2 PERKIN

Investigation of the kinetics of electron transfer processes involving fullerenes at liquid–liquid interfaces using scanning electrochemical microscopy: evidence for Marcus inverted region behaviour

Jie Zhang and Patrick R. Unwin *

Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL

Received (in Cambridge, UK) 26th March 2001, Accepted 18th June 2001
First published as an Advance Article on the web 18th July 2001

Electron transfer (ET) reactions between the anions of fullerenes (C_{60} and C_{70}) in chlorobenzene (PhCl) and $Fe(CN)_6^{3-}$ in an aqueous phase have been investigated using scanning electrochemical microscopy (SECM). Salts of the anion ClO_4^- were added to each phase to control the interfacial potential drop and maintain charge neutrality during the ET process. The rate constants of ET between C_{60}^- and $Fe(CN)_6^{3-}$ were similar to those between C_{70}^- and $Fe(CN)_6^{3-}$. Although the measured ET kinetics were found to depend on the interfacial potential drop, the rate constant for the oxidation of the fulleride anion (reduction of aqueous $Fe(CN)_6^{3-}$) decreased when the ClO_4^- concentration in the aqueous phase increased, even though this corresponds to an increase in driving force. It is suggested that this could be due to inverted region behaviour predicted by Marcus theory.

Introduction

Following the initial discovery,[1] fullerene research has continuously expanded due to both fundamental interest and wide ranging potential applications.[2] Electrochemical methods have played an important role in the characterisation of fullerene materials in solution[3] and in the solid state.[4] Voltammetric measurements in solution have provided much useful information on the electronic structure of fullerenes.[3b] Notably, Echegoyen and co-workers[5] detected stable C_{60}^{n-} ($n = 1$ to 6) in a mixed acetonitrile–toluene (1 : 5) solvent, proving the theoretical prediction that C_{60} was able to accept at least 6 electrons upon reduction.[6] In the area of solid-state voltammetry, processes occurring during and after the reduction of fullerene microcrystals, mechanically attached to electrodes,[4b–e] have been investigated. Electrochemical methods have also been used to study processes involving electro-generated fulleride anions. For example, Cliffel and Bard[7] examined the protonation of C_{60}^- and C_{60}^{2-} in *o*-dichlorobenzene, identifying that C_{60}^- was a very weak base while C_{60}^{2-} was a strong base. Niyazymbetov and Evans[8] used electro-generated C_{60}^- and C_{60}^{2-} as bases to catalyse nucleophilic addition reactions.

Scanning electrochemical microscopy (SECM)[9] has proven powerful for the measurement of kinetics at a wide range of interfaces, including solid–liquid,[10] liquid–liquid[11] and liquid–gas interfaces.[12] SECM has also found some application in the study of processes involving fullerenes.[4a,13,14] Bard and co-workers[4a] investigated the voltammetric behaviour of thin fullerene films. In later work,[13] it was shown that the rate constant of C_{60} reduction at a Pt ultramicroelectrode (UME) could be measured using SECM in a thin layer cell configuration with a mercury pool electrode. Most recently, Bard and co-workers[14] studied the interaction of C_{60}^- with a calixarene, by electrochemical reduction of *tert*-butylcalix[8]arene–C_{60} films, using SECM combined with a quartz crystal microbalance.

Many processes of fundamental,[15] industrial[16] and applied[17] significance occur at the interface between two immiscible electrolyte solutions (ITIES). There has been considerable interest in characterising charge transfer reactions at ITIES,[18] including both electron transfer (ET)[19] and ion transfer.[17,20] Redox reactions of transition metal complexes with fullerenes and related materials are also of wide interest.[21] However, there have not yet been any investigations of chemical reactions at ITIES involving fullerenes.

