

Marangoni flow in micro-channels

Hye Jin Lee^a, David J. Fermín^a, Robert M. Corn^b, Hubert H. Girault^{a,*}

^a *Laboratoire d'Electrochimie, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

^b *Department of Chemistry, University of Wisconsin, Madison, WI, USA*

Received 13 April 1999; received in revised form 26 April 1999; accepted 26 April 1999

Abstract

A novel electrochemical method for driving fluids in micro-channels is presented. The principle is based upon the onset of Marangoni flow along the interface between an aqueous solution (mobile phase) and an organic electrolyte polymer gel coated on the inner walls of the micro-channel. The gradient of surface tension responsible for the fluid motion arises from local changes in the surface charge. The excess charge is determined by the ionisation of surfactant species at the gel coating|aqueous electrolyte interface which is effectively dependent on the Galvani potential difference. Potential differences of less than a volt between two closely spaced silver band electrodes along the micro-channel can generate zones of high and low surface tension, promoting the motion of the aqueous electrolyte. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Marangoni flow; Liquid|polymer gel interfaces; Micro-channel networks; Surfactant

1. Introduction

Developments in micro-analysis have been hindered to some extent by the lack of efficient fluid pumping systems. The fluid movement in micro-channel networks built in glass, silica or polymeric materials is usually driven either by hydrostatic or electro-osmotic pumping [1–7]. While the former requires micro-pumps which impose limitations on the design of channel networks, electro-osmotic pumping involves high-voltage inputs through electrodes in contact with the solution. An alternative for controlling fluid motion is by capillary flow [8–10]. However, this process relies on chemical modifications of the surface properties, which in turn establish restrictions on the flow direction and rate.

A novel approach has been recently introduced by Abbott et al. [11,12] in which fluid pumping on millimetre-sized band electrodes is driven by gradients of surface tension. The difference in surface tension is created by local changes in the surface excess charge at two separated points along the channel. These authors employed ferrocene surfactants in order to generate zones of lower surface tension around the cathode with respect to the anode, leading to a flux of the mobile phase towards it. This phenomenon, known as Marangoni flow, can also be achieved at interfaces between two

immiscible electrolyte solutions (ITIES) as demonstrated by Girault and Schiffrin [13].

In the present communication, we demonstrate the Marangoni displacement of an aqueous electrolyte along a channel coated with an organic polymer electrolyte gel. The gradient of surface tension is developed by ionisation of the surfactant L- α -phosphatidylcholine (PC) at two localised points in the channel. As well as effective vectorial control of the fluid displacement, spatial resolution in the micrometer range can be achieved upon applying potential differences of the order of a volt.

2. Experimental

2.1. Electrolyte solutions

The polymer electrolyte gel was composed of high molecular weight polyvinylchloride (PVC) and 2-nitrophenyl-octylether (NPOE), in which tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl) was employed as the supporting electrolyte. An aqueous solution of potassium chloride (KCl) was used as the mobile phase. All reagents were of analytical grade or higher. Purified water from a Milli-Q 185 system was used for the aqueous solutions. The preparation of the organic supporting electrolyte has been reported elsewhere [14].

* Corresponding author. Tel.: +41-21-693-3151; fax: +41-21-693-3667; e-mail: hubert.girault@epfl.ch

2.2. Fabrication of micro-channel and polymer gel coating

The schematic diagram of the channel arrangement is displayed in Fig. 1(a) and (b). Two parallel grooves 40 μm wide, 35 μm deep and 10 000 μm long, separated by a distance of 3000 μm were photoablated in a polyethyleneterephthalate (PET) substrate with a UV Excimer laser. The photoablation process of the channel has been described previously [10]. The grooves were filled with a silver ink and cured at 70°C to form two parallel electrodes. A micro-channel 200 μm wide, 70 μm deep and 22 mm long was photoablated on the opposite side of the substrate, in a direction perpendicular to the two electrodes. The channel depth was such that the electrodes were effectively exposed at the bottom. The micro-channel was subsequently filled with a solution containing TBATPBCl and the surfactant, L- α -phosphatidylcholine (PC), dissolved in a mixture of NPOE/tetrahydrofuran (THF) (60% v/v) and PVC (2.8% m/m). THF was evaporated in order to form a gel coating on the channel wall. The micro-photograph, shown in Fig. 1(c), revealed the coating layer inside the channel. The last step was to enclose the main channel by a thermal lamination technique with PET (30 μm thick)/polyethylene (PE) (5 μm thick) at 125°C for 1 or 2 s in order to create a flow channel. The polarisation of the two silver bands was performed using a computer-controlled potentiostat.

