Osmosis and pervaporation in polyimide submicron microfluidic channel structures

Jan C. T. Eijkel, Johan G. Bomer, and Albert van den Berg

BIOS/Lab-on-a-Chip Group, MESA+ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Osmosis and pervaporation of water through the roof of all-polyimide channels of 500 nm height is described. The phenomena cause both a liquid flow in the channels and a concentration change of dissolved salt. Both effects are amplified due to the thin channel roof and the small channel height. Osmotic movement of demineralized water was observed towards a salt solution and towards ethanol and isopropanol. Water movement by pervaporation was observed from a salt solution towards the atmosphere. Flow velocities of up to 70 μm/s were generated in the channels. The results are in accordance with predictions from the solution-diffusion model for membrane transport. The observed phenomena can be applied in a nanofluidic osmotic pump or for an osmotic or pervaporative concentrator. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2046727]

Polymer membranes are widely used in the chemical industry for separation processes and for reverse osmosis.[1] Recently it was shown that one-dimensional nanochannels with polyimide walls of a few micrometers thickness and heights of 100 and 500 nm can be fabricated using the simple cleanroom methods of spinning and thin film deposition.[2] Since the thin walls of these channels can be considered as membranes, transport processes like osmosis (transport from liquid to liquid phase) and pervaporation (transport from liquid to vapor phase) can be expected to occur across the walls and it was the objective of this study to investigate this. On-chip applications of these phenomena can be similar to applications of polymer membranes, i.e., separation or concentration, with the added convenience of easy patterning of the flow structure. It will also be possible to manufacture an osmotic pump. Osmotic pumping can be regarded as a valuable addition to evaporative pumping,[3] in the same manner as solute concentration by osmosis can be regarded as a valuable addition to the same process by evaporation.[4–6]

Nanochannels with polyimide walls [4 mm long, 500 nm high, arranged in arrays of 16 parallel channels of 2–30 μm width, see Figs. 1(a) and 1(b)] were manufactured using a combination of spinning of a photopatternable polyimide and sacrificial-layer etching of aluminium.[1] Parts of pipette tips were glued to both channel entrance areas to serve as solution reservoirs. The channel array was filled with a 0.1 M KNO$_3$ solution and the channel roof in the permeation area was exposed to air with a relative humidity of 30% [Fig. 1(c)]. It is expected that water pervaporates from the solution to the atmosphere, down its chemical potential gradient. Such pervaporation would cause a concentration increase of KNO$_3$ and indeed the channel conductance (monitored with a HP 4194A impedance analyzer using a 100 mV ac electrical signal between 100 and 500 Hz) was observed to increase in time [Fig. 1(d)]. When the channel solution was refreshed with 0.1 M KNO$_3$ by applying suction to one of the reservoirs, conductance returned to approximately the initial value, to increase again by continued pervaporation. From the data the flow velocity from each reservoir to the exchange area was calculated using a simple model accounting for the counteracting effect of KNO$_3$ dif-

fusion. Calculated initial velocities in different experiments were 2–4 μm/s from each reservoir. An estimate of the resulting KNO$_3$ concentration under the exchange zone after 50 min was 0.7 M, an increase by a factor of 7.

For osmosis experiments a branched nanochannel structure was used with an increased permeation area [Fig. 2(a)]. Channels were 500 nm high and 30 μm wide. The length of the 16-fold branched permeation area in these chips was 1 mm. In a first experiment, the branched structure was filled with demineralized water, and 100 μl of demineralized water was deposited on top of the permeation area. In this situation no water chemical potential gradient exists over the channel roof and the meniscus stayed in place. Subsequently 50 μl of saturated NaCl solution was mixed with the demineralized
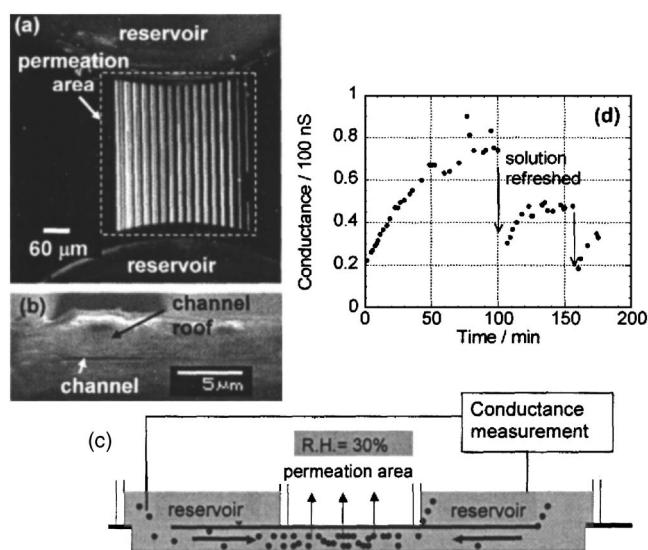

