquid interfaces, the uncompensated resistance of the organic phase is undoubtedly a major source of error which is difficult to circumvent. The second paper addresses the problem of extracting kinetic information when the faradaic and diffusion processes are poorly separated. As will be discussed, the mechanisms of ion transfer reactions are not very different from those of ion transport in electrolyte solutions (e.g., diffusion), and consequently the case treated in Ref. 69 is particularly relevant to ion transfer reactions. In this publication, VanderNoot concluded that it is only possible to extract valid estimates of the kinetic parameters from nonlinear regression analysis of ac impedance data (fitted to a classical Randles circuit) if the faradaic time constant, t_f , equal to $R_{CT}C$, where R_{CT} is the charge transfer resistance and C , the interfacial capacitance, is less than 30 times the time constant for diffusion, t_d , equal to $2(R_{CT}/2\sigma)^2$, where σ is the Warburg impedance classically defined as

$$\sigma = \frac{RT}{n^2 F^2 A 2^{1/2}} \left(\frac{1}{D_\alpha^{1/2} C_\alpha} + \frac{1}{D_\beta^{1/2} C_\beta} \right) \quad (19)$$

However, it would appear⁷¹ that the faradaic time constant at a

liquid–liquid interface is often greater than that for diffusion, and VanderNoot concluded that any ac impedance, ac polarographic, or for that matter any transient technique is not really suitable for the determination of kinetic parameters unless a linear regression method is used to entangle the kinetics from the diffusion process. Other techniques such as convolution linear sweep voltammetry, chronopotentiometry or chronocoulometry, where the data are acquired principally in the diffusion-controlled time domain and extrapolated back to time $t = 0$ for the determination of the kinetic parameters, do not suffer from these limitations. However, they suffer from the fact that the passage of a dc faradaic current across the interface is more likely to disturb its equilibrium structure than an ac current. In particular, if we consider the cotransport of solvent molecules with the transferring ions, there is a danger that ion transfer can cause a change in the dielectric constant profile.

In conclusion, there is no ideal method to study the kinetics of charge transfer reactions across a liquid–liquid interface. Any techniques can provide valuable information, as long as the results obtained are discussed taking into consideration the above limitations.

(ii) *Butler–Volmer Relationship*

The proportionality of $\ln(k_f)$ to the applied potential difference (also called Tafel behavior) was observed back in 1975 by Gavach *et al.*⁴ and has been corroborated ever since by many groups (e.g., Ref. 53, 54, 56, 57). The results of Shao and Girault,⁶¹ illustrated in Fig. 7, show beyond any doubts that a Butler–Volmer relationship (as described by Eq. (10)) accounts very well for the experimental data. In the case of the metal–electrolyte solution interface, such an equation is rationalized by the fact that the applied potential difference, $\Delta\phi$, the driving force for the electron transfer reaction, is located at the interface and that the variation of the activation energy with $\Delta\phi$ is a fraction of the variation of the electrical driving force.

In the case of liquid–liquid interfaces, we have seen that the potential drop across the mixed solvent layer is very small and that, therefore, any variation of the applied Galvani potential difference is translated into a tiny variation of the potential drop

across the mixed solvent layer. Consequently, if the electrical potential gradient was the driving force of the ion transfer reactions, this would mean that the apparent charge transfer coefficient defined by Eq.(16) should be negligible, which has never been verified experimentally.

It has been proposed many times (e.g., Ref. 71) that the true standard rate constant, k_t , [given by Eq. (15)] is potential-independent and that the variation of the Galvani potential difference results only in the variation of the surface concentrations of the transferring ion [see Eq. (14)]. The work of Samec *et al.*,^{51,54} which dedicated a lot of effort to the calculation of k_t , is not very conclusive, as the values obtained are less potential-dependent than their apparent counterpart but are nevertheless not really constant. In any case, if this assumption was to be valid the apparent charge transfer coefficient should be equal to the ratio of the potential drop in the diffuse layer over the overall Galvani potential difference²⁵:

$$\alpha_{\text{app}} = \frac{\phi_2}{\Delta_o^w \phi} \quad (20)$$

This point can be easily validated by varying the concentration of the supporting electrolytes in the adjacent phases [see Eq. (4)], but unfortunately experimental results do not seem to corroborate that view.⁷³

Recently, Shao, Campbell, and Girault⁶² looked at ion transfer, not from a kinetic viewpoint where the driving force is the concentration-independent part of the energy, i.e., the "electrochemical standard" energy ($\mu^\circ + zF\phi$), but with a phenomenological approach [see Eq. (21)]. In this case, the driving force for an ion transfer reaction is the electrochemical potential gradient. The question is how to relate this interfacial electrochemical potential difference to the applied electrical potential difference. This correlation can be carried out with the help of the schematic diagrams illustrated in Fig. 8. At equilibrium, the electrochemical potential of the species, i , is constant between the two phases, but it is the sum of 3 components: the standard chemical profile, assumed to be a step function for simplicity (a); the electrical profile $zF\phi$, showing that the Galvani potential difference at equilibrium, $\Delta\phi_{\text{eq}}$, is

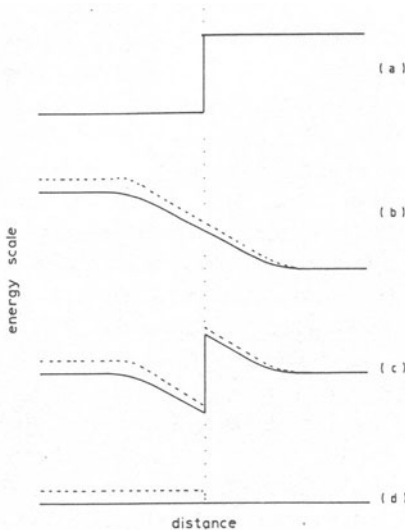


Figure 8. Schematic energy profiles (see text for details). (Reprinted from Ref. 62 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

distributed mainly between the two back-to-back diffuse layers(b); and finally the concentration term resulting from the Boltzmann distribution law, $RT \ln C$, which smoothes the profile obtained by addition of the first two terms (c). When we externally apply a Galvani potential difference, $\Delta\phi$, greater than the equilibrium value, $\Delta\phi_{\text{eq}}$ (as represented by the dashed line), the concentration term will adjust very quickly. If we assume for the sake of the argument that no ion transfer has the time to occur during the double-layer charging, then the electrochemical potential profile appears as a step function centered on the interfacial layer (d), which provides the limiting step in the ion transfer mechanism. The gist of the argument developed by Girault *et al.*⁶² is that all the applied electrical energy provided to the system $zF(\Delta\phi - \Delta\phi_{\text{eq}})$ appears entirely as an electrochemical driving force, $\Delta\tilde{\mu}$, across the interfacial layer, through which the ion transfer takes place despite the fact that very little of the applied electrical potential difference is effective across the mixed solvent layer.

In conclusion, we can postulate that the apparent rate constant is potential-dependent. This effect is not simply due to the potential dependence of the surface concentration. The local electrochemical driving force is the total applied potential difference. However, no experimental studies have been able to

relate the values of charge transfer coefficient to the different Butler-Volmer equations that have been proposed and reported above.

(iii) *Activation Energy and Linear Gibbs Energy Relationship*

In the early work of Gavach, ion transfer was considered as a chemical reaction involving a desolvation-resolvation process and the activation energy was assumed to be related to this inner solvation shell change. For example, in Ref. [5] the authors assumed that the activated state for the transfer of a tetraalkylammonium ion was that corresponding to the ion being located at the interface, with 3 alkyl chains in one phase and with the fourth in the other phase. In 1979, Samec⁶⁴ also supposed that ion transfer occurs via "the penetration through a static repulsion barrier of a certain height." This approach was pursued further after Gurevich and Kharkats published a stochastic approach to ion transfer,⁶⁵ and Samec *et al.*⁶⁶ still concluded in 1986 that a "potential energy barrier of 20–30 kJ mol⁻¹ was likely at the interface, the barrier arising from both the short-range interactions between the ion and solvent molecules in the inner layer and the reorganization of the solvent around the ion."

In 1985, Girault and Schiffrin²⁵ pointed out that the energetics of ion transfer were very similar to those of ion transport in electrolyte solutions. As a result, they proposed a model where the activation process of ion transfer was very similar to that proposed by Eyring for ionic conductivity. Usually, ionic motion is treated using linearized equations by assuming that the local driving force is small. The phenomenological equation for ionic flux is

$$J = -C\tilde{\mu} \text{ grad } \tilde{\mu} = -D \text{ grad } C - \frac{DC}{RT} \text{ grad } \mu^\circ - \frac{zFDC}{RT} \text{ grad } \phi \quad (21)$$

where $\tilde{\mu}$ is the electrochemical mobility. Shao *et al.*⁶² have shown that the linearization of the Butler-Volmer equation in its simplest form reduces to Eq. (21). Recently, Kakiuchi⁷⁴ followed a similar approach and integrated Eq. 21 across the mixed solvent layer

where all the standard chemical gradient is assumed to occur. The current–potential expression obtained is then given by

$$J = -\frac{D}{\Delta x} \left[C^w \left(\frac{ye^y}{\sinh y} \right) - C^o \left(\frac{ye^{-y}}{\sinh y} \right) \right] \quad (22)$$

with

$$y = \frac{zF}{2RT} [\Delta\phi - \Delta\phi^\circ].$$

The current–potential curves obtained by this approach, which does not assume *a priori* the existence of an activation energy barrier, resemble curved Tafel plots.