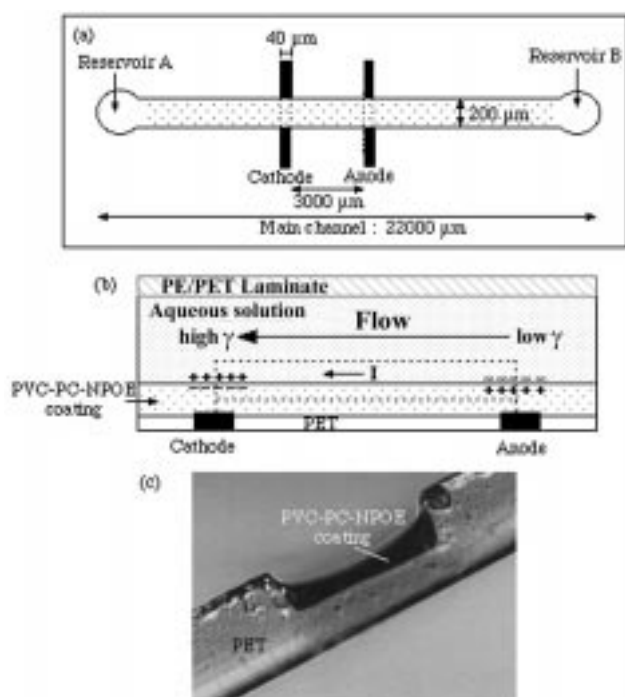


Fig. 1. Schematic diagram of top (a) and cross-section views (b) of the micro-channel arrangement. Aqueous electrolyte solution contained 10 mM KCl. Micro-photograph of the main flow channel coated with a solution of 2.8% (m/m) of 2-nitrophenyloctylether-polyvinylchloride gel in the presence of phosphatidylcholine (c).

3. Results and discussion

The excess charge across the gel coating|aqueous electrolyte interface as a function of the applied potential can be studied by differential capacitance measurements employing a cell, the arrangement of which is shown in Scheme 1.

In Fig. 2, the differential capacitance in the presence and absence of PC is displayed as a function of the potential drop between the electrodes in contact with the polymer gel and the aqueous phase ($\Delta E = E_{\text{gel coating}} - E_{\text{water}}$). It was observed that the capacitance increased as the gel layer containing PC was polarised positive with respect to the aqueous phase. Changes in the differential capacitance were negligible in the absence of the surfactant. The potential dependence of the surface tension can be estimated by double integration of the differential capacitance. The decrease of the surface tension with increasing applied potential (see Fig. 2) is associated with the protonation of the phosphate groups exposed to the aqueous side [13]. The protonation effect arises as a result of changes in the interfacial pH with the Galvani potential difference. The solution of the Boltzmann distribution for protons at the interface establishes that the pH relationship between the surface (pH_S) and bulk (pH_B) follows:

$$\text{pH}_S = \text{pH}_B - \frac{F}{2.3RT} E_{\text{water}} \quad (1)$$

where E_{water} corresponds to the potential drop developed in the aqueous phase [15–17]. Consequently, the interfacial pH

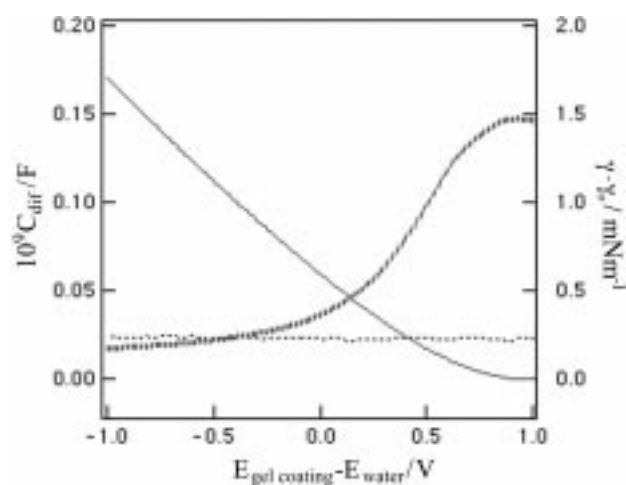
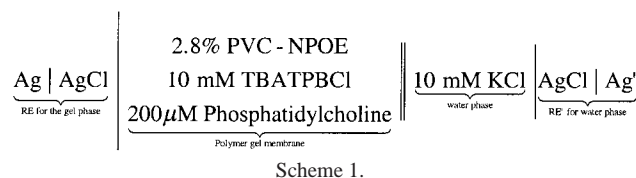


