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Short Communication

Electrokinetic energy conversion in microchannels using polymer solutions

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ABSTRACT

Electrokinetic energy conversion in microfluidic systems is a subject of intense research at present, where the main objective is to improve the thermodynamic efficiency of the process. As a novel strategy to the problem, this work focuses on the fluid dynamic properties of the working fluid. It is shown that polymer solutions with wall depletion can substantially increase the conversion efficiency in comparison to simple electrolytes under the same operating conditions. The effect is given by a reduction of the hydrodynamic conductance, while the streaming current is unaltered. It is also found that the maximum efficiency of electrokinetic power generation differs from that of electroosmotic pumping, in contrast to the case of simple electrolytes. This is due to the non-Newtonian character of polymeric fluids, which leads to nonlinear electrokinetic relations.

1. Introduction

Energy conversion in microsystems is a subject of intense research at present. In particular, the generation of electric current by means of electrokinetic phenomena, which has been known for many years [1], has experienced a renascence with the advent of nanofluidics and microfluidics [2–7]. The main goal of researchers in the field is to improve the thermodynamic efficiency of the converters [8–11].

Electrokinetic phenomena in microchannels require the presence of interfacial charge, with the associated electric double layer (EDL) of ions. When a flow rate Q is established by applying a pressure difference ΔP between microchannel ends (Fig. 1a), the convective transport of excess ions in solution produces the so-called streaming current in the direction of the flow. A streaming potential ΔV is also generated, which induces a conduction current in the opposite direction. Thus the net electric current I that may be supplied to an external load results from the difference between the forward (streaming) and the backward (conduction) fluxes of charge. In the case of simple electrolyte solutions, under steady and isothermal conditions, the coupled flows of fluid and electricity are described by Onsager relations for electrokinetic phenomena [12],

$$Q = L_{11}\Delta P + L_{12}\Delta V, \qquad (1)$$

$$I = L_{21}\Delta P + L_{22}\Delta V, \qquad (2)$$

where the coefficient L_{11} is the hydrodynamic conductance, $L_{12} = L_{21}$ represents electroosmosis/streaming phenomena (Onsager reciprocal relation), and L_{22} comprises the electric conductance.

The thermodynamic efficiency of the energy conversion is defined as the ratio of the useful electrical power to the mechanical power consumption, $\chi = I\Delta V/Q(-\Delta P)$ [1–3,8]. By using Eqs. (1) and (2), and considering that $L_{12}\Delta V \ll L_{11}\Delta P$ (see also [3]), the maximum value of χ is reached at $\Delta V = -L_{21}\Delta P/(2L_{22})$, and can be expressed as

$$\chi_{\max} = \frac{1}{4}\frac{L_{12}^2}{L_{11}L_{22}}. \qquad (3)$$

Therefore, obtaining better performance of electrokinetic energy converters requires a maximization of the ratio $L_{12}^2/L_{11}L_{22}$, as demonstrated in [8]. Accordingly, the efforts to improve $\chi_{\max}$ are invariably addressed to increase L_{12} and/or decrease L_{11} and L_{22}. For example, a special advance has been the introduction of liquid slip that significantly enhances the streaming effect [10,11]. On the other hand, energy dissipation due to back conduction can be eliminated by using liquid microjets [5]. The hydrodynamic conductance is normally minimized by reducing channel radius R up to the limit where its size approaches the EDL thickness λ (nano-scale fluidic channels), a situation in which $\chi_{\max}$ presents a peak [2,4,8].

Further diminution of L_{11} by increasing the fluid viscosity is unfeasible with simple liquids, because the viscosity also enters L_{12} and the overall result is a diminution of $\chi_{\max}$. As an alternative, this work discusses the use of viscous polymer solutions as working fluid. The key aspect is that the polymer must undergo wall depletion, so that the interfacial region where the streaming current takes place is free of polymer molecules, and the local viscosity is that of the pure solvent (Fig. 1b). It means decreasing L_{11}