To conclude on the physical meaning of the activation energy, or the lack of it, is not very easy yet. The only safe conclusion is to state that the local driving force at the interface is much higher than that involved in ionic diffusion or ionic conductivity, as soon as we depart from the equilibrium Galvani potential difference. Consequently, linearized equations such as the Nernst–Planck equation do not apply outside the narrow potential range, where the charge transfer resistance can be measured.

There is no doubt that ionic motion in liquid involves a collective motion of the surrounding solvent molecules, with perhaps the creation of a temporal cavity in the vicinity of the ion and a rearrangement of the dielectric surrounding. Although molecular dynamics models are not very suited to put in evidence the formation of activated states in ionic motion, there is no doubt that a classical kinetic model such as the transition state theory can be used. In this context, it is likely that the activated step of an ion transfer reaction is not very different from that of ion motion in electrolytes. In particular, it is probable that only a small part of the inner solvation shell does get exchanged in the mixed solvent layer, and consequently ion transfer is accompanied by a cotransport of solvent molecules which get exchanged later in the bulk.

In 1983 Samec, Marecek, and Homolka⁵² introduced the concept of the Brønsted relationship between the standard Gibbs energy of activation for ion transfer and the standard Gibbs trans-

fer energy. Early experimental results appeared to corroborate this hypothesis,^{52-54,61} but in 1991 Girault *et al.*⁶² questioned this approach on the basis that the Gibbs energy of transfer, defined as the difference between the Gibbs hydration and the Gibbs solvation energies, has no specific sign. Therefore, it was pointed out that it was difficult to justify a correlation between a value of which the sign is defined arbitrarily to an absolute value, i.e., the standard Gibbs energy of activation which refers to a symmetrical activation energy barrier. To account for the experimental data reported in Ref. 62, it was then proposed that the activation energy for ion transfer is in fact related to the Gibbs solvation energies of the ion in the adjacent phases by

$$k^\circ = Z \exp \left[- \frac{\lambda^\alpha / \Delta G_s^\alpha + \lambda^\beta / \Delta G_s^\beta}{RT} \right] \quad (23)$$

This empirical equation can be easily rationalized in the context of a Butler-Volmer treatment as it stems from the definition of the standard rate constant that

$$k^\circ = (k_f^\circ)^\alpha (k_b^\circ)^{1-\alpha} \quad (24)$$

where k_f° and k_b° are the rate constants at the absolute zero of the Galvani potential difference scale, similar to those introduced in Eq. (10), and α is the apparent charge transfer coefficient defined by Eq. (10) and Eq. (16). In the Butler-Volmer framework the coefficients λ^α and λ^β can be assigned to be equal to the apparent charge transfer coefficient.

The reason why the Brønsted relationship had shown agreement with the experimental data in the work of Samec *et al.*^{52,54} is due to the fortuitous fact that, for the series of ions studied by these authors, the Gibbs solvation energy was proportional to the Gibbs hydration energy (as shown in Ref. 62).

(iv) Diffusion Coefficient and Standard Rate Constant

In certain cases, a direct proportionality between the diffusion coefficient and the standard rate constant has been observed,⁶¹ although other works have shown that it was not a general

rule.^{57,62} This relationship was observed in the cases where the parameter varied was the viscosity of one of the solvents at constant dielectric constant. The variation of the Gibbs energy of solvation was therefore not caused by the electrostatic or Born component of this energy but by the work of cavity formation. It is very likely that the standard Gibbs activation energy for ion transfer can also be split into a neutral component related to the work of formation of a cavity in the interfacial region, and a solvent reorganization energy related to the electrostatic solvation energy. From these considerations, it appears that the observed proportionality indicates that the neutral component of the activation for ion transfer is directly proportional to the neutral part of the Gibbs solvation energy.

III. FACILITATED ION TRANSFER

The first electrochemical observation of a facilitated ion transfer reaction was reported in 1979 by Koryta *et al.*⁹ They studied the transfer of potassium from water to nitrobenzene, facilitated by the crown ether ionophore dibenzo-18-crown-6. This original publication has heralded an important part of the field of electrochemistry at liquid-liquid interfaces. The Prague group at the Heyrovsky Institute dedicated a lot of attention to this particular subject, resulting in a large number of publications.⁷⁵⁻⁸⁷ The ionophores investigated included nonactin,^{75,78} monensin,^{76,82,85} calcium ionophore,^{75,79} dibenzo-18-crown-6,^{78,87} tetracycline,⁸³ valinomycin,^{80,85} and nigericin.⁸⁴

Following the work of Koryta *et al.*,⁹ Freiser and his group started to investigate these phenomena⁸⁸⁻⁹⁵ and questioned the location of the complexation reaction. The 1980s have been marked by a controversy regarding the mechanisms of facilitated ion transfer reactions. The participants to the debate also included Senda *et al.*,⁹⁵ Makrlik *et al.*,⁹⁷⁻¹⁰³ Wendt *et al.*,^{104,105} and Wang *et al.*¹⁰⁶⁻¹⁰⁹ Unfortunately, the debate was not helped by the use of vocabulary borrowed from the field of classical electrode kinetics and the mechanisms proposed were referred to as E, EC, CE, etc. In order to clarify this ambiguous situation, a new terminology has

been introduced¹¹⁰ and is illustrated in Fig. 9. The different mechanisms are referred to as

- ACT aqueous complexation followed by transfer
- TOC transfer followed by complexation in the organic phase
- TIC transfer by interfacial complexation
- TID transfer by interfacial dissociation

The mechanism of facilitated ion transfer reactions is not unique, as it depends on the different concentrations of both the cation and the ligand in the two phases, and also on the association constant values for the complexation equilibria in the water and organic phases. Different limiting situations can be obtained for the different systems discussed here, but any intermediate situation can only be resolved by solving the set of differential equations for mass transport of the different species involved. Furthermore, the liquid-liquid interface, not being a sharp physical boundary, makes it difficult to differentiate cases where the ionophore is distributed between the two phases.

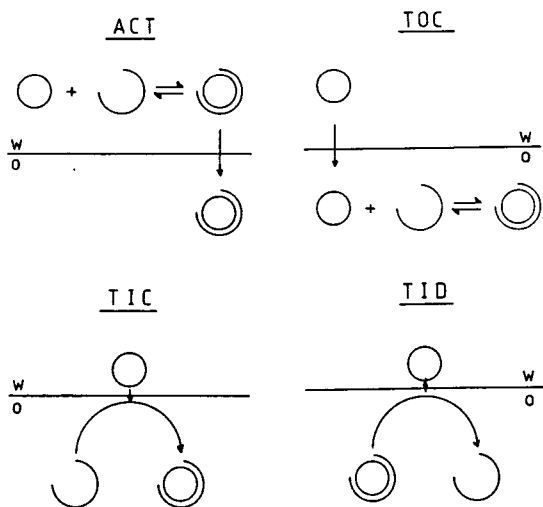


Figure 9. Schematic mechanisms of ion transfer. (Reprinted from Ref. 110 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

However, these difficulties can be circumvented by the choice of "easy systems" as shown by the numerous publications in this area. Indeed, the main success of this branch of liquid-liquid electrochemistry is undoubtedly because it can provide a rather simple electrochemical route to the measurement of the stoichiometry and association constant of ion-ionophore complexes in organic solvents. Indeed, if we consider the thermodynamic equilibria for a facilitated transfer, for which we assume that

Concentration of the metal ion in water is in excess compared to that of the ligand in the organic phase;

Partition coefficient of the ligand is so large that its aqueous concentration can be neglected;

Complex formation in the organic phase is high so that the metal concentration in the organic phase can be neglected;

then, the polarographic wave, for what can be classified as a TIC transfer (transfer by interfacial complexation), is given by⁹⁶

$$\Delta_o^w \phi = \Delta_o^w \phi^{1/2} + \frac{RT}{zF} \ln \left(\frac{I}{(I_l - I)^n} \right) \quad (25)$$

with

$$\begin{aligned} \Delta_o^w \phi^{1/2} = & \Delta_o^w \phi^{o'} + \frac{RT}{2zF} \ln \left(\frac{(D_L/n^2\pi t)^n}{D_{LM}/\pi t} \right) \\ & - \frac{RT}{zF} \ln(K_a^o C_0^w) \end{aligned} \quad (26)$$

It can be seen from this expression that the stoichiometry is obtained by plotting $\log[(I_l - I)^n/I]$ versus $\Delta\phi$, where I_l is the diffusion-limited current. The association constant in the organic phase, K_a^o , can be obtained by varying the metal ion concentration in the aqueous phase, plotting the variation of the half-wave potential as a function of $\ln(C_M^w)$ and extrapolating to zero concentration. This simple approach has been used many times to study ionophores such as crown ethers, which are very good ligands for alkali metal ions, as illustrated in Fig. 10 from the work of Samec and Papoff.⁸⁷

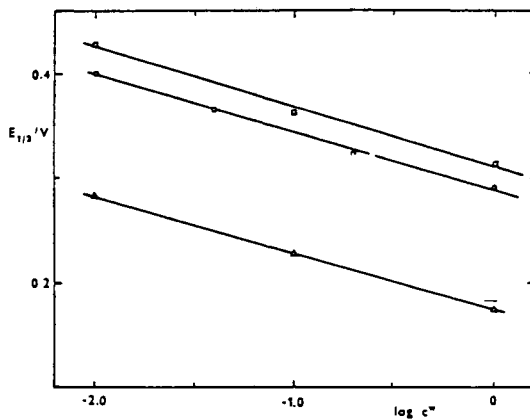


Figure 10. Dependence of the reversible half-wave potential on the concentration c^w of the K^+ cation in the aqueous phase in the presence of $B_{218}C_6$ (\square), $B_{224}C_8$ (\circ), and $B_{230}C_{10}$ (\triangle) in 1,2-DCE: aqueous phase, $KCl + 0.5 M MgSO_4$; organic solvent phase, $0.01 M TPAsDCC + 1 mM$ crown ether. (Reprinted from Ref. 87 with permission. Copyright the American Chemical Society.)

