# Ion-Transfer Processes across Liquid/Liquid Interfaces Promoted by a Convective Flux.

**Natalia Wilke, Rodrigo Alejandro Iglesias, Sergio Gustavo Chesniuk, Sergio Alberto Dassie, and Ana María Baruzzi***

Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Departamento de Fisicoquímica,
Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, 5000 Córdoba, Argentina.

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Convective flux produced by stirring either the aqueous or the organic phase is proposed as a mechanistic tool to study the ion-transfer processes at ITIES. The dependence of the voltammetric response on the sweep rate and the rotation frequency was used to differentiate the simple transfer of $TEA^+$ from the assisted transfer of $K^+$ by DB18C6 at a water 1,2-dichloroethane interface.

Charge transfer at phase boundaries consists of several steps, which include the transport of reactants to the reaction site and removal of the reaction products from the reaction surface. A distinct difference between solid/liquid and liquid/liquid interfaces is that when charge transfer across a liquid interface is considered, these steps take place at both sides of the interface. In this sense, any attempt to distinguish whether the reacting species are coming from one or the other side of the interface would be helpful to understand the transfer mechanism. Additionally, studies of the true kinetics of heterogeneous reactions require the elimination of problems introduced by mass transport of the reacting species. The elucidation of a charge-transfer mechanism at ITIES has been a matter of great interest, and many examples have been published that show how electrochemistry can be used to obtain thermodynamic and kinetic information about assisted and non-assisted transfer processes.[1–6] The new terminology proposed by Girault et al. [7,8] overcomes the controversy related to the different types of assisted transfer mechanisms reported so far. In that paper the acronym ACT (*aqueous complexation transfer*) is used to indicate aqueous complexation followed by transfer to the organic phase. This mechanism is only possible if the ligand is also soluble in the aqueous phase. In many cases, however, this does not happen and the transfer occurs by interfacial complexation (TIC/TID—*transfer by interfacial complexation/dissociation*—). Additionally, complexation in the organic phase after the cation transfer is also possible (TOC—*transfer by organic complexation*—).

The distinction between all of these possibilities is not always obvious when cyclic voltammetry is applied to a macro ITIES. In the case of assisted transfer by complex formation, the shape of the voltammograms depends on the stoichiometry and on the nature of the process (ACT, TIC and TOC mechanisms) if the stoichiometry is not 1 : 1. In this sense, simulation of the responses obtained under different experimental conditions, has already been published as a way to clarify the transfer process.[8–13]

An important experimental approach so far used to understand the mechanism of transfer at ITIES is the use of micro ITIES at the tip of a micropipette,[7,14–18] generating in this way asymmetry of the diffusion field. One of the advantages of micro ITIES is the mass-transport enhancement in one of the phases, which provides useful kinetic and mechanistic information.

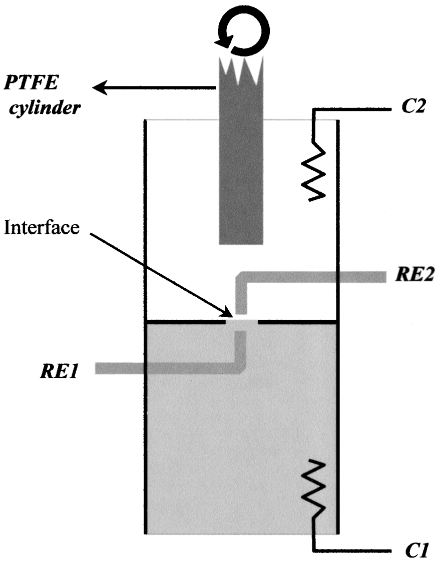
In this paper, a new technique which consists of alternately stirring the aqueous or the organic phase during a potential sweep is proposed to elucidate the mechanisms of transfer across liquid/liquid interfaces. In order to show the advantages and possibilities of controlling the convective flux in either the organic or the aqueous phase, two well-known transfer processes were chosen and analyzed under different experimental conditions: the direct transfer of tetraethylamonium and the facilitated transfer of $K^+$ assisted by DB18C6 (TIC/TID mechanism).