In this paper, we report the kinetics of the ET reaction between electro-generated fulleride anions (C_{60}^- and C_{70}^-) in chlorobenzene (PhCl) and aqueous $Fe(CN)_6^{3-}$ at the ITIES. The interfacial potential drop across the ITIES was controlled using ClO_4^- as a common ion in the two phases, which also served to maintain charge neutrality in the two phases during ET. PhCl was used as the organic phase since fullerenes have a reasonable solubility in this solvent,[22] while PhCl is insoluble in water.[23] The study is of intrinsic fundamental interest, since the potential-dependence of ET kinetics at ITIES is currently an active area, but the nature of ET processes across this type of interface is not yet clear.[24] Fullerenes could be an ideal species for this type of study, because they are insoluble in polar and H-bonding solvents,[22] and electro-generated fulleride anions are also likely to be insoluble, particularly since they are expected to form water insoluble ion-pairs with organic phase cations,[14] due to the low relative permittivity of PhCl.[22]

Experimental

Chemicals

Potassium hexacyanoferrate (A.R.), NaCl (A.R.) (Fisons), C_{60} (98%), C_{70} (99%), $NaClO_4 \cdot xH_2O$ (A.R.), PhCl (HPLC grade) (Sigma-Aldrich) and tetra-*n*-hexylammonium perchlorate (THAP, crystalline, Alfa) were used as received. All aqueous solutions were prepared from Milli-Q reagent water (Millipore Corp.).

Apparatus and procedures

All electrochemical measurements were made using a two-electrode arrangement. A silver quasi-reference electrode (AgQRE) or saturated calomel electrode (SCE) served as the reference electrode, and a glass-coated Pt disc UME (25 μm diameter) functioned as the working electrode tip. The electrodes were fabricated and polished as described previously.[25]

Since the density of PhCl is higher than that of water,[26] to simplify the measurement we used a method in which the aqueous solution was held as the lower phase in a glass tube

DOI: 10.1039/b102734b

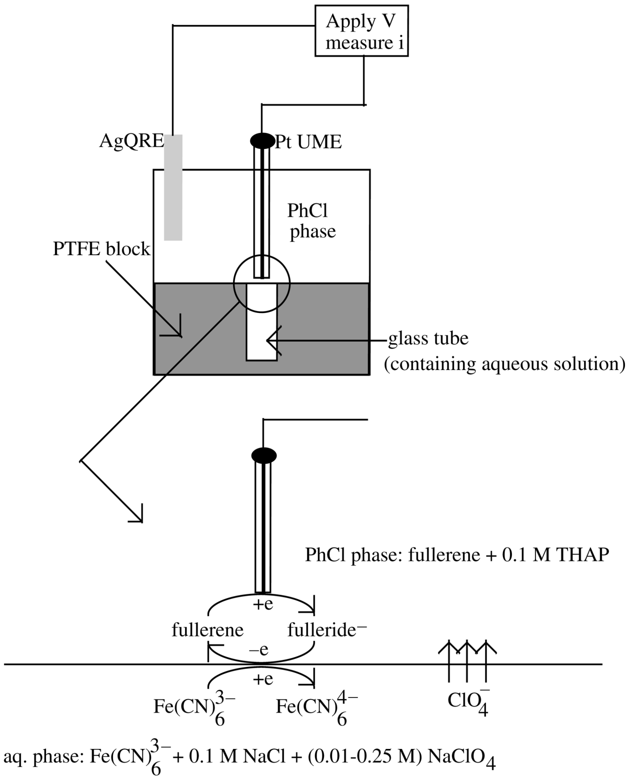

Fig. 1 Schematic of the application of SECM in the measurement of ET reactions at an ITIES.

positioned through the PTFE base of the cell (Fig. 1).[27] This configuration was stable as the water phase was held in contact with the tube by surface tension. The bottom aqueous phase contained 0.5–2.0 mM $Fe(CN)_6^{3-}$, 0.1 M NaCl and 0.01–0.25 M $NaClO_4$, while the PhCl (top) phase contained both 1 mM of the fullerene of interest and 0.1 M THAP. In this configuration, the tip UME was positioned in the PhCl phase and used to locally generate the fulleride anion by the diffusion-limited reduction of the fullerene. The fulleride anion diffuses to the ITIES, where the redox reaction with $Fe(CN)_6^{3-}$ occurs, converting the fulleride back to its initial (fullerene) form.