In addition to polarography with an electrolyte-dropping electrode, cyclic voltammetry is another easy and useful method to measure the stoichiometry of the complexation reaction when the listed conditions are satisfied. Indeed, Homolka *et al.*⁷⁹ had shown that for a TIC transfer limited by the diffusion of the ionophore to the interface, and that of the complexed ion away from the interface, the peak separation in cyclic voltammograms is equal to 59, 87, and 112 mV for stoichiometry (cation to ligand) of 1:1, 1:2, and 1:3, respectively. Cyclic voltammetry can also be used, in the case of 1:1 stoichiometry, to measure the association constant in the organic phase from the half-wave potential dependence on metal ion concentration, as given by Eq. (26) (with $n = 1$).

Matsuda *et al.*¹¹¹ have published a general theoretical equation for reversible polarographic current-potential curves, for ion transfer facilitated by a neutral ligand distributed between the two phases. Even in 1:1 stoichiometry, the equations obtained are too complicated to be reproduced or used directly. However, the two

limiting cases $C_M \gg C_L$ and $C_L \gg C_M$, for a 1:1 stoichiometry, are well worth considering:

When $C_M \gg C_L$, we have

$$\Delta_o^w \phi = \Delta_o^w \phi^{1/2} + \frac{RT}{zF} \ln \left(\frac{I}{I_l - I} \right) \quad (27)$$

with

$$\Delta_o^w \phi^{1/2} = \Delta_o^w \phi^o - \frac{RT}{zF} \ln \xi + \frac{RT}{zF} \ln \left(\frac{1 + \xi K_{p,L} + K_a^w C_M^w}{K_{p,L} K_a^o C_M^w} \right) \quad (28)$$

where $\xi = (D_o/D_w)^{1/2}$, with the assumption that the diffusion coefficients of the aqueous species are all equal to D_w and those of the organic phase are all equal to D_o ; where $K_{p,L}$ is the partition coefficient of the ligand between the two phases ($= C_L^o/C_L^w$); and where K_a^o 's are the association constants. The concentration dependence of the half-wave potential is shown in Fig. 11 and can be divided into 3 regions. If $1 + \xi K_{p,L} > 20 K_a^w C_M^w$, then the half-wave potential varies by 60/z mV per decade of concentration of metal ion in the aqueous phase as in Eq. (25). This inequality is often verified for what we defined earlier as the TIC mechanism.

If $20(1 + \xi K_{p,L}) < K_a^w C_M^w$, then the half-wave potential is

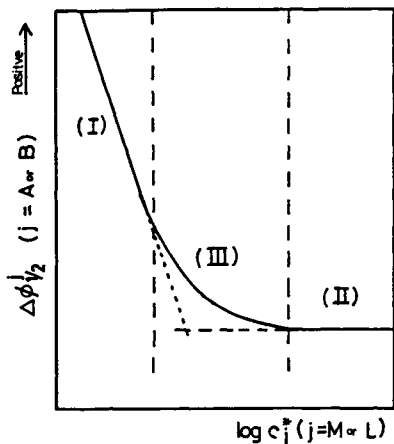


Figure 11. Schematic diagram showing the concentration dependence of the half-wave potential. $\Delta\phi_{1/2}^A$ vs. $\log c_M^*$ plot for (A) $C_M \gg C_L$; $\Delta\phi_{1/2}^B$ vs. $\log c_L^*$ plot for (B) $C_L \gg C_M$. (Reprinted from Ref. 111 with permission. Copyright The Chemical Society of Japan.)

independent of C_M^w . The half-wave potential then corresponds to that of ML and is simply given by

$$\Delta_o^w \phi^{1/2} = \Delta_o^w \phi^{o'} - \frac{RT}{zF} \ln \left[\frac{K_{p,L} K_a^o}{K_a^w} \right] \quad (28a)$$

This case corresponds to an ACT mechanism where the aqueous complexation constant is large.

Finally, if $1 + \xi K_{p,L} \sim K_a^w C_M^w$, then there is a mixed regime.

Matsuda *et al.*¹¹¹ proceeded to define further another function, F_A , such that

$$\begin{aligned} F_A &= \exp \left[\frac{zF}{RT} \Delta \phi^{1/2} - \Delta \phi^{o'} \right] \\ &= \frac{K_a^w}{\xi K_{p,L} K_a^o} + \left\{ \frac{1 + \xi K_{p,L}}{\xi K_{p,L} K_a^o} \right\} \frac{1}{C_M^w} \end{aligned} \quad (29)$$

As seen from this equation, the plot of the function F_A versus $1/C_M^w$ yields a straight line from which one can calculate K_a^w and K_a^o if $K_{p,L}$ is known. In the first limit, i.e., when $1 + \xi K_{p,L} > 20K_a^w C_M^w$, the straight line passes through the origin and the slope yields the association constant in the oil phase K_a^o . In the second limit, i.e., when $20(1 + \xi K_{p,L}) < K_a^w C_M^w$, then the straight line is horizontal and the intercept on the vertical axis yields $K_a^w / \xi K_{p,L} K_a^o$.

When $C_L \gg C_M$, then Eq. (27) remains valid, but the half-wave potential now reads

$$\begin{aligned} \Delta_o^w \phi^{1/2} &= \Delta_o^w \phi^{o'} + \frac{RT}{zF} \ln \xi \\ &+ \frac{RT}{zF} \ln \left(\frac{1 + \xi K_{p,L} + \xi K_a^w C_L^o}{\xi K_{p,L} K_a^o C_L^o} \right) \end{aligned} \quad (30)$$

Since Eq. (30) is obtained by replacing C_M^w by ξC_L^o , the discussion presented above applies similarly to this case.

Matsuda *et al.*¹¹¹ successfully tested this analysis by studying

the transfer of Na^+ , Cs^+ , Ba^{++} , and H_3O^+ , facilitated by dibenzo-18-crown-6 and 18-crown-6. Tan *et al.*¹¹² recently applied the methodology proposed by Matsuda to study the transfer of potassium transfer assisted by monoaza-18-crown-6. Unlike 18-crown-6, this ionophore is a weak base which can be protonated at a pH lower than the pK_a . By measuring the partition coefficient of the ionophore $K_{p,L}$ which was found to be equal to 0.2 between 1,2-dichloroethane and water, they applied Eq. (29) to measure the association constants between potassium and the ionophore in the two phases. Having measured the Gibbs energy of transfer of the protonated ionophore, Tan *et al.* calculated the pK_a of the azacrown in the organic phase. This illustrates how electrochemistry at a liquid-liquid interface can be used to obtain all the thermodynamic information required to calculate the pH dependence of the bulk concentrations of the different species, as shown in Fig. 12. It can be seen from this figure that at high pH, the

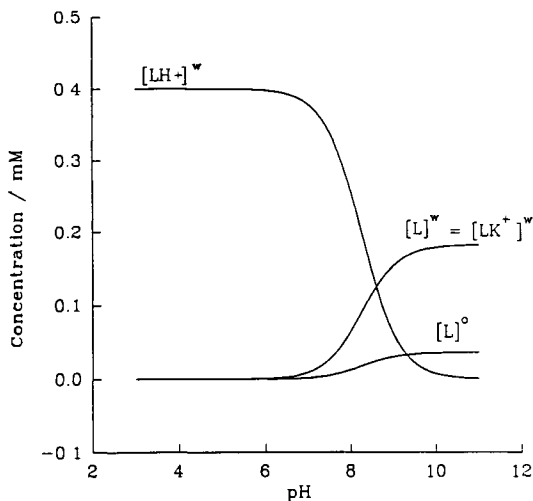


Figure 12. Variation of the concentration of the free ionophore $[\text{L}]$, the protonated ionophore $[\text{LH}^+]$, and the potassium-ionophore complex $[\text{LK}^+]$ with pH. (Reprinted from Ref. 112 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

facilitated transfer observed will include both the transfer of complexed ionophores (ACT mechanism) and transfer controlled by the diffusion of the ionophore in the organic phase to the interface (TIC mechanism). Since there is no thermodynamic difference between the two mechanisms, the distinction stems in fact from the mass transport processes involved: diffusion of the complexed ion in the aqueous phase in the former, diffusion of the uncomplexed ionophore in the organic phase in the latter. Such a difference can be experimentally observed when using micro liquid-liquid interfaces supported at the tip of micropipettes (*vide infra*).