Fig. 2. Differential capacitance in the presence (---) and absence (---) of PC as a function of the potential drop between the gel coating and the aqueous phase. The frequency and amplitude of potential modulation were 118 Hz and 1 V (rms), respectively. The potential dependence of the surface tension (—) was obtained by double integration of the differential capacitance curve. γ_0 corresponds to the constant resulting from the double integration of the differential capacitance with respect to the applied potential.

decreases as the potential difference ΔE decreases, leading to the surface protonation of the surfactant and the effective drop of the excess charge in the aqueous side [18].

A potential drop across the two band electrodes along the channel will generate zones of different polarisations between the gel coating and the aqueous phase. The ion mobility in the aqueous electrolyte is substantially higher than in the polymer gel, therefore, it is expected that the surface tension of the polymer gel|aqueous junction near the cathode will be higher than over the anode (see Fig. 1(b)). This gradient of surface tension is able to onset the Marangoni flow of the aqueous phase as exemplified in Fig. 3. In this sequence of images, a spherical particle is displaced along a 670 μm channel towards the cathode. Typical water front speeds have been estimated of the order of 100 $\mu\text{m s}^{-1}$. No flow was observed in the absence of the surfactant.

One of the most important features from an application point of view is that reversing the electrode polarisation results in inversion of the flow. This property indicates the vectorial control of the flow within the channel. The correlation between applied potential and flow rate is rather difficult to rationalise due to the complicated potential distribution under this arrangement. However, it was observed that the onset potential was 0.5 V, while no detectable changes in the flux occurred at potentials higher than 2 V. The effect of the inter-electrode distance was also studied and optimal values were obtained in the range of 3 to 5 mm.

The pH of the aqueous solution also plays a fundamental role. The maximum flow is observed between pH 5 and 6. No flow was observed at pH either lower than 3 or higher

than 9. This effect clearly indicates that the gradient in surface tension is connected to the local protonation of the surfactant whose bulk $\text{p}K_{\text{a}}$ values for the phosphate and amino groups are 1.4 and 11.6, respectively [19]. Outside the pH range from 3 to 9, the excess charge becomes independent of the Galvani potential difference as the surfactant remains either fully protonated or deprotonated. Only at pH close to 5 can local protonation be induced upon polarisation of the interface leading to surface tension gradient.

4. Conclusions

It is demonstrated that a surface tension gradient along the interface between a gel coating and an aqueous electrolyte provides an effective driving force for fluid pumping in micro-channels. The origin of this effect is related to local protonation of surfactant species adsorbed at the gel|aqueous electrolyte interface. In comparison to electro-osmotic and capillary flow methods, this new approach offers a full vectorial control of the fluid displacement in the micrometer range using low voltages. It is envisaged that complicated fluid motions in micro-channel networks could be achieved by applying small potential differences across the various nodes.

Acknowledgements

The authors wish to acknowledge the financial support given by the Fonds National pour la Recherche Scientifique Suisse under Grant No. FN 5002-045020. Thanks are also expressed to Daniele Laub of the CIME Service, Ecole Polytechnique Fédérale de Lausanne, for optical microscopy photography. Laboratoire d'Electrochimie is part of the European Training & Mobility Network on 'Organization, Dynamics and Reactivity at Electrified Liquid|Liquid Interfaces' (ODRELLI).