ClO_4^- was the only ion common to both liquid phases in all SECM experiments. The electroneutrality of both phases was maintained by the transfer of this ion when ET reactions occurred at the ITIES. The ratio of the bulk activities of ClO_4^- in the aqueous and organic phases determined the interfacial potential drop. At standard temperature and pressure, assuming experimental conditions where the activity coefficients of ClO_4^- in the aqueous and PhCl phases are constant, within the concentration range of interest, eqn. (1) should hold.[24]

$$\Delta_w^o\phi = \Delta_w^o\phi^{o\prime} - 0.059\log\frac{[ClO_4^-]_w}{[ClO_4^-]_o} \qquad (1)$$

$\Delta^o{}_w\phi = \phi_o - \phi_w$, where ϕ_o and ϕ_w are the potentials of the organic and water phases, respectively. $\Delta^o{}_w\phi^{o\prime}$ is the formal transfer potential for ClO_4^- which is given by eqn. (2), where

$$\Delta_w^o\phi^{o\prime} = \Delta_w^o\phi^o - 0.059\log\frac{\gamma_w}{\gamma_o} \qquad (2)$$

$\Delta^o{}_w\phi^o$ is standard transfer potential for ClO_4^-; γ_w and γ_o are the activity coefficients of ClO_4^- in the aqueous and PhCl phases, respectively. The formal potential of a redox process (fullerene reduction) at an electrode in PhCl, measured with respect to an aqueous reference electrode, should thus shift by 59 mV to more negative values with a decade increase in $[ClO_4^-]_w$.

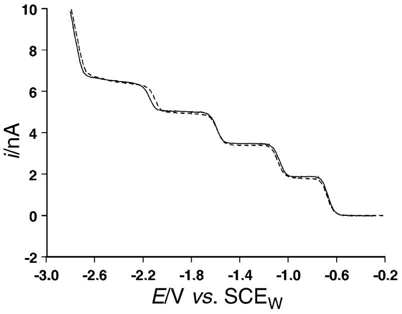

Fig. 2 Steady-state voltammograms for the reduction of fullerenes, C_{60} (solid line) and C_{70} (dashed line), in PhCl at a 25 µm diameter Pt UME. The PhCl phase contained 1 mM fullerene and 0.1 M THAP. An SCE was placed in the aqueous (w) solution, which contained 0.1 M NaCl and 0.1 M $NaClO_4$.

The basic apparatus used for SECM has been described previously.[10c,d] Approach curves were obtained by translating the tip UME towards the ITIES and recording the steady-state diffusion-limited current for fullerene reduction as a function of the distance, *d*, between the tip and the ITIES. When the tip attained the distance of closest approach to the ITIES, there was a sudden change in current, which is due to the preferential wetting of the hydrophilic tip by water. Typically, a 25 µm diameter tip could be approached to a closest distance of *ca.* 2–3 µm from the ITIES. To determine this distance precisely, negative feedback experiments were always run without any redox-active species in the bottom phase and data analysed with negative feedback theory similar to that of Kwak and Bard.[28] This procedure is essential to ensure that the tip to interface distance is known with high precision. All of the measurements were carried out inside a glovebox (Glovebox Technology, Huntingdon, UK) in the absence of O_2, at ambient temperature (23 ± 1 °C).

Results and discussion

Potential drop across the ITIES

The relative values of the interfacial potential drop across the ITIES were obtained by adopting a procedure described previously,[24] in which the reversible half-wave potential for the reduction of fullerene was measured against SCE in the aqueous phase, with different ratios of $[ClO_4^-]_w/[ClO_4^-]_o$.

Typical steady-state linear sweep voltammograms of fullerene reduction in PhCl at a 25 µm diameter Pt UME are shown in Fig. 2. Four well-defined waves were measured corresponding to four one-electron transfer reductions, which agrees well with previous voltammetric studies in a similar solvent.[14] From the plateau current of the first reduction wave, a diffusion coefficient, *D*, of 3.9×10^{-6} $cm^2\ s^{-1}$ for C_{60} and 3.7×10^{-6} $cm^2\ s^{-1}$ for C_{70} was calculated on the basis of eqn. (3),[29] where i_{lim} is the

$$i_{lim} = 4nFDac \qquad (3)$$

steady-state diffusion-limited current, *n* is the number of electrons transferred, *F* is Faraday's constant, *a* is the electrode radius and *c* is the fullerene concentration in the bulk solution.