The transfer of protons by neutral organic bases had also received a lot of experimental attention after Makrlik *et al.* had shown in 1983,^{98,99} that aniline and 2,4-dinitro-N-picryl-1-naphthylamine acted as proton carriers from water to the non-aqueous phase. The transfer of protons facilitated by neutral molecules containing amino groups was then thoroughly studied by Homolka *et al.*¹¹³ and by Yoshida and Freiser,⁸⁸ who studied the transfer of protonated phenanthroline. Wang *et al.*^{106,108} later used the same approach to study teramycin (an oxytetracycline antibiotic) and acridine, a dye with weak basicity. In all these works, the half wave potential of the protonated species was observed to be linearly dependent on pH, with a slope of 59 mV/pH. Although Yoshida and Freiser⁸⁸ saw in this dependence an evidence that the transfer observed is that of the protonated amine followed by ion pair formation in the organic phase (in their case with TPB⁻), it is clear nowadays that the treatment proposed recently by Matsuda *et al.*¹¹¹ accounts for all the published data. In particular, Homolka *et al.*¹¹³ could not explain why the 59 mV/pH dependence was not observable in low pH solutions in the case of aniline and phenanthroline, and it is clear from above that at such a high concentration of protons, the condition $1 + \xi K_{p,L} > 20K_a^w C_M^w$ is not satisfied anymore.

The transfer of protons facilitated by anionic bases was recently studied by Senda *et al.*,^{114,115} who were interested in proton transfer facilitated by uncouplers of oxidative phosphorylation in mitochondria. They derived an expression for the half wave potential based on the following assumptions. The aqueous phase is ideally buffered and the proton activity is kept constant; the concentration of protons in the organic phase is negligible compared

to that of A^- and AH ; and only A^- is initially present in the organic phase.

$$\Delta_o^w \phi^{1/2} = \Delta_o^w \phi_{H^+}^{\circ'} + \frac{RT}{zF} \ln \left[\frac{K_{p,AH} K_d^o}{K_d^{ww}} \right] + \frac{RT}{zF} \ln \left[\frac{[D_A^o/D^w]^{1/2}}{1 + [C_{H^+}/K_d^w][1 + K_{p,AH}(D_{AH}^o/D^w)^{1/2}]} \right] \quad (31)$$

where the K_d 's are the dissociation constants of AH and where D^w is the mean diffusion coefficient of the uncoupler in the aqueous phase; i.e.,

$$D^w = \frac{D_{AH}^w + (K_d^w/C_{H^+}) D_A^w}{1 + (K_d^w/C_{H^+})} \quad (32)$$

There are 2 interesting limiting cases

1. When $K_{p,AH}(D_{AH}^o/D^w)^{1/2} \gg 1$, i.e., when the partition coefficient of the neutral protonated uncoupler is large (which is always the case for hydrophobic neutral organic molecule) and when $[C_{H^+}/K_d^w][K_{p,AH}(D_{AH}^o/D^w)^{1/2}] \gg 1$ (in very acidic solutions) then Eq. (32) reduces to

$$\Delta_o^w \phi^{1/2} = \Delta_o^w \phi_{H^+}^{\circ'} + \frac{RT}{zF} \ln \left[\frac{(D_A^o)^{1/2} K_d^o}{(D_{AH}^o)^{1/2}} \right] - \frac{RT}{zF} \ln [C_{H^+}] \quad (33)$$

Equation 33 corresponds to the transfer of protons from water to oil facilitated by A^- . In this case, the half-wave potential is linearly dependent on pH.

When $K_{p,AH}(D_{AH}^o/D^w)^{1/2} \gg 1$ but when $[C_{H^+}/K_d^w][K_{p,AH}(D_{AH}^o/D^w)^{1/2}] \ll 1$ (that is, in slightly acidic to basic solution) Eq. (32) reduces to

$$\Delta_o^w \phi^{1/2} = \Delta_o^w \phi_{H^+}^{\circ'} + \frac{RT}{zF} \ln \left[\frac{K_{p,AH} K_d^o [D_A^o/D^w]^{1/2}}{K_d^w} \right] \quad (34)$$

which corresponds to the half-wave potential for the transfer of A^- from oil to water.

Senda *et al.*^{114,115} applied this theory to the transfer of 2,3,4-trinitrophenol (picric acid), 2,4-dinitrophenol, carbonylcyanide *p*-trifluoromethoxyphenylhydrazine (FCCP) and 3,5-di(ter-butyl)-4-hydroxybenzylidenemalonitril (SF6847).

The transfer of charged dyes across a liquid-liquid interface is very similar in nature to proton transfer facilitated by neutral or anionic bases, as demonstrated by Wang *et al.*¹¹⁶⁻¹¹⁸ Both acidic dyes, like bromocresol green or bromophenol blue, and basic dyes, like rhodamine and methylgreen were investigated. In the case of an acidic dye AH_2 , with pK_1 and pK_2 in the range 2-10, the half-wave potential is given by

$$\Delta_o^w \phi^{1/2} = \Delta_o^w \phi_{AH^-}^{\circ'} - \frac{RT}{2nF} \ln \left(\frac{D_{AH_2}^w}{D_{AH_2}^o} \right) - \frac{RT}{nF} \ln \left(\frac{C_{H^+}}{K_{d1}} + 1 + \frac{K_{d2}}{C_{H^+}} \right) \quad (35)$$

as illustrated in Fig. 13 for bromocresol green and bromocresol purple. A similar expression could be obtained for basic dyes.

The coupling of proton transfer to metal ion transfer is very important to biological and solvent extraction processes. Koryta *et al.*⁸²⁻⁸⁴ addressed this fundamental problem and studied proton and sodium transfer facilitated by monensin and nigericin. Monensin is a carboxylic (HX), acyclic complexing agent which forms cyclic complexes with sodium by closing the ligand with hydrogen bonding. HX acts as a sodium carrier whereas NaX acts as a proton carrier. In both cases, however, the transferred species is $NaHX^+$. Koryta *et al.* above shown, by solving the set of differential equations for diffusion of HX, NaX, and $NaHX^+$, that the half-wave potential is

$$\Delta \phi^{1/2} = \frac{RT}{zF} \ln \left(\frac{k_1}{C_{Na^+}} + \frac{k_2}{C_{H^+}} \right) \quad (36)$$

with $k_1 = \exp[F \Delta \phi_{Na^+}^{\circ} / RT] / K_{Na^+}$, K_{Na^+} being the association constant in the oil phase between Na^+ and HX, and with $k_2 = \exp[F \Delta \phi_{H^+}^{\circ} / RT] / K_{H^+}$, K_{H^+} being the association constant between H^+ and NaX.

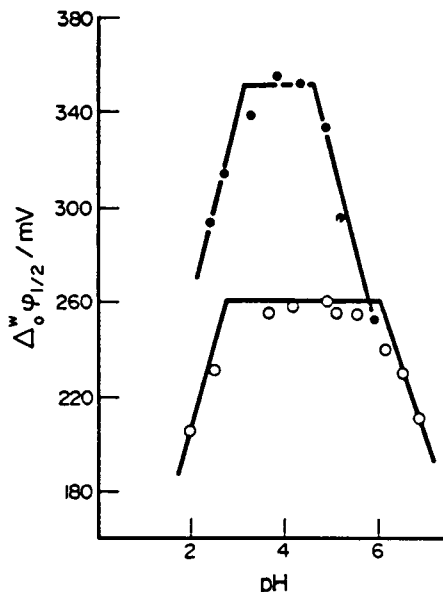


Figure 13. The $\Delta_0 \phi_{1/2}^w$ -pH curves of the transfer of acidic dyes BCG and BCP across the W/NB interface; W: 0.01 M LiCl, B-R buffer; NB: 0.01 M TBATPB; ●-BCG, ○-BCP, $\Delta_0 \phi_{1/2}^w$ vs. TBA⁺ISE. BCG: bromocresol green; BCP: bromophenol blue. (Reprinted from Ref. 118 with permission. Copyright Pergamon Press, Oxford, U.K.)

Due to their relevance in solvent extraction and metal recovery, the facilitated transfer of transition metal ions has been investigated by the type of electrochemical methodology described above. This electrochemical approach has in fact proven to be a valuable tool for the study of the mechanism of solvent extraction processes. Wendt *et al.*^{104,105} studied the transfer of Fe, Ni, and Zn assisted by bidentate nitrogen bases, such as phenanthroline and bipyridine. Similar studies were carried out by Wang *et al.*¹⁰⁷ and by Doe and Freiser,^{119,120} who also studied the transfer of cadmium assisted by diphenylthiocarbazone, a weak monobasic acid.⁹⁵ Solomon *et al.*¹²¹ studied terpyridine as an extractant for transition metals. An interesting result from this type of work is

the observed additivity of the Gibbs energies of transfer of complexes with different stoichiometries, as illustrated in Fig. 14 from the work of Solomon *et al.*¹²¹ Recent work at Edinburgh University, aimed at measuring the Gibbs energy of transfer of bare transition metal ions, has corroborated the value obtained by extrapolation in Fig. 14.