## Experimental

Cyclic voltammetry experiments were carried out in a four-electrode system using a conventional glass cell having an interfacial area of 0.25 $cm^2$. Two platinum wires were used as counter-electrodes (C1 and C2), and the reference electrodes (R1 and R2) were $Ag/AgCl/Cl^-$. The reference electrode in contact with the organic solution was immersed in an aqueous solution of $1.0 \times 10^{-2}$ M tetraphenylarsonium chloride (TPAsCl) (Merck p.a.). The potential values reported are the applied potentials, which include $\Delta\phi^\circ_{tr} = 0.364$ V for the transfer of the reference ion, $TPAs^+$.

The aqueous base electrolytes were MCl ($M = Na^+$ and $K^+$) (Backer p.a.) in ultrapure water (18 MΩ), MilliQ system. The organic base electrolyte was $1.0 \times 10^{-2}$ M tetraphenylarsonium dicarbollylcobaltate (TPAsDCC) in 1,2-dichloroethane (DCE) (Dorwil p.a.). TPAsDCC was prepared as described by Baruzzi and Wendt.[19] Tetraethylammonium bromide (TEABr, Mallinckrodt), and dibenzo-18-crown-6 (DB18C6, Sigma) were commercially available and used without further purification.

Voltammetric experiments were performed using a potentiostat, which eliminates the IR drop automatically by means of a periodic



Scheme 1.

current-interruption technique[20] An L. Y. P. Electrónica Argentina waveform-generator and a computer for data acquisition were also employed.

Agitation was performed with a PTFE cylinder analogue to a rotating-disc electrode, controlled by a PINE disc rotator (Scheme 1).

## Results and Discussion

As stated before, two well-known transfer processes were analyzed under different experimental conditions: the direct transfer of tetraethylammonium and the facilitated transfer of $K^+$ assisted by DB18C6 (TIC/TID mechanism).

**1. Agitation of the Organic Phase.** Figure 1 shows voltammetric profiles obtained for both systems while stirring the organic phase in comparison with those obtained in unstirred solutions.

In Fig. 1a the current-potential profiles for the direct transfer of tetraethylammonium cation ($TEA^+$) are shown. The forward peak corresponds to the diffusion-controlled transfer of this cation from the aqueous phase to the organic phase. As can be observed, the shape and the current values are the same under both stirred and unstirred conditions; that is, the transfer to the organic phase is not appreciably affected by agitation of the organic phase. On the other hand, the backward peak, that is, the return of the species to the aqueous phase, decreases and the ratio $Ip^+/Ip^-$ fails to be one. This result is easily explained by considering that as soon as the ion reaches the organic phase, it is removed from the interface by stirring, and thus decreasing its interfacial concentration.

Figure 1b shows cyclic voltammograms corresponding to the facilitated transfer of $K^+$ assisted by DB18C6(L) in quiescent and stirred organic phases when the ligand concentration was lower than the cation concentration ($C_L << C_M$), in which case, the ligand mass transport rate is the current controlling process. When the organic phase is stirred, the ligand is pushed to the interface. This results in an increase in the positive current, $K^+$ transfer to the organic phase, up to a limiting current value determined by the stirring frequency ($f$). The backward peak becomes smaller, which is a clear indication that the potassium complex is formed on the organic side of the interface during the forward scan, and is pushed away to the bulk of the organic phase, thus decreasing its interfacial concentration.