FIG. 1. (a) Top view of the polyimide channel array used for pervaporation experiments. The permeation area is indicated by the dashed rectangle. (b) Cross section of one channel. Roof thickness is 2.3 μm. (c) Schematic of the pervaporation experiment. Dots indicate dissolved KNO$_3$. Pumping indicated by arrows coincides with a change in salt concentration measured as a change in channel conductance. (d) Change in channel conductance observed as a result of water pervaporation through the channel roof. The channel solution is refreshed at $t=100$ and $t=155$ min, restoring original conductance.
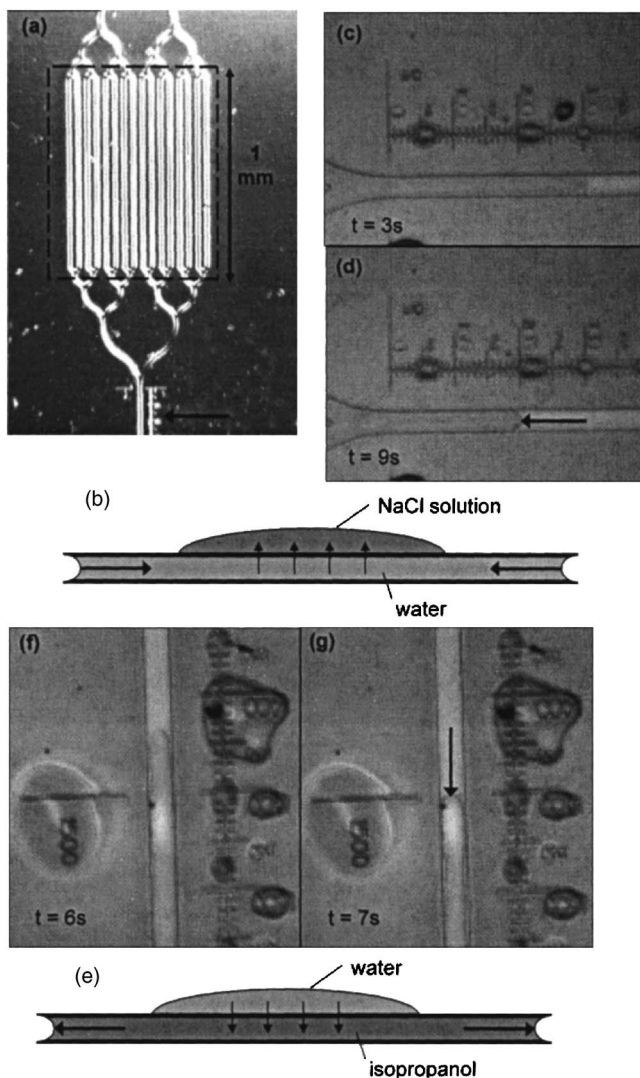
FIG. 2. (a) Branched channel structure used for osmotic experiments. The permeation area is indicated by the dashed rectangle. The meniscus speed was observed at the location of the arrow [compare (c) and (d)]. (b) Schematic of the first osmosis experiments with water permeating out of the channel towards a NaCl solution on top of the permeation area. (c)–(d) Observed water meniscus movement; the indicated times are after addition of NaCl. (e) Schematic of the second osmosis experiments with water permeating into the channel towards an alcohol (isopropanol or ethanol). (f)–(g) Observed isopropanol meniscus movement; the indicated times are after placing a water drop on the exchange area.

water on top of the permeation area [Fig. 2(b)]. The resulting water chemical potential gradient draws the water out of the channel and Figs. 2(c) and 2(d) show the resulting meniscus movement. The response time for meniscus movement to start was about 3 s. The average velocity recorded over a time period of 6 seconds was about 16 μm/s. The observed change of curvature of the meniscus is due to a buckling of the polyimide roof at the location reached at $t=9$ s.