The dependence of the reversible half-wave potential ($E_{1/2}$) on log ($[ClO_4^-]_w$), deduced from such measurements, is shown in Fig. 3. The slopes of *ca.* −58 mV per decade increase in $[ClO_4^-]_w$ for each of the fullerenes are consistent with eqn. (1).

Potential dependence of ET rates

Initial studies involved changing the ratio of redox reactants in the two phases in order to identify the optimum conditions for subsequent ET kinetic measurements. For these studies, the

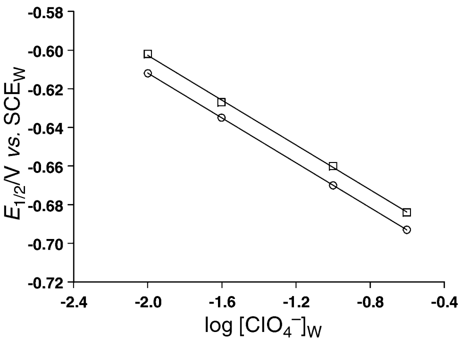

Fig. 3 Dependence of the half-wave potentials, $E_{½}$, for the reversible first reduction of fullerenes, C_{60} (□) and C_{70} (○), in PhCl on $[ClO_4^-]_w$, with [THAP] = 0.1 M.

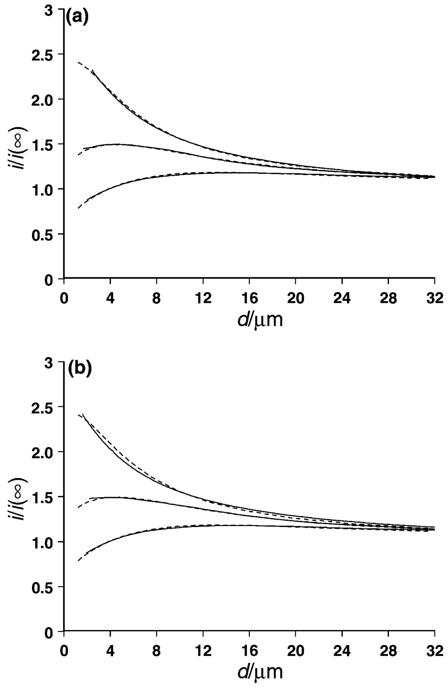

Fig. 4 Effect of K_r on SECM approach curves for the oxidation of the anion of fullerenes, C_{60} (a) and C_{70} (b), by aqueous $Fe(CN)_6^{3-}$. $[ClO_4^-]_o = [ClO_4^-]_w = 0.1$ M together with 1 mM fullerene in PhCl and 0.1 M NaCl in the aqueous phase. From top to bottom the solid experimental curves are for $K_r = 2$, 1 and 0.5. The corresponding theoretical (dashed) curves are for $k = 15$ cm s^{-1} M^{-1} in all cases.