**2. Agitation of the Aqueous Phase.** Figure 2a shows a

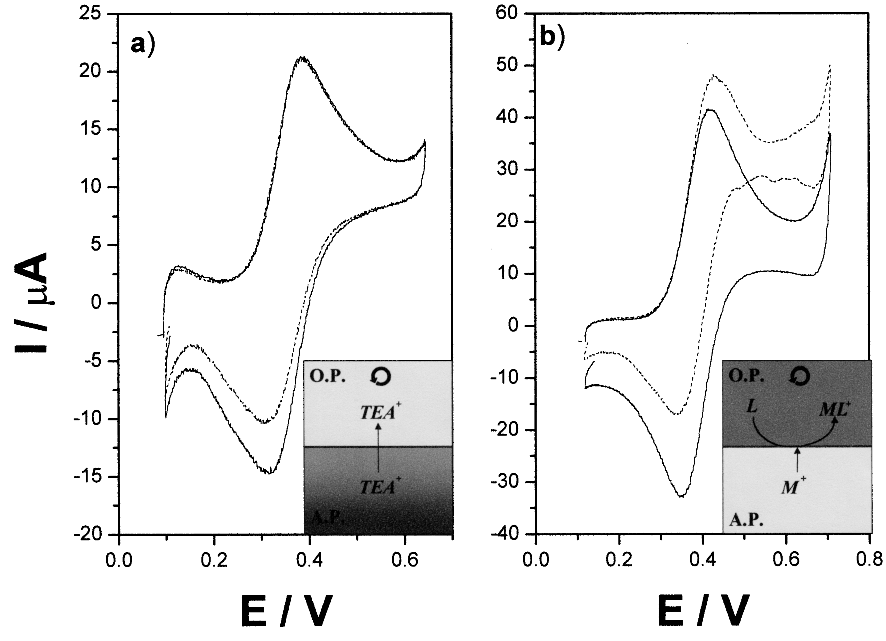


Fig. 1. Cyclic voltammograms for the transfer of $TEA^+$ (a), and for the transfer of $K^+$ assisted by DB18C6 (b); at 0.025 V $s^{-1}$. Quiescent solutions (—) and *organic phase agitated* at 600 rpm (- - -). (a) Organic phase (O.P.): $1.0 \times 10^{-2}$ M TPADCC. Aqueous phase (A.P.): KCl $1.0 \times 10^{-2}$ M + $8.0 \times 10^{-4}$ M TEABr. (b) O.P.: $1.0 \times 10^{-2}$ M TPADCC + $2.1 \times 10^{-3}$ M DB18C6. A.P.: KCl $1.0 \times 10^{-2}$ M.

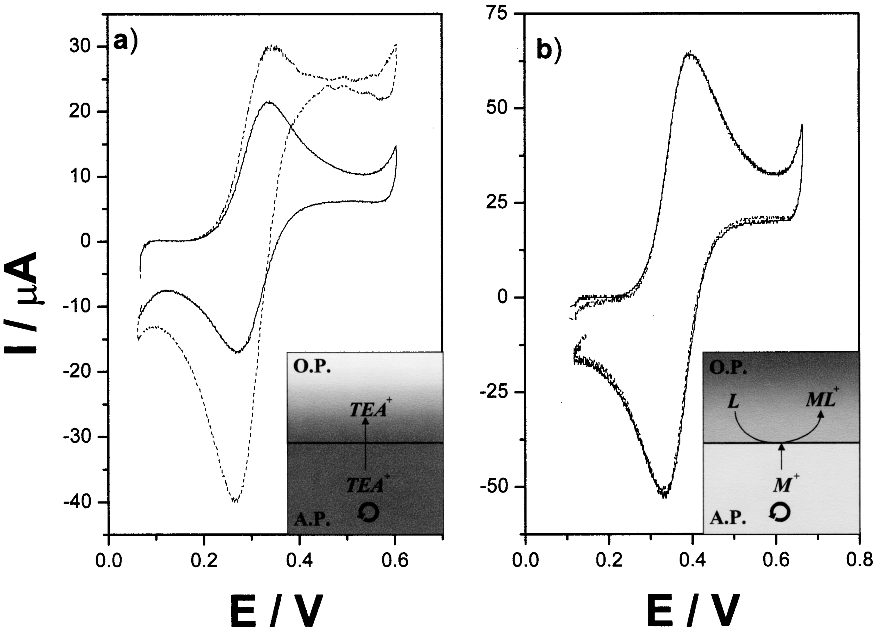


Fig. 2. Cyclic voltammograms for the transfer of TEA$^+$ (a), and for the transfer of K$^+$ assisted by DB18C6 (b). Sweep rate: 0.025 V s$^{-1}$. Quiescent solutions (—) and *aqueous phase agitated* at 600 rpm (- - -). Experimental conditions are the same as in Fig. 1a and 1b.