In a second experiment, the branched channel structure [Fig. 2(a)] was filled with isopropanol. Subsequently 100 μl of demineralized water was deposited on top of the branched structure (permeation area) [Fig. 2(e)]. The polyimide channel wall is assumed to have a large selectivity for water transport over alcohol transport.[1,7,8] Due to the gradient in chemical potential created, water starts permeating into the channels and Figs. 2(f) and 2(g) show the resulting meniscus movement. The response time was about 2 s and the average

velocity recorded was about 70 μm/s. Comparable flow velocities were obtained when the channel structure was filled with ethanol.

The data obtained here allow some general conclusions to be drawn. First we can conclude that pumping in polyimide channel structures can be generated by gradients in water chemical potential over the channel roof. Such gradients were created between demineralized water and air of 30% RH, between a salt solution and demineralized water and between an alcohol and demineralized water. It was also shown that the pervaporative pumping was accompanied by a concentration change in the pumped solution. Furthermore an enhancement of pumping speed due to the use of channel branching [Fig. 2(a)] was demonstrated.

The solution-diffusion model for membrane pervaporation and osmosis[9,10] can be used to calculate theoretical water transport rates. Here the transport rate is calculated from the chemical potential gradient of the transported substance over a membrane and a pervaporation coefficient. From the chemical potentials of -1.65×10^8 Pa (Refs. 11 and 12) in the atmosphere (RH=30%) and -5×10^5 Pa in the channel (0.1 M KNO$_3$), a membrane thickness of 2.3 μm and a water permeability coefficient of 9×10^{-15} m^3 m/(s m^2 Pa),[13,14] a flow velocity of 3 μm/s from each reservoir was calculated for the pervaporation experiments, corresponding satisfactorily with the values derived from the conductivity increase ($2-4$ μm/s). In the osmosis experiment with isopropanol and water, the branched structure showed a pumping velocity of about 70 μm/s at a comparable difference in water potential. This difference is close to the 27-fold enhancement in pumping speed expected from the difference in exchange area between the branched (Fig. 2) and nonbranched (Fig. 1) structures. Capillary forces can be excluded as driving force in the osmosis experiment because an identical meniscus existed on both sides of the exchange structure.

The observed effects offer numerous possibilities for application in micro-or nanofluidic devices, sample concentration and pumping. In general all the processes applied in the membrane industry can be used in a geometrically controlled manner on the chip scale. The manufacturing technique used furthermore enables multilayer construction, which would allow for controlling and responding layers. The observed response times of a few seconds are suitable for a fast-responding on-chip pumping system. Another possible application area is osmotically-driven drug release from microfluidic systems like what was demonstrated for osmotic capsules.[15]

[1]A. Jonquières, R. Clément, and P. Lochon, Prog. Polym. Sci. **27**, 1803 (2002).
[2]J. C. T. Eijkel, J. G. Bomer, N. R. Tas, and A. van den Berg, Lab Chip **4**, 161 (2004).
[3]N. Goedecke, J. C. T. Eijkel, and A. Manz, Lab Chip **2**, 219 (2002).
[4]C. S. Effenhauser, H. Harttig, and P. Kramer, Biomed. Microdevices **4**, 27 (2002).
[5]G. M. Walker and D. J. Beebe, Lab Chip **2**, 57 (2002).
[6]B. H. Timmer, K. M. van Delft, W. Olthuis, P. Bergveld, and A. van den Berg, Sens. Actuators B **91**, 342 (2003).
[7]H. Yanagisita, D. Kitamoto, K. Haraya, T. Nakane, T. Tsuchiya, and N. Koura, J. Membr. Sci. **136**, 121 (1997).

[8]J. Kim, K. Lee, and S. Kim, J. Membr. Sci. **169**, 81 (2000).
[9]J. G. Wijmans and R. W. Baker, J. Membr. Sci. **107**, 1 (1995).
[10]X. Feng and R. Y. M. Huang, Ind. Eng. Chem. Res. **36**, 1048 (1997).
[11]B. V. Derjaguin and N. V. Churaev, J. Colloid Interface Sci. **54**, 157 (1976).

[12]M. Tuller and D. Or, Water Resour. Res. **37**, 1257 (2001).
[13]J. L. Mrotek, M. J. Matthewson, and C. R. Kurkjian, J. Lightwave Technol. **19**, 988 (2001).
[14]J. Seo and H. Han, J. Appl. Polym. Sci. **82**, 731 (2001).
[15]F. Theeuwes, J. Pharm. Sci. **64**, 1987 (1975).