References

- [1] A. Manz, H. Becker, *Microsystem Technology in Chemistry and Life Science*, Springer, New York, 1998.
- [2] M.U. Kopp, A.J. Mello, A. Manz, *Science* 280 (1998) 1046.
- [3] P. Lenney, N.J. Goddard, J.C. Morey, R.D. Snook, P.R. Fielden, *Sensors and Actuators B* 38 (1997) 212.
- [4] R.S. Ramsey, J.M. Ramsey, *Anal. Chem.* 69 (1997) 1174.
- [5] Z. Fan, D.J. Harrison, *Anal. Chem.* 66 (1994) 177.
- [6] A. Manz, C.S. Effenhauser, N. Burggraf, D.J. Harrison, K. Seiler, K. Fluri, *J. Micromech. Microeng. Microfluidics, Special* (1994) 1.
- [7] D.J. Harrison, K. Fluri, K. Seiler, Z. Fan, C.S. Effenhauser, A. Manz, *Science* 261 (1993) 895.
- [8] M.A. Roberts, J.S. Rossier, B.J. Seddon, P. Bercier, H.H. Girault, *Anal. Chem.* 69 (1997) 2035.
- [9] E. Delamarque, A. Bernard, H. Schmid, B. Michel, H. Biebuyck, *Science* 276 (1997) 779.
- [10] E. Kim, Y. Xia, M. Whitesides, *Nature* 376 (1995) 581.

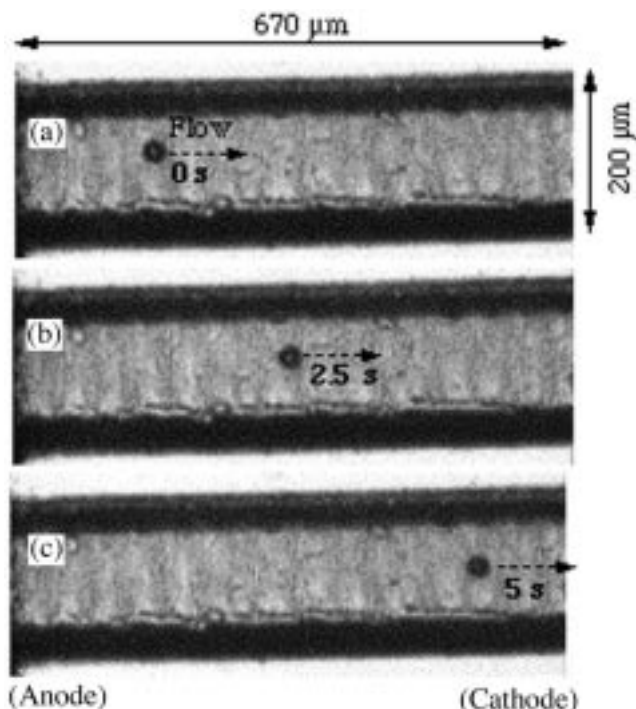


Fig. 3. Spherical particle displaced by the electrolyte flow along the channel at 2 V. The electrolyte pH was 5.

- [11] B.S. Gallardo, V.K. Gupta, F.D. Eagerton, L.I. Jong, V.S. Craig, R.R. Shah, N.L. Abbott, *Science* 283 (1999) 57.
- [12] N.L. Abbott, *Colloid Polym. Sci.* 103 (1997) 300.
- [13] H.H.J. Girault, D.J. Schiffrin, *J. Electroanal. Chem.* 179 (1984) 277.
- [14] H.J. Lee, C. Beriet, H.H. Girault, *J. Electroanal. Chem.* 453 (1998) 211.
- [15] R.R. Naujok, D.A. Higgins, D.G. Hanken, R.M. Corn, *J. Chem. Soc., Faraday Trans.* 91 (1995) 1411.
- [16] X. Zhao, S. Ong, H. Wang, K.B. Eisenthal, *Chem. Phys. Lett.* 214 (1993) 203.
- [17] P.-F. Brevet, H.H. Girault, in: A. Yolkov, D. Deamer (Eds.), *Liquid–Liquid Interfaces, Theory and Methods*, CRC Press, Boca Raton, FL, 1996, Ch. 6.
- [18] T. Kakiuchi, M. Nakanishi, M. Senda, *Bull. Chem. Soc. Jpn.* 62 (1989) 403.
- [19] T. Seimiya, S. Ohki, *Biochim. Biophys. Acta* 298 (1973) 546.