cyclic voltammogram of TEA$^+$ transfer. When compared with the response in the unstirred solution, a stationary current in the forward sweep and a higher current peak in the backward sweep are observed. The rate of mass transfer of the ion present in the aqueous phase is enhanced with stirring and a limiting current is reached if *f* is high enough. The shape of the backward peak is not affected but, as the amount of substance transferred to the organic phase is higher than that in the absence of convection, the negative peak increases.

The transfer of K$^+$ assisted by DB18C6 is shown in Fig. 2b. A negligible effect of stirring is observed in this case. This is a clear indication that the transfer process is controlled by the diffusion of the species present in the unstirred organic phase. This result is expected considering that the ligand concentration is lower than the cation concentration.

**3. Effect of the Sweep Rate and the Stirring Frequency.** Figure 3a shows cyclic voltammograms at equal forward and different backward sweep rates ($v$) for TEA$^+$ transfer when the aqueous phase was stirred at 600 rpm. In this way, the initial condition for the backward scan was always the same. In the same figure, a good agreement between the experimental and theoretical data considering a reversible diffusion-controlled mechanism is shown. The analysis of the voltammograms obtained under these experimental conditions at different *f* indicates that the negative peak current ($I_p^-$) increases linearly with $v^{1/2}$ (Fig. 3b). The intercept value is non zero due to the difficult determination of the background current, which was taken as the limiting current value of the forward scan. It is also very important to observe in this figure the increase in the slope with the stirring frequency. This is a consequence of TEA$^+$ accumulation on the organic side of the interface (vide infra).

In Figs. 4a and b the effects of *v* and *f* on the response are compared. The most important differences between the stirred and unstirred experiments are observed at low sweep rates and