The analysis of the facilitated transfer of transition metal ions is complicated by the sometimes slow kinetics of complexation in the bulk phases, and by the high stoichiometry of the metal complexes. Consequently, a thorough analysis requires knowledge of the different association constants and rate constants. Even in the cases of fast complexation kinetics and reversible ion transfer reactions, the high stoichiometry leads to unusual electrochemical behaviour as recently shown by Kakiuchi and Senda¹²² who used a

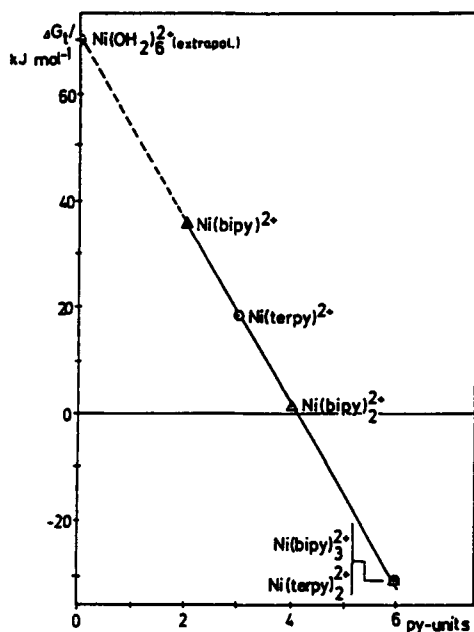


Figure 14. $\Delta G_{tr}^{\circ}(w \rightarrow o)$ of Ni-bipyridine and Ni-terpyridine complexes vs. the number of pyridyl units. (Δ) From Ref. 104; (\circ) this work. (Reprinted from Ref. 121 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

finite difference method to calculate the cyclic voltammetric responses for facilitated transfers having a possible stoichiometry of 1:2 (metal:ligand). The results, illustrated in Fig. 15, showed that, even if the concentration of the metal in the aqueous phase is in excess compared to that of the ligand in the organic phase, the voltammograms obtained for different values of the reduced associated constant, $b_1 = K_1 C_L^o$ (with K_1 the association constant for the 1:1 complex in the organic phase and C_L^o the ligand concentration in the bulk of that phase), exhibit either one peak when b_1 is large with respect to the reduced association constant for the second complexation, $b_2 = K_1 K_2 (C_L^o)^2$, or two peaks when b_1 is small compared to b_2 . The single peak corresponds to a transfer by simultaneous formation of ML and ML_2 , whereas the first of the two peaks corresponds to the transfer by formation of ML_2 and the second that of ML governed mainly by the backward diffusion of ML_2 to the interface. This work clearly showed the complexity of this type of reaction.

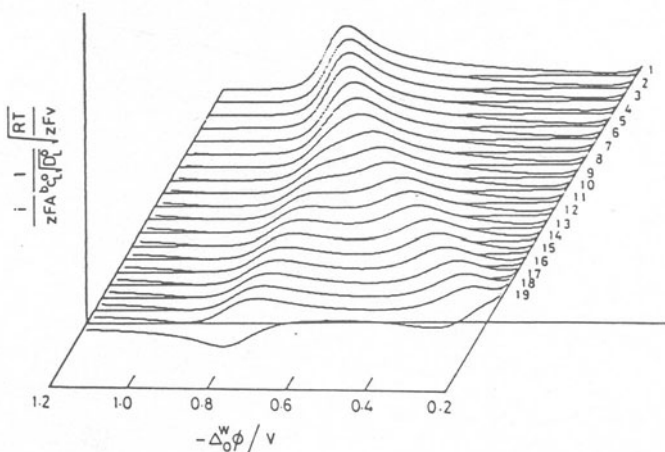


Figure 15. Cyclic voltammograms calculated for $\lambda = 100$, $\zeta_M = \zeta_{ML} = \zeta_{ML_2} = 0.5$, $\xi_{ML} = \xi_{ML_2} = 1.0$, and $b_2 = 10^{10}$ with different values of b_1 : 5×10^{13} (1), 2×10^{13} (2), 10^{13} (3), 5×10^{12} (4), 2×10^{12} (5), 10^{12} (6), 5×10^{11} (7), 2×10^{11} (8), 10^{11} (9), 5×10^{10} (10), 2×10^{10} (11), 10^{10} (12), 5×10^9 (13), 2×10^9 (14), 10^9 (15), 5×10^8 (16), 2×10^8 (17), 10^8 (18), and 5×10^7 (19). $\lambda = C_M^w / C_L^o$ and $\zeta = (D^o / D^w)^{1/2}$. (Reprinted from Ref. 122 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

Very little has been done regarding the kinetic study of assisted ion transfer reactions. Senda *et al.*⁹⁶ studied the transfer of sodium at the water-nitrobenzene interface facilitated by dibenzo-18-crown-6 in order to elucidate the mechanism of the transfer, and concluded that the transfer occurred by a TIC mechanism. Recently, Shao⁷³ revisited this system at the water-1,2-dichloroethane interface. The results obtained for the following charge transfer reactions are illustrated in Fig. 16.

1. The facilitated transfer of potassium from water to oil, in the case where the concentration of the ion is in excess in water compared to the concentration of dibenzo-18-crown-6 in the organic phase (TIC mechanism because of the low solubility of the ionophore in water).

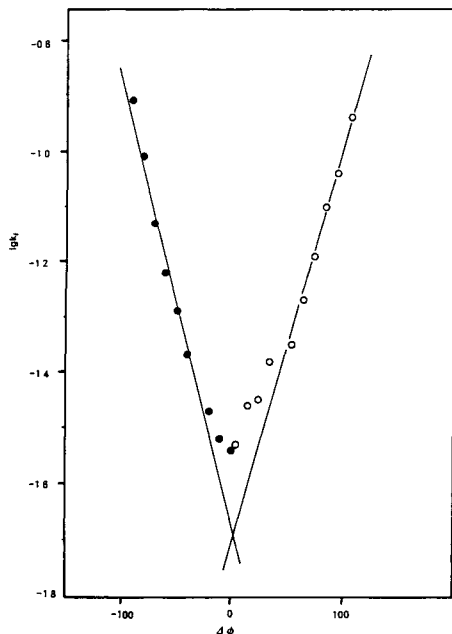


Figure 16. Dependence of rate constant on the applied potential. (○) K^+ transfer facilitated by DB18C6 from water to 1,2-DCE phases. (●) K^+ DB18C6 transfer from 1,2-DCE to water phases.

2. The transfer of potassium from oil to water, where the potassium salt (potassium tetrphenylborate) is dissolved in the organic phase with an equimolar concentration of the ionophore. Recent work using micro liquid-liquid interfaces supported at the tip of micropipettes has shown this process to occur by TID mechanism (transfer by interfacial dissociation).

It can be seen in Fig. 16 that this type of facilitated ion transfer seems to follow a Butler-Volmer relationship as do normal ion transfer reactions.

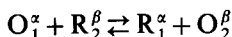
Many questions remained unanswered regarding facilitated ion transfer reactions. The overall macroscopic mechanism is no longer an issue, as it can be elucidated by the methodology described above. However, the microscopic aspects of the transfer and in particular the interfacial aspects such as the loss of the solvation molecules during the replacement by the "solvating" ionophore, still are.

The other important question which will certainly be a challenge for future work is: How does the measurement of the electrochemical rate of the facilitated transfer relate to the interfacial mechanism?

IV. ELECTRON TRANSFER

Heterogeneous electron transfer reactions at liquid-liquid interfaces are involved in many chemical systems such as phase transfer catalysis, and in many biological systems, if a lipid bilayer membrane can be assimilated to a liquid membrane. The two pioneering works, where electron transfer reactions were associated with the passage of an electrical current across a liquid-liquid interface, are the work of Guainazzi *et al.*¹²³ who reduced aqueous Cu(II) to metallic copper using tetrabutylammonium hexacarbonylvanadate in 1,2-dichloroethane, and the work of Samec *et al.*¹²⁴ who measured the current associated with the oxidation of ferrocene in nitrobenzene by ferricyanide in water.

The Nernst equation for the electrochemical equilibrium



is

$$\Delta_{\alpha}^{\beta}\phi = \Delta_{\alpha}^{\beta}\phi^{\circ} + \frac{RT}{nF} \ln \left(\frac{a_{\text{O}_1}^{\alpha} a_{\text{R}_2}^{\beta}}{a_{\text{R}_1}^{\alpha} a_{\text{O}_2}^{\beta}} \right) \quad (37)$$

where the standard potential for the reaction, $\Delta_{\beta}^{\alpha}\phi^{\circ}$, is equal to

$$\Delta_{\alpha}^{\beta}\phi^{\circ} = E_{\text{O}_1/\text{R}_1}^{\circ,\alpha} - E_{\text{O}_2/\text{R}_2}^{\circ,\alpha} + \frac{\Delta G_{i,\text{R}_2}^{\circ,\alpha \rightarrow \beta} - \Delta G_{i,\text{O}_2}^{\circ,\alpha \rightarrow \beta}}{nF} \quad (38)$$

The second term of Eq. (38) represents the difference between the redox scales in the two solvents, α and β . Indeed, we have

$$E_{\text{O}/\text{R}}^{\circ,\beta} = E_{\text{O}/\text{R}}^{\circ,\alpha} + \frac{\Delta G_{i,\text{O}}^{\circ,\alpha \rightarrow \beta} - \Delta G_{i,\text{R}}^{\circ,\alpha \rightarrow \beta}}{nF} \quad (39)$$

One of the original aspects of electron transfer reactions at liquid-liquid interfaces is that, contrary to what happens in bulk solutions, a strong reducing agent in one phase can coexist in contact with an easily reducible species in the other phase, if the Galvani potential difference between the two phases is such that the Gibbs energy for equilibrium is positive.