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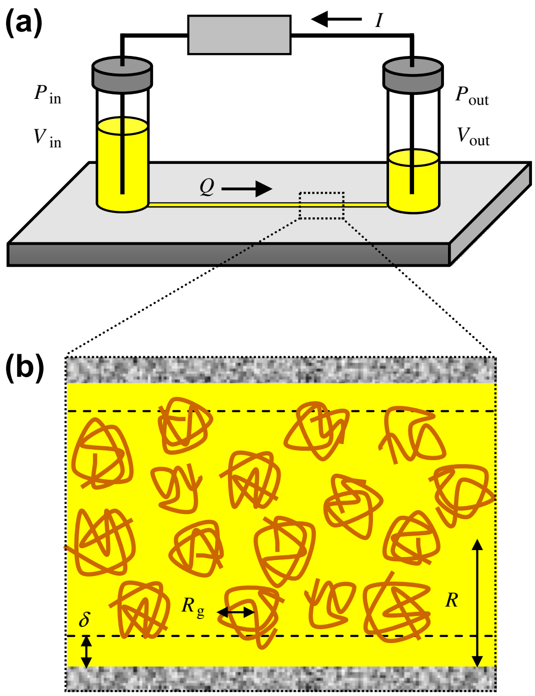

Fig. 1. (a) Drawing of an elementary electrokinetic generator consisting of a microchannel, fluid reservoirs, and electrical connections to an external load. (b) Schematic representations of a solution of nonadsorbing polymers into the microchannel (not to scale; see text for definitions).

without affecting L_{12}. Indeed, this effect has been recently investigated [13] for electroosmotic pumping. The present paper shows how polymer solutions can substantially improve the thermodynamic efficiency of electrokinetic power generation, in comparison to simple electrolyte solutions under the same operating conditions.

2. General considerations

Polymer solutions are normally constituted by a background electrolyte, the "solvent," and a certain concentration of dissolved polymers. The viscosity of the solvent is a constant coefficient μ_s, while the viscosity of polymer solution, $\eta(\dot{\gamma})$, depends on the shear rate $\dot{\gamma}$, and is always higher than μ_s [14]. The radius of gyration of polymer molecules (R_g, Fig. 1b) can be several tenths of nanometers; thus micro-scale fluidic channels need to be considered to satisfy the continuum hypothesis ($R \ll R_g$). Further, in polymer solutions $\lambda < 10$ nm; hence the thin EDL approximation is used. Given these assumptions, the electrokinetic flow equations reported below are addressed to microchannels and moderate ionic strength.

The efficiency attained with simple electrolytes (solvent) is taken as a reference. Theoretical expressions of the conductance coefficients are available for straight microchannels with cylindrical cross section and uniform surface properties [1,8,13]. In particular, for $\lambda \ll R$, these expressions are $L_{11} = -AR^2/(8\mu_s l)$, $L_{12} = L_{21} = A\varepsilon\zeta/\mu_s l$, and $L_{22} = -A\sigma/l$, where A and l are the cross-sectional area and length of the channel, respectively, ζ is the electrokinetic potential, ε is the dielectric permittivity, and σ is the electrical conductivity of the fluid. The minus sign is related to the definition of pressure and potential differences ($\Delta P = P_{\text{out}} - P_{\text{in}}$, $\Delta V = V_{\text{out}} - V_{\text{in}}$; Fig. 1a). Substituting these coefficients into Eq. (3) yields $\chi^{(s)}_{\max} = 2(\varepsilon\zeta)^2/(R^2\mu_s\sigma)$, where the superscript s indicates solvent. It is evident that the efficiency decreases when the fluid viscosity increases, and that channel radius is a critical factor. For instance, given a microchannel with $R = 10$ μm, filled with an aqueous solution of 1 mM KCl, and $\zeta = 100$ mV, $\chi^{(s)}_{\max} \sim 10^{-5}$. This value is far from the conversion efficiency reached with nanochannels and very low ionic strength, $\chi^{(s)}_{\max} \approx 3$–$5\%$ [4,6]. Precisely, it is worth noting that the value predicted here is valid for microchannels and moderate ionic strength, which is the framework needed here to discus the effect of polymer solutions.