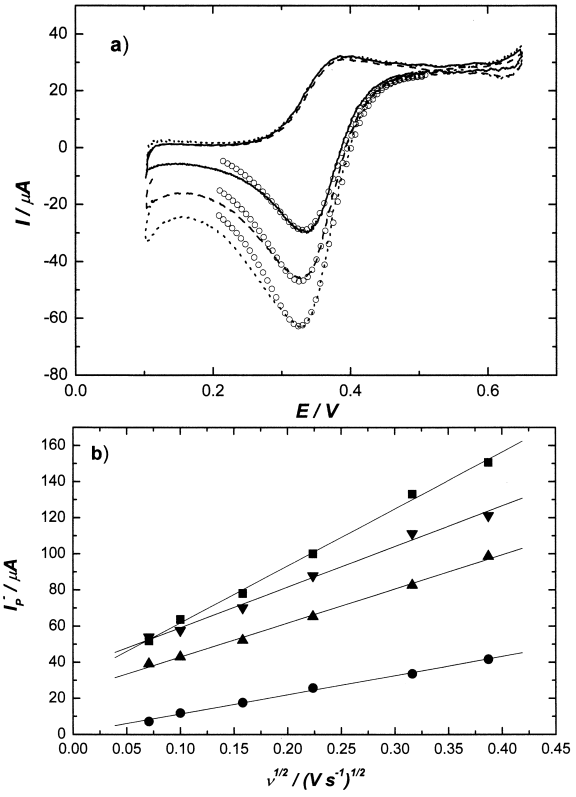


Fig. 3. (a) Cyclic voltammograms for the transfer of TEA$^+$ *agitated in aqueous phase* at 600 rpm. Forward scan: 0.025 V s$^{-1}$. Backward scan: (—) 0.005 V s$^{-1}$, (- - -) 0.025 V s$^{-1}$ and (• • • •) 0.050 V s$^{-1}$. Open circles correspond to theoretical data. (b) $I_P^-$ vs $v^{1/2}$ plots *agitated in aqueous phase* at different stirring frequencies: (●) 0, (▲) 400, (▼) 600 and (■) 800 rpm. Forward scan: 0.025 V s$^{-1}$. Organic phase: 1.0 × 10$^{-2}$ M TPADCC. Aqueous phase: KCl 1.0 × 10$^{-2}$ M + 8.0 × 10$^{-4}$ M TEABr.