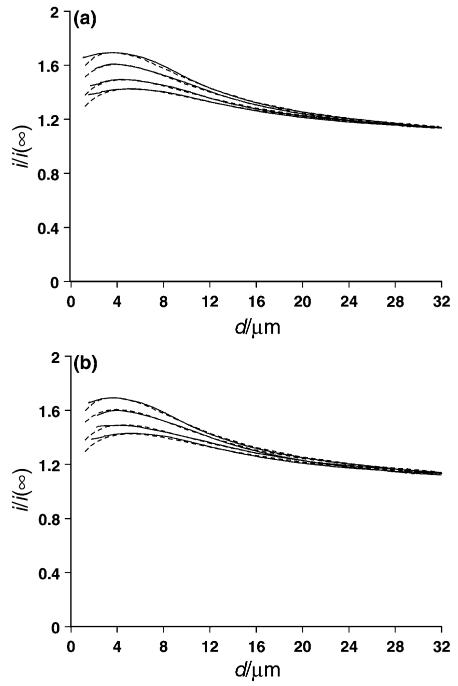

Fig. 5 Approach curves for the oxidation of the electro-generated anions of fullerenes (C_{60} (a) and C_{70} (b)) by aqueous $Fe(CN)_6^{3-}$ on $[ClO_4^-]_w$ with 1 mM fullerene and 0.1 M THAP in PhCl. From top to bottom, the solid lines are the experimental curves for $[ClO_4^-]_w = 0.01$, 0.025, 0.1 and 0.25 M together with 1 mM $Fe(CN)_6^{3-}$ and 0.1 M NaCl. The best fits to theory[11d] (dashed lines) were obtained for (top to bottom): 30, 22, 15 and 12 cm s^{-1} M^{-1} for both (a) and (b).

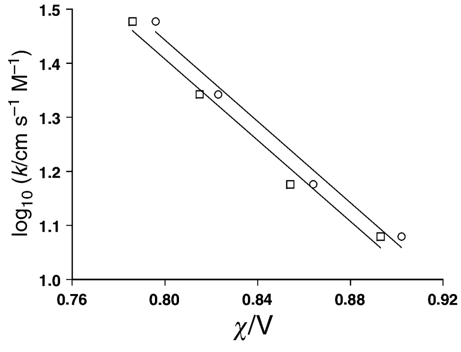

Fig. 6 log k–χ plot of the data from Fig. 5: C_{60} (□); C_{70} (○).

effective bimolecular rate constant (k/cm s^{-1} M^{-1}) was measured with 0.1 M ClO_4^- as the potential determining ion in both the aqueous and the PhCl phases. The bulk concentration of fullerene remained constant at 1 mM, while the bulk concentration of $Fe(CN)_6^{3-}$ was changed from 0.5 to 2.0 mM. This yielded a ratio $K_r = c_w/c_o$ (where c_w and c_o are the bulk concentration of $Fe(CN)_6^{3-}$ and fullerene, respectively) in the range 0.5 to 2. Typical experimental SECM approach curves are shown in Fig. 4. Using a model outlined elsewhere,[11d] these data were found to be consistent with $k = 15$ cm s^{-1} M^{-1} for both C_{60} and C_{70}.

The system with $K_r = 1$ was selected for further potential-dependent experiments, because the shape of SECM approach curves was likely to be most sensitive to the ET kinetics.[11d] In these experiments, the interfacial potential drop was varied by maintaining the THAP concentration constant, while changing the ClO_4^- concentration in the aqueous phase. Typical SECM approach curves obtained from these measurements are shown in Fig. 5. The results show that the ET kinetics depend only weakly on $\Delta^{o}_{w}\varphi$ and that, strikingly, the highest rate constant is observed when the aqueous ClO_4^- concentration is lowest, which corresponds to the lowest driving force for the ET reaction. This can be seen more clearly in Fig. 6 which shows plots of log k *versus* χ. $\chi = \Delta E^{0\prime} - \Delta^{o}_{w}\phi$ is the driving force for the reaction, where $\Delta E^{0\prime} = E^{0\prime}(\mathrm{Fe(CN)}^{3-/4-}) - E^{0\prime}$-(fullerene$^{0/-1}$) is the difference in the formal potentials of the two redox couples. This overall behavior is consistent with Marcus theory.[30,31] Neglecting work terms, which is valid because fullerenes are neutral species and fulleride anions are likely to form neutral ion-pairs with the electrolyte cation in PhCl, the energy of activation for the ET reaction is given by eqn. (4),

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{0\prime}}{\lambda}\right) \qquad (4)$$

$\Delta G^{0\prime}$ is given by eqn. (5).[9f]

$$\Delta G^{0\prime} = -F\chi \qquad (5)$$

In eqn. (4), λ is the reorganization energy, which is defined as $\lambda = \lambda_o + \lambda_i$, where λ_o and λ_i are the outer and inner sphere reorganization energies, respectively.

