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Manipulation of fluid flow direction in microfluidic paper-based analytical devices with an ionogel negative passive pump

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ABSTRACT

Microfluidic paper-based analytical devices (μPADs) are a relatively new group of analytical tools that represent an innovative low-cost platform technology for fluid handling and analysis. Nonetheless, μPADs lack in the effective handling and controlling of fluids, which leads to a main drawback for their reproducibility in large volumes during manufacturing, their transition from the laboratory into the market and thus accessibility by end-users. Herein we investigate the applicability of ionogel materials based on a poly(*N*-isopropylacrylamide) gel with the 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid as fluid flow manipulator in μPADs using the ionogel as a negative passive pump to control the flow direction in the device. A big challenge undertook by this contribution is the integration of the ionogel materials into the μPADs. Finally, the characterisation and the performance of the ionogel as a negative passive pump is demonstrated.

1. Introduction

Ionic liquids (ILs) are drawing an incredible amount of attention both from academics and the industry due to their environment-friendly properties, and particularly their potential in green chemistry. The rapid growing number of publications and patents can be considered proof of the large amount of research and investment in this area and their potential applicability has been revealed by some inspiring results [1,2]. ILs are salts, completely composed of ions with melting temperatures below 100 °C, a result of their low-charge density and low symmetry ions [1,3–5]. ILs are categorised as "green" solvents thanks to their unique properties, such as negligible vapour pressure, large range of temperatures at liquid stage [4], conventional non-flammability, non-volatility, and their outstanding solvation potential [2,6–10]. Besides, due to their ionic character, most aprotic ILs display high thermal stability with decomposition temperatures around 300–500 °C, high chemical stabilities (extremely redox robustness), high ionic conductivity, and high solvation ability for organic, inorganic and organometallic compounds with improved selectivity [1–3,11–14]. They are generally described as "designer solvents" and their potential is further extended due to the fact that their physical and chemical properties (such as their thermophysical properties, biodegradation ability or toxicological features, as well as their hydrophobicity and solution behaviours) may be delicately tuned by varying both the cation and the anion [1,3,15–19]. Moreover, their tunable properties are enabling rapid advances in devices and processes for the production, storage and efficient use of energy [1,20].

However, for material applications, the main requirement is immobilising ILs in solid devices while keeping their specific properties, which is highly challenging [21]. Ionogels form a new class of hybrid materials that preserve the main properties of the ILs (liquid-like dynamics and ion mobility) but in a solid or gel like

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structure, while allowing easy shaping and thus, increasing considerably the potential use of ILs in key areas such as energy, environment and analysis [21,22]. In the case of ionogels, a further dimension is achieved: the ability of keeping the ILs, and their properties, in a solid support, which can be referred to as "flexibility space" [21]. Additionally, the properties of the final ionogel are different from the simple combination of each pure component. Ionogels offer a way to further use ionic liquids in technological applications [22]. The combination of gels, with diversified applications of ionic liquids, enables the design of a thrilling combination of functional tailored materials, allowing materials to be custom designed for a wide range of applications such as sustainable chemistry, energy, electronics, medicine, food or cosmetics, among others [22].

"Lab-on-a-Chip" (LOC) or "micro-Total Analysis Systems" (μTAS) have the greatest potential for integrating multiple functional elements into a small device to produce truly sample-in/answer-out systems [23]. The design, fabrication, flow control, analysis and connection techniques are under continuous development improving among others, the throughput and the automation while at the same time leading to reduced costs [24]. However, the development of fully integrated microfluidic devices is still facing some significant obstacles, including the lack of robust fundamental building blocks for fluid control, the miniaturisation or elimination of external fluidic control elements [23,25]. The control and movement of flows in microchannels comes from microvalves and micropumps. In the case of active valves and pumps, the actuation depends on external power supplies and they require relatively complex procedures for integration into the microfluidic devices which pose a drawback for the device. On the other hand, passive valves/pumps have recently received an overwhelming amount of interest since they do not need any external actuation components and are easy to fabricate [24]. They can be regarded as a response to the need of simple and effective fluid control elements for building low cost and sophisticated lab-on-a-chip devices. These valves are essentially fabricated from stimuli responsive polymer gels [24]. Gels consisting of either physical or chemical cross-links can undergo controlled and reversible shape changes in response to an applied field [26]. In other words, they demonstrate substantial and reversible changes in equilibrium degree of swelling in response to weak changes in their surroundings (solvent composition, temperature, pH, and supply of electric field, light, etc.) [27–30]. They are referred to, as smart materials, since they are able to perform functions though an external stimulus without the need of any human input, demonstrating potential for "smart" applications, including biomedical devices, drug delivery carriers, scaffolds for tissue engineering, filters and membranes for selective diffusion, sensors for on-line process monitoring and artificial muscles among others [28,31].