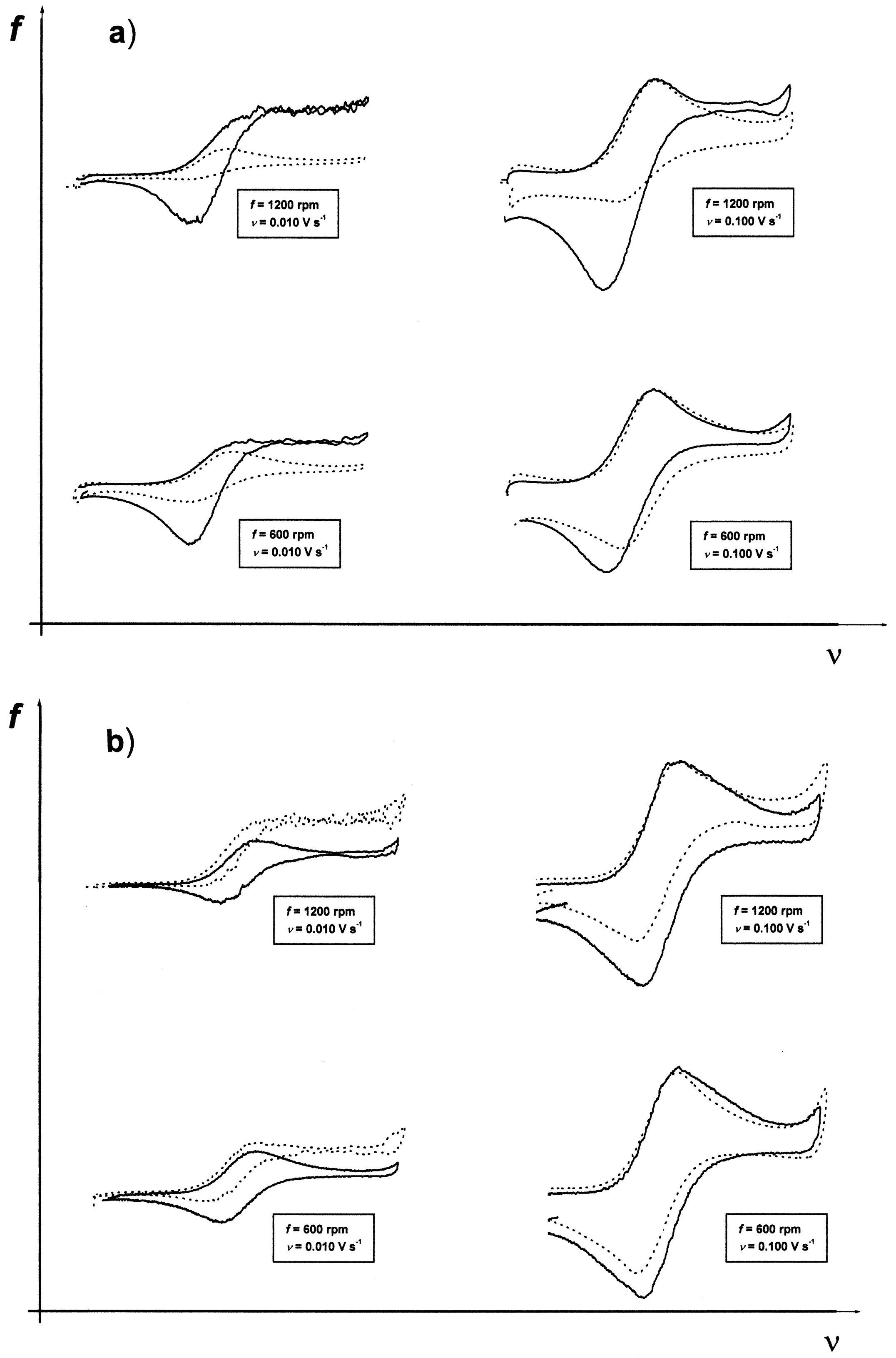


Fig. 4. Diagrams showing qualitative voltammograms at different sweep rates and stirring frequencies. (—) *Aqueous phase agitated* and (- - -) *Organic phase agitated.* (a) Organic phase: $1.0 \times 10^{-2}$ M TPADCC. Aqueous phase: KCl $1.0 \times 10^{-2}$ M + $8.0 \times 10^{-4}$ M TEABr. (b) Organic phase: $1.0 \times 10^{-2}$ M TPADCC + $2.1 \times 10^{-3}$ M DB18C6. Aqueous phase: KCl $1.0 \times 10^{-2}$ M.

when the current controlling species is present in the agitated phase. This means on the other hand, that under these experimental conditions, stirring offers the most relevant advantages as a mechanistic tool. It is important to remark that relatively

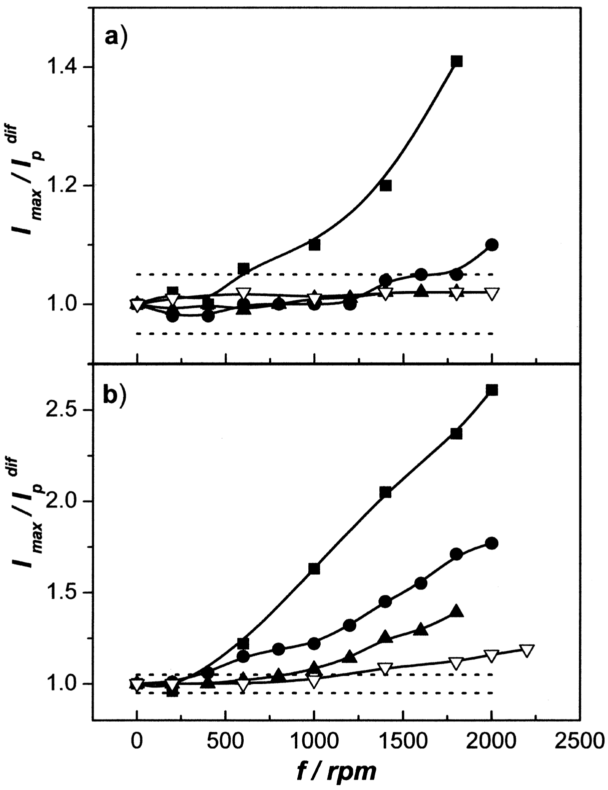


Fig. 5. $I_{max}/I_p^{dif}$ vs $f$ plots at different sweep rates: (■) 0.010 V s$^{-1}$, (●) 0.025 V s$^{-1}$, (▲) 0.050 V s$^{-1}$ and (▽) 0.100 V s$^{-1}$. Organic phase: $1.0 \times 10^{-2}$ M TPADCC + $2.0 \times 10^{-3}$ M DB18C6. Aqueous phase: KCl $1.0 \times 10^{-2}$ M. Full lines are not simulated data; they are there only to clarify the behavior. Dotted lines show an interval corresponding to an error of 5%. (a) *Aqueous phase agitated.* (b) *Organic phase agitated.*