Although there is some information on λ values for fullerenes,[32,33] no measurements have been made in PhCl. λ for ET reactions involving fullerenes can be calculated from Marcus theory.[31] λ_i is 39.7 kJ mol^{-1} for $Fe(CN)_6^{3-/4-}$,[34] while λ_i of $C_{60}^{0/-}$ can be taken as being close to zero, because λ_i is negligibly small compared to λ_o for many organic species,[35] and the rigid framework of C_{60} remains unchanged in C_{60}^- keeping λ_i small.[33] For the bimolecular ET process, λ_i can be taken as the mean value for these two redox couples. λ_o for the bimolecular ET process at the ITIES is given by eqn. (6),[31b] where D_i^{op} is the optical relative permittivity and D_i^s is the static relative permittivity for the two phases (labelled $i = 1$ or 2). The distances, d_1 and d_2, refer to the displacement of reactants 1 and 2, respectively, from the interface. $R \approx d_1 + d_2$, Δe is the charge transferred, while a_1 and a_2 are the radii of the two reactants.

A λ_o value of 58 kJ mol^{-1} was calculated from eqn. (6) using

$$\begin{aligned}\lambda_o = {} & \frac{(\Delta e)^2}{2a_1}\left(\frac{1}{D_1^{op}} - \frac{1}{D_1^s}\right) + \frac{(\Delta e)^2}{2a_2}\left(\frac{1}{D_2^{op}} - \frac{1}{D_2^s}\right) - \\ & \frac{(\Delta e)^2}{4d_1}\left(\frac{D_2^{op} - D_1^{op}}{D_1^{op}(D_2^{op} + D_1^{op})} - \frac{D_2^s - D_1^s}{D_1^s(D_2^s + D_1^s)}\right) - \\ & \frac{(\Delta e)^2}{4d_2}\left(\frac{D_1^{op} - D_2^{op}}{D_2^{op}(D_2^{op} + D_1^{op})} - \frac{D_1^s - D_2^s}{D_2^s(D_2^s + D_1^s)}\right) - \\ & \frac{2(\Delta e)^2}{R}\left(\frac{1}{D_1^{op} + D_2^{op}} - \frac{1}{D_1^s + D_2^s}\right)\end{aligned} \qquad (6)$$

standard parameters[23,26] together with tabulated radii of the redox species: $Fe(CN)_6^{3-}$ (0.45 nm)[34] and C_{60} (hydrodynamic radius of 0.64 nm).[36] A λ value for the bimolecular reaction of 78 kJ mol^{-1} thus results. This implies that the Marcus inverted region for ET between $Fe(CN)_6^{3-}$ and fullerides will appear when $\Delta E^{0\prime} + \Delta^{\circ}_{w}\phi$ is greater than 0.8 V, based on eqn. (4). In the experimental measurements, the difference between the measured half-wave potentials of the two redox couples, with respect to the same reference electrode in the aqueous phase, gives an absolute value of the driving force.[11c] In the present study, the driving force is in the range of 0.79–0.90 V, which is just in the inverted region. This observation of inverted region behavior adds further weight to similar recent deductions based on SECM studies of other systems at native ITIES[11d] and ITIES with adsorbed phospholipid monolayers.[11b]

Conclusions

The kinetics of the ET reaction between fulleride anions in PhCl and aqueous $Fe(CN)_6^{3-}$ have been measured, as a function of interfacial potential drop, using SECM. Similar ET rate constants were obtained for systems involving C_{60} and C_{70} under the same conditions. The kinetics were found to depend rather weakly on the interfacial potential drop, with the rate constant decreasing with increasing driving force, consistent with Marcus inverted region behaviour for ET.

Acknowledgements

We thank the EPSRC and Avecia for support. J.Z. also gratefully acknowledges scholarships from the ORS scheme and University of Warwick. We are grateful to Dr Anna L. Barker for providing a program for SECM approach curve analysis.

References

1 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.

2 M. S. Dresselhaus and G. Dresselhaus, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996.

3 (*a*) C. A. Reed and R. D. Bolskar, *Chem. Rev.*, 2000, **100**, 1075; (*b*) L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.