Very few experimental observations, or electrochemical studies, of electron transfer across a liquid-liquid interface have been reported. This paucity is due to the difficulties associated with the choice of systems for which the Gibbs energy of transfer of both the reactants and products are well known, so as to ensure that the measured currents are due to electron transfer and not ion transfer. Other difficulties, associated with the nature of the supporting electrolytes often used in the organic phase, also hindered early progress in this area (e.g., tetraphenylarsonium can oxidize ferrocene, or tetraphenylborate can be easily oxidized thereby reducing the size of the potential window). The pioneering work of Samec *et. al.*¹²⁴⁻¹²⁶ was based on the oxidation of ferrocene in the organic phase by ferricyanide in the aqueous side. Although ferricinium is water-soluble, it was demonstrated that the current observed for this oxidation was not coupled to the transfer of the product of the oxidation process.¹²⁷ However, the fact that ferricinium could partition did not help the elucidation of the reaction mechanism.

Gblewicz and Schiffrin^{128,129} have studied the system $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in water–Lutetium biphthalocyanine in 1,2-dichloroethane, and very recently Cheng and Schiffrin¹³⁰ investigated the systems $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in water–bis(pyridine) *meso*-tetraphenylporphyrinato iron(II) and ruthenium(III) in 1,2-dichloroethane. These systems have the advantage that none of the products of the reaction would cross the interface, thereby impeding the measurements.

Kihara *et al.*¹³¹ investigated a series of redox couples and analyzed their data using the steady-state current–potential expression derived by Samec.¹³²

$$\Delta\phi = \Delta\phi^\circ + \frac{RT}{n_1 n_2 2F} \ln \left[\frac{(D_{\text{O}_1})^{n_2} (D_{\text{R}_2})^{n_1}}{(D_{\text{R}_1})^{n_2} (D_{\text{O}_2})^{n_1}} \right] + \frac{RT}{n_1 n_2 F} \ln \left(\frac{(I_{\text{dR}_1} - I)^{n_2} (I_{\text{dO}_2} - I)^{n_1}}{(I_{\text{dO}_1} - I)^{n_2} (I_{\text{dR}_2} - I)^{n_1}} \right) \quad (40)$$

where I_d is the diffusion limiting current, which is proportional to the concentration and to the mass transfer coefficient. From this equation, it is possible to calculate the half-wave potential. However, care must be taken when using this type of analysis for extracting kinetic information. Indeed, as clearly shown by Stewart *et al.*¹³³ in the case of cyclic voltammetry, the diffusion of the two reactants and the two products of the heterogeneous electron transfer reactions can lead to “funny” voltammograms, or steady-state curves which do not exhibit the familiar criteria of reversibility for a classical electrochemical reaction coupled with linear diffusion. In the case of cyclic voltammetry, the current for a reversible electron transfer reaction is calculated as the root of the quadratic equation:

$$AI(t)^2 + BI(t) + C = 0 \quad (41)$$

where the coefficients A , B , and C are

$$A = \frac{\theta S(t)}{(D_{\text{R}_1} D_{\text{O}_2})^{1/2}} - \frac{1}{(D_{\text{O}_1} D_{\text{R}_2})^{1/2}}$$

$$B = \theta S(t) \left[\frac{C_{\text{R}_1}}{(D_{\text{O}_2})^{1/2}} + \frac{C_{\text{O}_2}}{(D_{\text{R}_1})^{1/2}} \right] + \frac{C_{\text{O}_1}}{(D_{\text{R}_2})^{1/2}} + \frac{C_{\text{R}_2}}{(D_{\text{O}_1})^{1/2}}$$

$$C = C_{\text{R}_1} C_{\text{O}_2} \theta S(t) - C_{\text{O}_1} C_{\text{R}_2}$$

and where $\theta S(t)$ is classically defined as a function of the starting potential, $\Delta\phi_s$, and the sweep rate, v , by

$$\theta = \exp \left[\frac{nF(\Delta\phi_s - \Delta\phi)}{RT} \right]$$

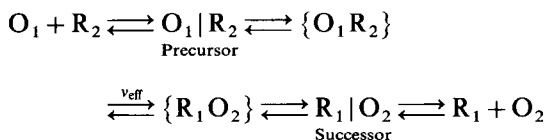
$$S(t) = \exp \left[\frac{-nFvt}{RT} \right]$$

Numerical integration of Eq. (41) clearly shows that the conditions for pseudo-first-order reactions can only be obtained if the reactants in excess in one phase are of equal concentrations, e.g.,

$$C_{O_1} = C_{R_1} \gg C_{O_2} \quad \text{and} \quad C_{R_2}$$

This condition should also be fulfilled for the half wave, or more precisely the midpeak potential, to be equal to the standard transfer potential (as defined by Eq. (38), assuming further the equality of the diffusion coefficients of the reactants and products.

Although experimental studies have been difficult and scarce, theoretical models have been forthcoming. The use of the precounter model for electron transfer reactions at liquid-liquid interfaces.



leads to the following expression of the overall rate constant:¹³⁴

$$k_{\text{obs}} = Z \exp \left[-\frac{w_p}{RT} \right] k_{\text{et}} \quad (42)$$

where Z is the preexponential factor, k_{obs} the observed rate constant, both having a dimension of $\text{cm}^4 \text{mol}^{-1} \text{s}^{-1}$ and where k_{et} is the first-order rate constant for the electron transfer reaction within a precursor. The latter is given by

$$k_{\text{et}} = v_{\text{eff}} \exp \left(-\frac{(\lambda + \Delta G^{o'} + w_p - w_s)^2}{4\lambda RT} \right) \quad (43)$$

where ν_{eff} is the effective electron hopping frequency, w_p is the work to bring reversibly the reactants to a distance, r , to form a precursor, w_s is the work to separate reversibly the products from the successor, ΔG° is the concentration independent part of the Gibbs energy for the electron transfer reaction, and λ is the reorganization energy.

The latter is classically defined as the sum of a solvent reorganization energy, λ_0 , and of a vibrational reorganization term, λ_i . An expression for λ_0 was proposed in 1985 by Kharkats and Volkov,¹³⁵ and recently R. A. Marcus treated the simple model where the liquid-liquid interface is represented as a planar boundary separating two homogeneous dielectric media.^{136,137} From the continuum dielectric theory, λ_0 was found to be

$$\begin{aligned} \lambda_0 = & \frac{(\Delta e)^2}{2a_1} [\varepsilon_{\text{op1}}^{-1} - \varepsilon_{\text{st1}}^{-1}] + \frac{(\Delta e)^2}{2a_2} [\varepsilon_{\text{op2}}^{-1} - \varepsilon_{\text{st2}}^{-1}] \\ & - \frac{(\Delta e)^2}{4d_1} \left[\frac{\varepsilon_{\text{op2}} - \varepsilon_{\text{op1}}}{\varepsilon_{\text{op1}}(\varepsilon_{\text{op1}} + \varepsilon_{\text{op2}})} - \frac{\varepsilon_{\text{st2}} - \varepsilon_{\text{st1}}}{\varepsilon_{\text{st1}}(\varepsilon_{\text{st1}} + \varepsilon_{\text{st2}})} \right] \\ & - \frac{(\Delta e)^2}{4d_2} \left[\frac{\varepsilon_{\text{op1}} - \varepsilon_{\text{op2}}}{\varepsilon_{\text{op2}}(\varepsilon_{\text{op1}} + \varepsilon_{\text{op2}})} - \frac{\varepsilon_{\text{st1}} - \varepsilon_{\text{st2}}}{\varepsilon_{\text{st2}}(\varepsilon_{\text{st1}} + \varepsilon_{\text{st2}})} \right] \\ & - \frac{2(\Delta e)^2}{2R} \left[\frac{1}{\varepsilon_{\text{op1}} + \varepsilon_{\text{op2}}} - \frac{1}{\varepsilon_{\text{st1}} + \varepsilon_{\text{st2}}} \right] \end{aligned} \quad (44)$$

where ε_{op} and ε_{st} are the optical and static dielectric constants, Δe is the charge transferred, d_i is the perpendicular distance from the center of the reactant, i , to the interfacial boundary, R is the center-to-center separation distance between the two reactants, and a_i is the radius of the reactants.

The preexponential factor, Z , depends on the geometric position of the precursor *vis-à-vis* the interface. In the case of the metal-electrolyte interface, where the precursor is defined by the distance, R , between the reactant and the metal, Z is equal to $N_{\text{av}} \delta R$ (where δR is the thickness of the reaction layer, which is about 100 pm). In the case of liquid-liquid interfaces, it is difficult to predict the position of the precursor within the interfacial mixed solvent layer. If in a first instance, we assume the precursor to be

perpendicular to the boundary separating two dielectric continua, Marcus¹³⁶ has shown that Z is then equal to

$$Z = 2\pi(a_1 + a_2) N_{av}(\delta R)^3 \quad (45)$$

However, if the centres of the ions can penetrate the mixed solvent layer so that the precursor can lay parallel to the interface, then Z is given by:¹³⁶

$$Z = \pi(a_1 + a_2)^3 N_{av} \delta R \quad (46)$$

The work terms in Eqs. (42), (43) are more difficult to ascertain as they contain basically three contributions:

1. A change in the standard chemical potential of the reactants and products, associated with the difference in solvation energy between the interfacial region and the bulk

2. A change in the activity coefficient due to the change in ionic atmosphere between the interfacial region and the bulk, the two having different dielectric constants.