low rotation frequencies are enough to observe appreciable changes. In contrast, at high $f$, the interface becomes unstable and oscillations in the current appear. To show the extent of this effect, the peak or limiting current ($I_{max}$) was normalizad with respect to the peak current under the unstirred condition ($I_p^{dif}$), and the ratio ($I_{max}/I_p^{dif}$) was plotted versus $f$ (Fig. 5). Figure 5a shows $I_{max}/I_p^{dif}$ when the aqueous phase is stirred. A ratio of one should be observed at all $f$ (see Fig. 2b); however it fails to be one at a low sweep rate and a high $f$. The increase of $I_{max}/I_p^{dif}$ is due to a mechanical perturbation of the non-stirred phase induced by the stirred phase. This figure shows the mechanical stability range for this system at each sweep rate. Figure 5b shows $I_{max}/I_p^{dif}$ when the organic phase is stirred. As expected, this ratio increases at all sweep rates because convection becomes important at high enough $f$. From this type of experiment it is possible to determine the optimum working range to see the desired effects. For instance, at 0.025 V s$^{-1}$ the range is 500 rpm $< f <$ 1500 rpm.

In an additional experiment, the simultaneous electrochemical responses of both transfer processes were analyzed to make more evident the capabilities of this methodology (Fig. 6). For these experiments 0.8 mM TEABr + 10 mM NaCl and DB18C6 0.8 mM + TPADCC 10 mM were the compositions of the aqueous and the organic phase, respectively. In this experiment, $Na^+$ was used instead of $K^+$, as $K^+$ and $TEA^+$ transfers are overlapped. This change is irrelevant since both alkali cations are transferred by the same mechanism. In the absence of convection, two reversible diffusion-controlled peaks are observed in the forward and backward scans. When the organic phase is agitated (Fig. 6a), the first positive peak (I) remains unchanged while a stationary current is observed at potentials corresponding to the second process (II). During the backward scan, both peaks (III and IV) decrease. On the other hand, when the aqueous phase is agitated (Fig. 6b), the first process is enhanced while the second remains the same.

Figure 7 shows that besides the mechanistic information, analytical and extractive advantages can be achieved using this methodology. The simultaneous stirring of one phase and polarization of the interface at potentials where a transfer process occurs produce ion preconcentration. As already shown in Fig. 3, the slope of the $i_p$ vs $v^{1/2}$ graph depends on the mass accumulated at the interface. As a result of this enhancement in concentration, there is an increase in the electrochemical response, and therefore in the sensitivity, when cyclic voltammetry is used for analytical purposes.

## Conclusions

The aim of this paper is to show the possibilities of stirring the aqueous or the organic phase during polarization to obtain some insight into mechanistic elucidation. It was shown that in spite of agitation, experimental conditions of $f$ can be found where a well-defined and stable interface is established and, in consequence, proper polarization is obtained.

The convective flux in one phase produces an asymmetry of the diffusion field, that is, a selective decrease of the diffusion layer thickness on one side, which enables one to distinguish the direction of the ion transfer. In this sense, electrochemical measurements at a micro ITIES give analogue mechanistic information;[14,15,17] that is, to decrease the interfacial diameter is equivalent to increase the stirring frequency. To stir either the organic or the aqueous phase requires only a Teflon bar whose rotation frequency is controlled.

We can conclude that one advantage of this technique is the possibility to obtain mechanistic information with a very simple experimental set up. It is also possible to distinguish between different facilitated ion-transfer mechanisms. In this case we studied only a TIC/TID mechanism ($K^+$ transfer facilitated by DB18C6) but the results would be different if the related mechanism were an ACT. In other words, if the organic phase were stirred, the TIC mechanism (with $C_L << C_M$) would show a limiting positive current value, while in the ACT mechanism it would be unaffected. On the other hand, if the aqueous phase were stirred, the positive current value would not change for the TIC mechanism, while it would be higher, up to a limiting value, for the ACT mechanism.