4 (*a*) C. Jehoulet, Y. S. Obeng, Y. T. Kim, F. M. Zhou and A. J. Bard, *J. Am. Chem. Soc.*, 1992, **114**, 4237; (*b*) A. M. Bond, W. Miao, C. L. Raston, T. J. Ness, M. J. Barnes and J. L. Atwood, *J. Phys. Chem. B*, 2001, **105**, 1687; (*c*) A. M. Bond, W. Miao, C. L. Raston and C. A. Sandoval, *J. Phys. Chem. B*, 2000, **104**, 8129; (*d*) A. M. Bond, W. Miao and C. L. Raston, *J. Phys. Chem. B*, 2000, **104**, 2320; (*e*) M. F. Suárez, F. Marken, R. G. Compton, A. M. Bond, W. Miao and C. L. Raston, *J. Phys. Chem. B*, 1999, **103**, 5637.

5 Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978.

6 R. C. Haddon, L. E. Brus and K. Raghavachari, *Chem. Phys. Lett.*, 1986, **125**, 459.

7 D. E. Cliffel and A. J. Bard, *J. Phys. Chem.*, 1994, **98**, 8140.

8 M. E. Niyazymbetov and D. H. Evans, *J. Electrochem. Soc.*, 1995, **142**, 2655.

9 For reviews of SECM see for example: (*a*) A. J. Bard, F.-R. F. Fan, D. T. Pierce, P. R. Unwin and D. O. Wipf, *Science*, 1991, **254**, 68; (*b*) A. J. Bard, F.-R. F. Fan and M. V. Mirkin, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1993, p. 243; (*c*) A. J. Bard, F.-R. F. Fan and M. V. Mirkin, in *Physical Electrochemistry: Principles, Methods and Applications*, ed. I. Rubinstein, Marcel Dekker, New York, 1995, p. 209; (*d*) P. R. Unwin, *J. Chem. Soc. Faraday Trans.*, 1998, **94**, 3183; (*e*) A. L. Barker, M. Gonsalves, J. V. Macpherson, C. J. Slevin and P. R. Unwin, *Anal. Chim. Acta*, 1999, **385**, 223; (*f*) S. Amemiya, Z. Ding, J. Zhou and A. J. Bard, *J. Electroanal. Chem.*, 2000, **483**, 7; (*g*) A. L. Barker, C. J. Slevin, P. R. Unwin and J. Zhang, in *Liquid Interfaces in Chemical, Biological and Pharmaceutical Applications*, ed. A. G. Volkov, Marcel Dekker, New York, 2001, p. 283.

10 See for example: (*a*) A. J. Bard, M. V. Mirkin, P. R. Unwin and D. O. Wipf, *J. Phys. Chem.*, 1992, **96**, 1861; (*b*) B. R. Horrocks, M. V. Mirkin and A. J. Bard, *J. Phys. Chem.*, 1994, **98**, 9106; (*c*) J. V. Macpherson and P. R. Unwin, *J. Phys. Chem.*, 1995, **99**, 3338; (*d*) J. V. Macpherson and P. R. Unwin, *J. Phys. Chem.*, 1995, **99**, 14824; (*e*) S. B. Basame and H. S. White, *Langmuir*, 1999, **15**, 819; (*f*) Y. Selzer, I. Turyan and D. Mandler, *J. Phys. Chem. B*, 1999, **103**, 1509.

11 See for example: (*a*) C. Wei, A. J. Bard and M. V. Mirkin, *J. Phys. Chem.*, 1995, **99**, 16033; (*b*) Y. Selzer and D. Mandler, *J. Electroanal. Chem.*, 1996, **409**, 15; (*c*) M. Tsionsky, A. J. Bard and M. V. Mirkin, *J. Am. Chem. Soc.*, 1997, **119**, 10785; (*d*) A. L. Barker, P. R. Unwin, S. Amemiya, J. Zhou and A. J. Bard, *J. Phys. Chem. B*, 1999, **103**, 7260; (*e*) Y. Selzer and D. Mandler, *J. Phys. Chem. B*, 2000, **104**, 4903; (*f*) J. Zhang, A. L. Barker and P. R. Unwin, *J. Electroanal. Chem.*, 2000, **483**, 95.