3. An electrical component associated with the Galvani potential distribution across the two back-to-back, diffuse layers.

The first contribution contains the variation of the electrostatic part of the solvation energy as the reactant/product feels the influence of the dielectric constant of the adjacent phase, as discussed by Kharkats and Ulstrup⁴¹ (see Eqs. (7)–(9)). Marcus¹³⁷ has shown that this contribution to the work term is

$$w_p = - \left[\frac{(z_{O_1})^2}{4d_1 \epsilon_{st1}} - \frac{(z_{R_2})^2}{4d_2 \epsilon_{st2}} \right] \left[\frac{\epsilon_{st2} - \epsilon_{st1}}{\epsilon_{st1} + \epsilon_{st2}} \right] + \frac{2z_{O_1} z_{R_2}}{R(\epsilon_{st1} + \epsilon_{st2})} \quad (47)$$

for the work of formation of the precursor. Similarly, the work w_s to separate the products of the reaction is obtained by substituting the charge of the products for those of the reactants in the expression above.

The second contribution, linked to the variation of the activity coefficient, might not be negligible but is extremely difficult to quantify.

Finally, the third contribution is the easiest to calculate if one assumes that the potential drop in the diffuse layer can be

evaluated from the Gouy–Chapman theory (see Eq. (4)). In this case, we have

$$w_p = z_{O_1} F \phi_{2w} + z_{R_2} F \phi_{2o} \quad (48)$$

$$w_s = z_{R_1} F \phi_{2w} + z_{O_2} F \phi_{2o} \quad (49)$$

However, one of the advantages of liquid–liquid interfaces is the easy determination of the potential of zero charge. At this potential, the work terms given by Eqs. (48), (49) are obviously equal to zero making an evaluation of k_{et} easier from the measurement of k_{obs} .

The potential dependence of electrochemical rate constants for electron transfer reactions at liquid–liquid interfaces has not yet been studied. Since it has been established that very little of the applied Galvani potential difference occurs across the mixed solvent layer in which the electron transfer reactions are likely to take place, it is not clear if the driving force is affected by the polarization of the interface, and if the apparent electrochemical control of the reaction is not only due to the control of the surface concentrations of the reactants by the applied potential difference.

So at the end of 1991, it is safe to predict that experimental studies of electron transfer reactions at liquid–liquid interfaces, during the coming decade, will be dedicated to test the theories available. Contrary to ion transfer reactions where we possess interesting experimental results with no theory to rationalise the observations, we have interesting theories for electron transfer reactions not yet corroborated by experiments.

V. PHOTOINDUCED CHARGE TRANSFER REACTIONS

A considerable amount of work has been carried out to study photoelectrochemical reactions in micellar and microemulsion systems. In 1979, Calvin *et al.*¹³⁸ had shown, for example, that the change in hydrophobicity or hydrophilicity of an acceptor, or quencher, following a photoinduced electron transfer at a water–toluene interface, leads to a separation of the photoproducts. In the system investigated, i.e., the photooxidation of $[\text{Ru}(\text{bpy})_3]^{2+}$ in water, the aqueous quencher, hexadecyl-4,4'-bipyridinium

($C_{16}V^{2+}$), crosses to the toluene phase upon reduction hence ensuring a physical separation of the photoproducts. Such a reaction can be classified as a PE-IT in the nomenclature listed below.

The liquid-liquid interface provides many advantages compared to microemulsions. First, the potential distribution is much better understood and controllable; the interfacial structure does not depend on the surface state of a surfactant monolayer and is therefore more homogeneous; and finally, direct photocurrent can be measured.

There is a large combination of photoinduced reactions which will lead to the measurement of a photocurrent at the liquid-liquid interface:

PE-IT photoinduced electron transfer reactions followed by ion transfer

PC-IT photochemical reactions followed by ion transfer

IPET interfacial photoinduced electron transfer

IPA interfacial photoanation

PE-IT reactions were first investigated by Kuzmin *et al.*,¹³⁹⁻¹⁴¹ who studied two systems:

1. The photoinduced electron transfer between excited protoporphyrin (excitation 540–580 nm) and quinones, followed by the measured of the transfer of the reduced radical quinones.

2. The photoinduced electron transfer between excited quinones (excitation 313–365 nm) and tetraphenylborate (TPB^-), followed by the measurement of the transfer of a related anion (diphenylboronate (Ph_2BO^-) according to the authors, or more likely an intermediate between TPB^- and Ph_2BO^-).

The photochemical reaction scheme is shown in Fig. 17, where M is the light absorbing molecule, 1M and 3M denote the singlet and the triplet states respectively, and where k_q^S , k_q^T , k_d^S , k_d^T , k_r^S , k_r^T , and k_{ISC} are the quenching, diffusion, recombination, and intersystem crossing rate constants of the corresponding excited states and radical ion pairs.

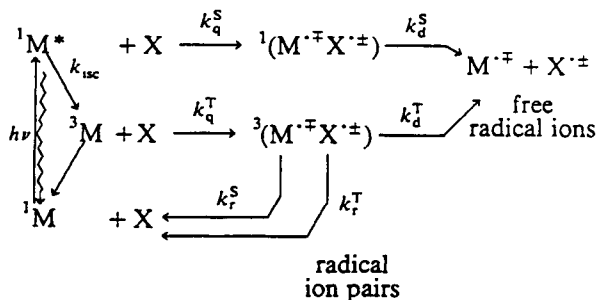


Figure 17. Photochemical mechanism for electron transfer reactions. + + +, Experimental data; —, calculated. (Reprinted from Ref. 141 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

The quantum yield for radical ions is that of a classical quenching reaction in the bulk, and is

$$\phi = \frac{\phi_0^S k_q^S \tau_0^S [X] + \phi_0^T \phi_T k_q^T \tau_0^T [X]}{(1 + k_q^S \tau_0^S [X])(1 + k_q^S \tau_0^S [X])} \quad (50)$$

where $\phi_0^S = k_d^S / (k_d^S + k_r^S)$ and $\phi_0^T = k_d^T / (k_d^T + k_r^T)$ are the limiting quantum yields of radical ions for the singlet and triplet states, τ_0^S and τ_0^T are the lifetimes of these states in the absence of quenchers, and ϕ_T is the triplet (intersystem crossing) quantum yield.

The differential equation for the crossing species should take into account the rate of formation, the diffusion, and the decay rate constants if applicable. Overall, it reads as

$$D \left(\frac{\partial^2 C}{\partial x^2} \right) + I_0 \phi_0 \varepsilon G^0 \exp[-ax] - k_1 C - 2k_2 C^2 = \frac{\partial C}{\partial t} \quad (51)$$

The region $x > 0$ corresponds to the organic phase containing the light absorbing reactant, D is the diffusion coefficient of the crossing species generating the photocurrent, C its concentration, I_0 is the incident photon flux, ϕ_0 is the quantum yield of the photo-reaction generating the crossing species, ε is the absorption coefficient, G^0 is the concentration of the ground state, a stems from the Beer-Lambert law and is equal to $\ln 10 \varepsilon G^0$, and k_1 and

k_2 are the decay rate constants in the first- and second-order process respectively.

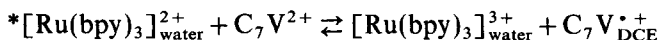
Kuzmin *et al.* have solved this equation using both a Fourier transformation¹⁴¹ and a semi-implicit numerical integration.¹⁴²

Very similar to PE-IT reactions are PC-IT, where a photochemical reaction is followed by measuring the photocurrent associated with an ion transfer. Such a mechanism occurs during the photodecomposition of tetraaryl ions (tetraphenylborate, tetrakis(4-chlorophenyl)borate, tetraphenylarsonium) by UV light in 1,2-dichloroethane.^{143,144} The species crossing the interface was assigned as a bridged phenyl intermediate, $(\text{Ph})_2\text{B}(\text{biphenyl})^-$. The differential equation for this system is that given above in Eq. (51) with $k_2 = 0$. The authors used a Laplace transformation to solve this equation and showed that the photocurrent could be expressed as

$$I(t) = \frac{nFADk'}{k' - Da} \left[-\left(\frac{a}{B}\right) (1 - \exp[-Bt]) \text{erfc}[a(Dt)^{1/2}] \right. \\ \left. - \left(\frac{k'}{CD}\right) \left(1 - \exp[Ct]\right) \text{erfc}\left[\left(\frac{k't}{D}\right)^{1/2}\right] \right] \\ + \left(\frac{k}{D}\right)^{1/2} \left(\frac{1}{B} + \frac{1}{C}\right) \text{erf}[(kt)^{1/2}] \quad (52)$$

with $A = I_0 \phi_0 \varepsilon G^0$, $B = k - Da^2$, and $C = k'/D - k$, where k' is the electrochemical rate of ion transfer and where the other terms have the meaning defined for Eq. (51). The results obtained experimentally have been curve-fitted to Eq. (51), as illustrated in Fig. 18, and yielded an intermediate lifetime value of 12 min, assuming a quantum efficiency of 0.22.