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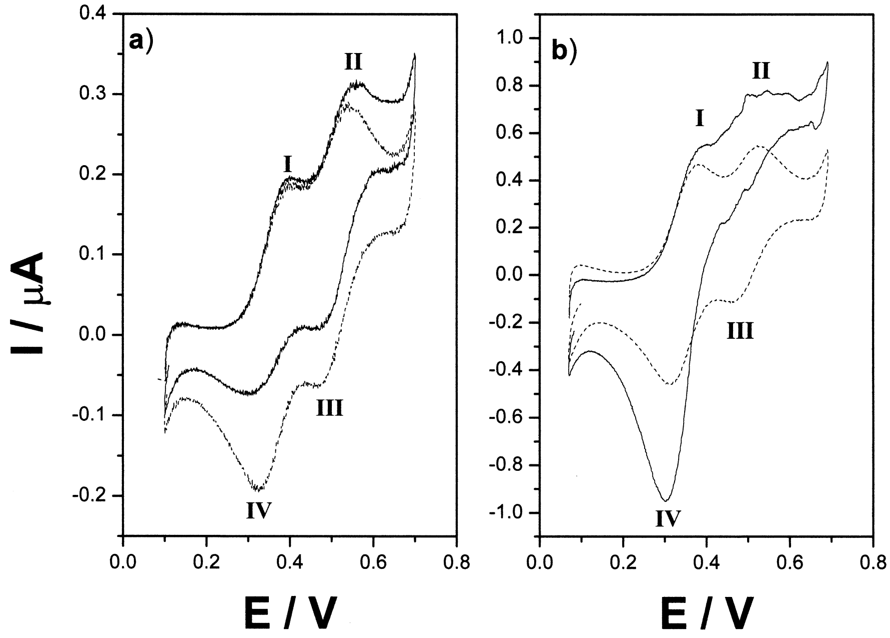

Fig. 6. Cyclic voltammograms for quiescent (- - -) and agitated solutions (—). Sweep rate: 0.025 V $s^{-1}$. Aqueous phase: KCl 1.0 × $10^{-2}$ M + 1.1 × $10^{-4}$ M TEABr. Organic phase: 1.0 × $10^{-2}$ M TPADCC + 9.0 × $10^{-4}$ M DB18C6. (a) *Organic phase agitated.* Stirring frequency: 600 rpm. Aqueous phase: KCl 1.0 × $10^{-2}$ M + 9.0 × $10^{-4}$ M TEABr. Organic phase: 1.0 × $10^{-2}$ M TPADCC + 9.0 × $10^{-4}$ M DB18C6. (b) *Aqueous phase agitated.* Stirring frequency: 400 rpm.

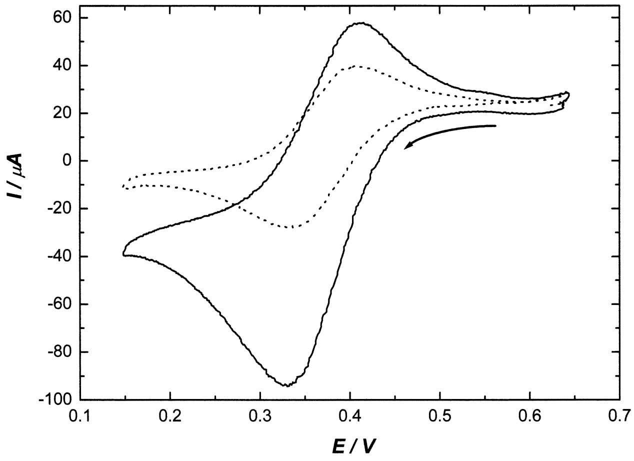

Fig. 7. Cyclic voltammograms beginning at 0.64 V after polarization at this potential. *Aqueous phase agitated.* Stirring frequency: 600 rpm (- - -) without polarization and (—) with polarization (60 s). Organic phase: 1.0 × $10^{-2}$ M TPADCC. Aqueous phase: KCl 1.0 × $10^{-2}$ M + 8.0 × $10^{-4}$ M TEABr.

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