12 (*a*) C. J. Slevin and P. R. Unwin, *J. Am. Chem. Soc.*, 2000, **122**, 2597; (*b*) C. J. Slevin, S. Ryley, D. J. Walton and P. R. Unwin, *Langmuir*, 1998, **14**, 5331; (*c*) C. J. Slevin, J. V. Macpherson and P. R. Unwin, *J. Phys. Chem. B*, 1997, **101**, 10851.

13 M. V. Mirkin, L. O. S. Bulhões and A. J. Bard, *J. Am. Chem. Soc.*, 1993, **115**, 201.

14 D. E. Cliffel, A. J. Bard and S. Shinkai, *Anal. Chem.*, 1998, **70**, 4146.

15 A. G. Volkov, D. W. Deamer, D. L. Tanelian and V. S. Markin, *Liquid Interfaces in Chemistry and Biology*, Wiley, New York, 1998.

16 (*a*) J. H. Atherton, *Res. Chem. Kinet.*, 1994, **2**, 193; (*b*) P. R. Danesi and R. Chiarizia, *CRC Crit. Rev. Anal. Chem.*, 1980, **10**, 1.

17 *Liquid Interfaces in Chemical, Biological, and Pharmaceutical Applications*, ed. A. G. Volkov, Marcel Dekker, New York, 2001.

18 H. H. Girault, D. J. Schiffrin, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1989, vol. 15, p. 1.

19 For examples see: (*a*) H. Jensen, J. J. Kakkassery, H. Nagatani and H. H. Girault, *J. Am. Chem. Soc.*, 2000, **44**, 10943; (*b*) Y. Cheng and D. J. Schiffrin, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2517.

20 For a review, see for example: *Liquid–Liquid Interfaces: Theory and Methods*, eds. A. G. Volkov and D. W. Deamer, CRC Press, Boca Raton, 1996.

21 A. L. Balch and M. M. Olmstead, *Chem. Rev.*, 1998, **98**, 2123.

22 R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, *J. Phys. Chem.*, 1993, **97**, 3379.

23 *The Merck Index*, 7th edn., Merck & Co. Inc., Rahway, 1989.

24 (*a*) J. Zhang and P. R. Unwin, *J. Phys. Chem. B*, 2000, **104**, 2341 and references therein; (*b*) M. Tsionsky, A. J. Bard and M. V. Mirkin, *J. Phys. Chem. B*, 1996, **100**, 17881 and references therein.

25 J. V. Macpherson and P. R. Unwin, *J. Phys. Chem.*, 1994, **98**, 1704.

26 *Handbook of Chemistry and Physics*, 80th edn., CRC Press, Boca Raton, 1999, p. 3–33.

27 Y. Shao, M. V. Mirkin and J. F. Rusling, *J. Phys. Chem. B*, 1997, **101**, 3202.

28 J. Kwak and A. J. Bard, *Anal. Chem.*, 1989, **61**, 1221.

29 Y. Saito, *Rev. Polarogr. Jpn.*, 1968, **15**, 177.
30 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.
31 (*a*) R. A. Marcus, *J. Phys. Chem.*, 1990, **94**, 1050; (*b*) R. A. Marcus, *J. Phys. Chem.*, 1990, **94**, 4152; (*c*) R. A. Marcus, *J. Phys. Chem.*, 1990, **94**, 7742; (*d*) R. A. Marcus, *J. Phys. Chem.*, 1991, **95**, 2010; (*e*) R. A. Marcus, *J. Phys. Chem.*, 1995, **99**, 5742.
32 D. M. Guldi, P. Neta and K. D. Asmus, *J. Phys. Chem.*, 1994, **98**, 4617.
33 H. Imahori, K. Hagiwara, T. Akiyama, M. Aoki, S. Taniguchi, T. Okada, M. Shirakawa and Y. Sakata, *Chem. Phys. Lett.*, 1996, **263**, 545.
34 Y. Cheng and D. J. Schiffrin, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 199.
35 L. Eberson, *Adv. Phys. Org. Chem.*, 1982, **18**, 79.
36 Q. C. Ying, J. Marecek and B. Chu, *J. Chem. Phys.*, 1994, **101**, 2665.