As for electron transfer reactions at an ITIES (see Chapter 4), the study of IPET or interfacial photoinduced electron transfer has been scarce because of the difficulty in identifying systems where the photoproducts do not cross the interface in the potential region where the IPET photocurrent can be measured. Thomson *et al.*¹⁴⁵ measured photocurrents for the system



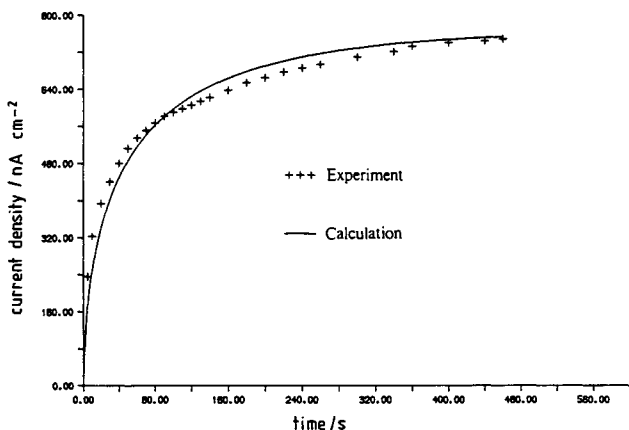


Figure 18. Photocurrent-time transients for 9.94 nM TBATPB. (Reprinted from Ref. 144 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

In this system, the aqueous photoproduct, $[\text{Ru}(\text{bpy})_3]^{3+}$, is more hydrophilic than the aqueous reactant, $[\text{Ru}(\text{bpy})_3]^{2+}$, and the organic photoproduct, C_7V^{*+} , is more hydrophobic than the organic reactant, C_7V^{2+} , guaranteeing that the photocurrent observed was purely electronic. Other systems, using $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photosensitizer in the aqueous phase and TCNQ [tetracyanoquinodimethane] as a reversible organic quencher, have recently been studied¹⁴⁶ and shown to be able to act as photoelectrical energy converters.

De Armond *et al.*^{147,148} have studied systems involving the quenching of excited $^*[\text{Ru}(\text{bpy})_3]^{2+}$ in the organic phase by methylviologen in water. However, because in these systems the photoproducts are more hydrophobic or hydrophilic than their respective reactants, the quantitative interpretation of the observed photopotentials and photocurrents was difficult. Furthermore, these studies were carried out at the water–nitrobenzene interface, and the possibility of nitrobenzene reduction by $^*[\text{Ru}(\text{bpy})_3]^{2+}$ was never considered in the analysis.

Finally, IPA or interfacial photoanation reactions have been observed at liquid–liquid interfaces by measurement of photocurrents.¹⁴⁹ The photoinduced exchange of ligands in the bulk is a well-characterized process. Brown¹⁴⁹ has observed

the exchange of bipyridyl by chloride in $[\text{Ru}(\text{bpy})_3]^{2+}$, and the photocurrent corresponding to the facilitated transfer of chloride as the resulting complex, $\text{Ru}(\text{bpy})_2\text{Cl}_2$, was neutral and not detectable electrochemically, even if it were to transfer in this potential domain.

VI. MICRO-ITIES

Microelectrodes, where the mass transport of the reactants and products of the electrode reaction is controlled by spherical-cylindrical diffusion, have shown many advantages compared with the larger electrodes.

First, in the case of microdiscs, microrings, and microhemispheres, the current reaches a steady state value. The ohmic loss is much smaller than on larger electrodes and the steady-state ohmic loss is independent of the electrode geometry. This allows electrochemical experiments to be carried out in resistive media.

There are basically two ways to support a micro-liquid-liquid interface: at the tip of a glass micropipette pulled to obtain a tip radius of few microns,¹⁵⁰ and in a small orifice in a thin material.¹⁵¹

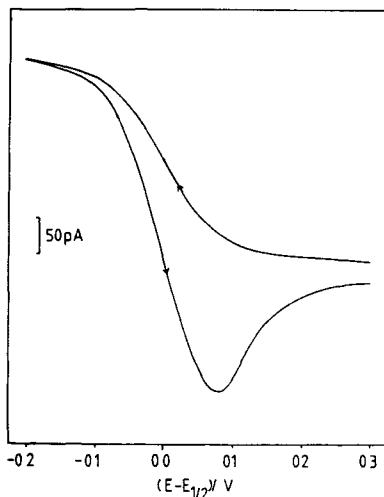


Figure 19. Cyclic voltammogram for the ingress transfer of TEA^+ , for the cell $\text{Ag}/\text{AgCl}|\text{TPBNa}$ (1 mM), NaCl (10 mM)| CVTPB (1 mM), TEATPB (60 μM)|| LiCl (1 mM) | AgCl/Ag at a 15- μm radius pipette. $E = \Delta_o^* \phi$. (This definition of E will be used throughout.) Reprinted from Ref. 152 with permission. Copyright Elsevier Science publishers, Amsterdam.)

In the case of micro-ITIES supported at the tip of a micropipette, the diffusion fields inside and outside are different. Indeed, mass transport of reactants to the interface outside the pipette occurs by spherical diffusion, whereas the mass transport of reactants to the interface inside the pipette occurs by linear diffusion. This asymmetry of diffusion fields is clearly observable in the case of ion transfer reactions, where ingress motion of ions into the pipette gives rise to steady state currents and egress motion of ions outwith the pipette generates peaked linear sweep voltammograms as illustrated in Fig. 19.¹⁵² Such a difference of diffusion regimes can be used as a tool to determine which ion limits the potential window. In the case of the systems shown in Fig. 20,¹⁵³ the potential window in the negative end (oil versus water) is limited by the transfer of lithium which exits the pipette in a linear fashion and reenters the pipette in a spherical manner as indicated by the absence of peaks on the return scan. Conversely, the positive end is limited by the transfer of tetrabutylammonium (TBA^+) which enters the pipette in a spherical way and exits the pipette in a linear manner as indicated by the peak on the return scan. Senda

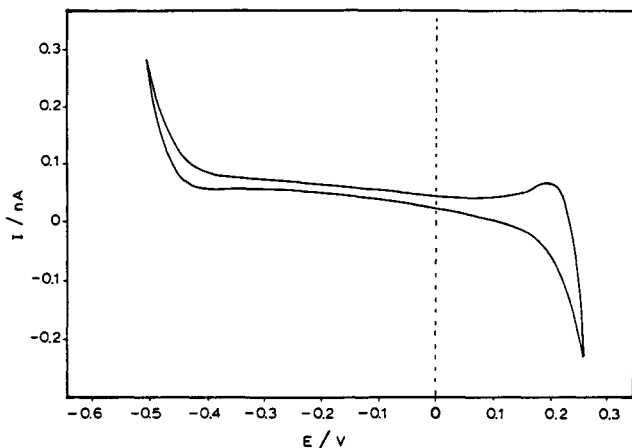


Figure 20. Potential window for the system: $\text{Ag}/\text{AgCl}/\text{LiCl}$ (10 mM) \parallel TBATPBCl (1 mM) \mid TBACl (1 mM) \mid AgCl/Ag . Organic phase, DCE. $E = \phi^o - \phi^w$ in the absolute scale. (The origin ($E = 0$) is determined by measurement of the potential of zero charge [4, 5]. (Reprinted from Ref. 152 with permission. Copyright Elsevier Science Publishers, Amsterdam.)

*et al.*¹⁵⁴ studied the transfer of acetylcholine across the water-nitrobenzene interface, with the organic phase in the pipette, and have shown that voltammetry of ion transfer using micropipettes offers a great potential in electroanalysis and perhaps in brain research.

The charge transfer reaction can, however, be made pseudo-first-order with respect to a reactant located inside the pipette (e.g., facilitated ion transfer with excess of metal ions in the pipette¹⁵⁵). Then the limiting mass transport is similar to redox reactions on metallic microelectrodes. In this case, the classical microelectrode methodology does apply *en bloc*. Such an example of direct transposition is the study of pseudo-first order transfer of sodium, facilitated by dibenzo-18-crown-6 from water to 1,2-dichloroethane, where the steady-state curve obeys the equation

$$\Delta_w^\circ \phi = \Delta_w^\circ \phi^{1/2} + \frac{RT}{zF} \ln \left[\frac{D_O}{D_R} \right] + \frac{RT}{zF} \ln \left[\frac{I_l - I}{I} \right] \quad (53)$$

When the organic phase contains small concentrations of supporting electrolytes,¹⁵⁶ it was further shown that the theory developed by Oldham¹⁵⁷ for explaining the observation of the oxidation of ferrocene in acetonitrile in the absence of supporting electrolyte¹⁵⁸ did apply.

The other approach to support a microelectrode is to drill a microhole in a thin inert membrane. Vanysek *et al.*¹⁵⁹ used high-voltage discharge to drill thin layers of glass but the minimum radius obtained by this technique was 65 μm which was much too high to be classified as a micro-ITIES. Campbell and Girault¹⁵¹ used UV excimer laser photoablation to drill thin polyester films (12 μm thick), and were able to obtain microholes (or microhole arrays) having a radius of few microns. In this case, Eq. (53) applies for any type of charge transfer reaction, including ion transfer.

VII. CONCLUDING REMARKS

Following the pioneering work of Gavach *et al.*, electrochemistry at liquid-liquid interfaces has developed very quickly

over the last decade. The understanding of the interfacial structure is rather well established, at least as far as the potential distribution is concerned.

Our lack of theoretical knowledge of ion transfer reactions simply reflects the general lack of understanding of the molecular mechanisms involved in ionic motion in liquids. Conversely, the study of electron transfer reactions at liquid-liquid interfaces benefits from the detailed knowledge we have of homogeneous electron transfer reactions.

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