3. Electrokinetic flow of polymer solutions

The electrokinetic flow of shear-dependent polymer solutions has been described in a previous work [15] by using different constitutive models of inelastic fluids. Results obtained with the "power law" model are used here; i.e., $\eta(\dot{\gamma}) = \beta\dot{\gamma}^{\alpha-1}$, where β is the consistency parameter and α is the flow behavior index [14]. As noted above, a crucial aspect is the existence of wall depletion of polymer molecules. This behavior is observed in nonadsorbing polymers, the concentration of which decreases steeply near the wall [16]. The thickness δ of the depletion layer is on the order of R_g (Fig. 1b). Therefore, and considering that $\lambda < \delta$, electrokinetic effects take place in the depletion layer, which is free of polymers, and the local viscosity is μ_s. Under these conditions, the coefficients L_{12}, L_{21}, and L_{22} of polymer solutions coincide with those of the solvent (further details are given in [15]). Nevertheless, the hydrodynamic conductance takes the following expression,

$$\mathscr{L}_{11}(\Delta P) = \frac{-AR^2}{8l}\left\{\frac{4(1-\delta/R)^{3+1/\alpha}}{(3+1/\alpha)\beta^{1/\alpha}}\left(\frac{R|\Delta P|}{2l}\right)^{1/\alpha-1} + \frac{1-(1-\delta/R)^4}{\mu_s}\right\}, \tag{4}$$

where the first term comes form the bulk polymer fluid, and the second is due to the layer of solvent adjacent to the wall (Fig. 1b). It is observed that $\mathscr{L}_{11}$ is not more of a coefficient but a function of the applied pressure ΔP, which directly influences the shear rate $\dot{\gamma}$, and hence the polymer viscosity [15]. Consequently Q is nonlinear with ΔP. This model has been validated against experimental data of electroosmotic pumping [13].

4. Conversion efficiency

According to the results above, the electric current is in principle unaffected by the polymer (Eq. (2) with coefficients reported in Section 2), and the flow rate is given by $Q = \mathscr{L}_{11}(\Delta P)\Delta P + L_{12}\Delta V$, with $\mathscr{L}_{11}$ from Eq. (4). With these expressions, the maximum efficiency of current generation results,

$$\frac{\chi^{(p)}_{\max}}{\chi^{(s)}_{\max}} = \frac{L_{11}}{\mathscr{L}_{11}(\Delta P)}, \tag{5}$$

where the superscript p indicates polymer. Three main features of Eq. (5) must be noted: (i) The conversion efficiency of the polymer solution is higher than that of the solvent, taking into account that the hydrodynamic conductance of a polymer solution is always lower than that of the solvent alone. (ii) The gain of the efficiency is entirely given by the diminution of the mechanical power consumption, while the generated power is unaltered. (iii) The relative efficiency depends on the applied pressure, and differs from the corresponding result for electroosmotic pumping (compare to Eq. (24) in [13]), which in turns depends on the applied electric potential. Actually, the predicted efficiencies for generation and pumping modes are identical only if $\alpha = 1$, i.e., if the polymer solution has a Newtonian viscosity μ_p and Q is linear with ΔP.

The case of Newtonian polymer solutions is analyzed first, for the sake of simplicity. Introducing $\alpha = 1$ and $\beta = \mu_p$ into $\mathscr{L}_{11}$ yields $\chi^{(p)}_{\max}/\chi^{(s)}_{\max} = [1 + (\mu_s/\mu_p - 1)(1-\delta/R)^4]^{-1}$. In the limit $\delta/R \ll 1$, $\chi^{(p)}_{\max}/\chi^{(s)}_{\max} = \mu_p/\mu_s$, which clearly shows the gain of thermodynamic