In particular ionogels can also be used as stimuli responsive gels. They have many advantages over conventional materials since their robustness, acid/base character, viscosity and other critical operational characteristics can be finely modified through the tailoring of chemical and physical properties of the ILs [24]. The characteristics of the ionogels can be tuned by simply changing the IL and so the actuation behaviour when used as microvalves in microfluidic devices can be more precisely controlled [24,32]. For instance, two interesting approaches that we took in order to control fluid movement in microfluidic devices, were the use of photo-responsive ionogels controlled by light [33] and the use of reversible thermoresponsive ionogel [34].

Although there have been significant developments and some very promising ones in the microfluidics field, still, the amount of commercial products based on microfluidics has, with few exceptions, remained low, due to the critical need of a large variety of costly high performance components (mixers, actuators, reactors, separators, valves and pumps etc.) for fluid control and transport in the devices. The increase of the cost of the devices resulted in the decrease of the market possibilities [35]. Therefore, "Lab on a paper" is being developed to provide an answer to deliver simple, cheap and autonomous devices which are easily manageable by the end-users [36]. These devices have the full potential of classical microfluidics but with a well-focused commercialisation path [37]. Paper is receiving a great amount of attention as a promising substrate material for microfluidic devices not only due to its extremely low cost and ubiquity but also due to its mechanical properties, comprising flexibility, lightness, and low thickness [36]. In particular, μPADs are a relatively new group of analytical tools, capable of analysing complex biochemical samples, within one analytical run, where fluidic manipulations, like transportation, sorting, mixing or separation are available [35,38].

Thanks to the capillary forces of paper, there is no requirement for external pumps to provide fluid transport inside the paper unlike traditional microfluidic platforms [35]. However this advantage also generates a drawback; the isotropic wicking behaviour of paper and the fluid transportation caused by any exposed surface area prevent the accurate control of the fluid transport on paper materials, making it highly challenging and complicated [39,40]. Lack of fluid control on paper is at this moment the main dragging force for researchers when looking for new capabilities of μPADs.

In our previous work [35], we offered a solution by presenting a new concept for fluid flow manipulation in μPADs by introducing two different ionogel materials as passive pumps which were drop-casted at the inlets where the analytes are introduced into the device. It was demonstrated that ionogels highly affected the fluid flow by delaying the flow from the inlet. They revealed two distinctive liquid flow profiles due to their different physical and chemical properties and thus water holding capacities.

In this study, we extend our investigations and introduce another new concept for fluid flow manipulation in μPADs. Here, we use the ionogel materials as negative passive pumps at the outlet of the μPADs. The ionogel is able to continuously drive fluids through the μPAD through the swelling effect, and so, to control the flow direction and flow volume that reach the outlet. In order to generate a useful, reproducible and operative device we investigated a new method for the integration of the ionogel materials into the μPADs. Finally, the characterisation and the performance of the ionogel as negative passive pump were carried out.

2. Experimental

2.1. Reagents and materials

Whatman Filter paper Grade 1, wax printer XEROX ColourQube 8580 and a hot plate (Labnet International Inc., USA) were provided in order to fabricate the μPADs. The design of the devices was carried out with the software application AutoCAD^{TM}.

For the synthesis of the ionogels, *N*-isopropylacrylamide, *N*,*N*′-methylene-bis(acrylamide), 2,2-Dimethoxy-2-phenylacetophenone photoinitiator and 1-ethyl-3-methylimidazolium ethyl sulfate were purchased from Sigma-Aldrich, Spain. For gasket fabrication, cyclic olefin copolymer (COP) was provided by Zeonex/Zeonor, Germany and the pressure sensitive adhesive layer (PSA) was gently provided by Adhesive Research, Ireland.

NaOH solution, and phenolphthalein, which are used for the observation of the colour change (pH) on the μPAD were provided by Sigma-Aldrich, Spain. For visual observation, blue food dye (McCormick, Sabadell, Spain) was used: 5 mL of water with 100 μL of food dye (high concentration).