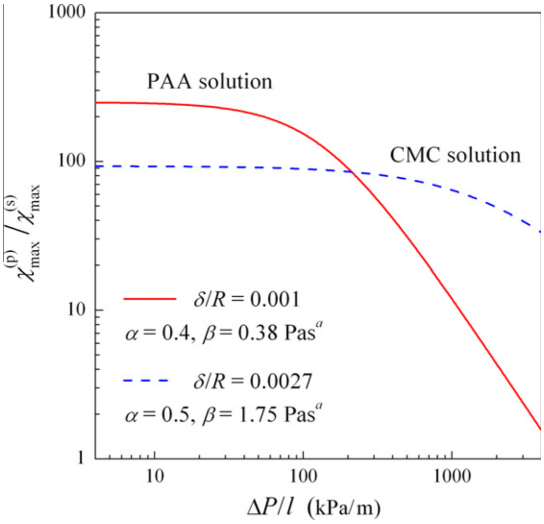

Fig. 2. Maximum efficiency, relative to that of the solvent, as a function of the applied pressure gradient, for polymer fluids with wall depletion in cylindrical microchannels. The full line represents a solution of 8.33 mM polyacrylic acid (PAA) at pH 8.2 and 25 °C; the background electrolyte is an aqueous solution of 10 mM Tris and 5 mM acetic acid [17]. Calculations were made for $R = 37\ \mu\mathrm{m}$ and $\delta = 100$ nm. The dashed line represents a solution of 1% carboxymethyl cellulose (CMC) at pH 7 and 25 °C; the background electrolyte is an aqueous solution of 15 mM phosphoric acid [18]. Calculations were made for $R = 10\ \mu\mathrm{m}$ and $\delta = 10$ nm.

efficiency in relation to simple electrolytes. On the other hand, in the limit $\mu_p/\mu_s \gg 1$, $\chi_{max}^{(p)}/\chi_{max}^{(s)} = [1-(1-\delta/R)^4]^{-1}$, and the ratio δ/R becomes the controlling factor. Therefore the largest efficiencies are expected for $\mu_p \gg \mu_s$ and $\delta \ll R$, which in practical terms means concentrated solutions of low molecular weight polymers.

The prediction of Eq. (5) for arbitrary values of α is illustrated in Fig. 2, by using data of polymer solutions previously employed in experiments of electroosmotic pumping: polyacrylic acid (PAA) [17] and carboxymethyl cellulose (CMC) [18]. It is observed that the conversion efficiency is two orders of magnitude higher than that obtained with simple electrolytes in the same experiment. However these polymers are shear thinning, and the efficiency decreases with the applied pressure (the opposite is expected for shear-thickening fluids). At low pressure gradients, where the viscosity is the highest, the efficiency is limited by the ratio δ/R, as explained above.

It is interesting to observe the interplay between the viscosity level (measured by β) and the depletion layer thickness in these examples. The size of PAA molecules is rather small ($\delta \approx 10$ nm); hence the solution presents a relatively high efficiency at low ΔP, but decreases rapidly at larger pressures. In contrast, CMC involve large molecules ($\delta \approx 100$ nm), which limit the efficiency at low ΔP, but yield relatively large efficiencies at high pressures, due to the large viscosity of the solution. In fact, this simple analysis shows how molecular weight and polymer concentration can be adjusted to improve the conversion efficiency. In addition, parameters α, β, and δ strongly depend on ionic strength, pH, and temperature, which enable further possibilities of optimization.

5. Conclusions

The calculations above indicate that $\chi_{max}^{(p)}/\chi_{max}^{(s)} \sim 10^3$ could be reached with proper formulations of the working fluid. Considering $\chi_{max}^{(s)} \sim 10^{-5}$, absolute efficiencies $\chi_{max}^{(p)} \sim 1\%$ are in principle achievable with polymer solutions. This value remains below the best performances obtained with nanochannels [4,6], but it involves microchannels and moderate ionic strength. Moreover, the restriction of $R \geqslant 10\ \mu\mathrm{m}$ included to satisfy the continuum hypothesis in modeling [15] can be relaxed in practice to provide even better efficiencies.

It had been suggested [8] that future work on electrokinetic power generation should be focused on the search of working fluids with improved physicochemical properties. In this sense, one may observe that the employment of polymer solutions is a promising strategy that deserves further investigation.

In addition to the problem of energy conversion, understanding the electrokinetic transport of polymeric liquids is of interest from a fundamental point of view (nonlinear electrokinetics), as well as for the development of microfluidic technology that manipulates complex fluids.

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