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Fabrication of smart supramolecular systems based on polyelectrolytes and surfactants in microfluidic environment

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Abstract. This work represents a process of fabrication of smart materials in a microfluidic confinement. Compared with macroscopic solutions, microfluidic convection-diffusion conditions create multiple additional factors that affect complexation in reacting polymer and surfactant flows. The system of convection-diffusion-reaction equations was solved to develop a polyelectrolyte-surfactant interaction model in a microchannel with laminar flows of reactants; phase formation and precipitation conditions in a microchannel were considered. The recommendations for control of phase behaviour in a microchannel were proposed by the design and operation mode of microfluidic devices used for synthesis of polymer-surfactant complexes and characterization of polymer-surfactant association process.

1. Introduction

Polymers and surfactants are typical representatives of complex supramolecular systems [1-3]. Their association behavior and properties can be controlled by various factors such as concentration ratios, individual characteristics of components, addition of solvent, etc. [4-6].

Microfluidic chips are becoming promising devices for fundamental and applied research for characterization of soft matter such as drug delivery systems, quantum dots, complexes of biopolymers, etc. [7-11]. In microfluidic chips, application of a broad variety of factors can be reduced to control of by microchip's design and operation. There is a growing interest of scientists to synthesis various smart supramolecular systems such as polymer-surfactant associates in microfluidic confinement [12-15].

It is of fundamental and practical importance to reveal operation modes and design parameters of microfluidic devices, which allow for controlling association processes in a microchannel.

The main objective of this research was to study association processes and hydrodynamic properties of resulting complexes for the anionic polyelectrolyte (polyacrylic acid – PAA) and cationic surfactant (cetyltrimethylammonium bromide – CTAB) solutions in microfluidic chips.

2. Experimental

The molds for microfluidic chips were fabricated by deposition of a negative photoresist SU-8 (MicroChem, USA) on a silicon wafer by spin-coating and further treatment by the UV radiation through a photomask according to SU-8 specifications.

The microfluidic devices were fabricated from polydimethylsiloxane (PDMS) Sylgard 184 by Dow Corning, USA. A required amount of PDMS was mixed with a curing agent according to the manufacturer's specifications. The mold was filled with PDMS to form a layer of 3-4 mm. A plastic

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Petri dish was then filled with remaining polymer to form a bottom layer with 2-3 mm thickness. PDMS was cured at 60°C for 4 hours. Cured PDMS layers was removed from a mold and a Petri dish and bonded together. Before bonding, PDMS surfaces were processed surfaces in oxygen plasma in Harrick Plasma Cleaner PDC-32G for 60 seconds.

Association of polymer-surfactant complexes in microchannels were characterized by Levenhuk D320 optical microscope equipped with Levenhuk M1400 Plus camera.

3D-modelling of polyelectrolyte-surfactant interaction in a microchannel was simulated in Matlab 2020a with partial differential equations toolbox.

Diffusion coefficients and hydrodynamic radii of polyelectrolyte macromolecules and polyelectrolyte-surfactant associates were determined by dynamic light scattering with Malvern Zetasizer Nano ZS.

Polyacrylic acid (PAA) by Polysciences, Inc., USA, with $Mw = 90\ 000,\ 25\ w.\ \%$ aqueous solution was used for an anionic polyelectrolyte. Cetyltrimethylammonium bromide, 98% by BDH Limited, Great Britain (CTAB) was used for a cationic surfactant. Aqueous CTAB solutions with 14 mmol/l surfactant concentration prepared from the CTAB powder were used in all experiments.

3. Theory

A general scheme of a microfluidic chip with reacting polymer, surfactant and solvent flows is shown on Fig. 1. This figure shows a combination of a microchip microscopy photo and the model of convection-diffusion-reaction processes occurring in a microchannel after junction of the inlet flows.

Diffusion of components to the center of the microchannel from the side flows results in the start of the complexation reaction and accumulation of the polymer-surfactant complex in the center of a microchannel.

The widths of polymer, surfactant and solvent flows are the Dirichlet boundary conditions for the junction face of the microchannel parallelepiped. Top, bottom and side faces of the microchannel are the Neumann boundary conditions reflecting zero flux of interacting particles through channel boundaries.



15 mm

Figure 1. A scheme of a 3-input microfluidic chip with reacting polymer and surfactant flows.

The behavior of reacting flows in a microchannel can be described by a combination of reaction, convection and diffusion partial differential equations with non-uniform initial conditions [16-18]. Association of a surfactant molecule with a monomer binding site in a macromolecular chain can be described by a general second-order reaction equation:

$$\begin{array}{c} A + B \stackrel{k_1}{\leftrightarrow} C \\ k_2 \end{array} \tag{1}$$

Where A and B are the reagents A and B, C is the product of their interaction. The rate law for the reagent A is:

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}\tau} = -\mathrm{k}_{1}\mathrm{C}_{\mathrm{A}}\mathrm{C}_{\mathrm{B}} + \mathrm{k}_{2}\mathrm{C}_{\mathrm{C}} \tag{2}$$

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Where C_A , C_B and C_C are concentrations of the reagents A, B and the product C; k_1 and k_2 are the rate constants of the direct and reverse reactions.

For a reaction occurring in a microfluidic channel, the diffusion term and the convection terms are the important components of the equation:

$$\frac{dC_A}{d\tau} + U\frac{\partial C_A}{\partial l} = D_A \Delta C_A - k_1 C_A C_B + k_2 C_C$$
(3)

Where D_A is the diffusion coefficient of the reagent A molecules, U is the flow velocity derived from the flowrate, Δ is the Laplacian, and l is the axial coordinate a microchannel.

To simplify this equation, consider a steady-state flow if reactants and two second-order derivatives representing radial and vertical diffusion in a microchannel (the axial diffusion is neglected):

$$U\frac{\partial C_A}{\partial l} = D_A \left(\frac{\partial^2 C_A}{\partial w^2} + \frac{\partial^2 C_A}{\partial h^2}\right) - k_1 C_A C_B + k_2 C_C$$
(4)

These equations are non-linear second-order convection-diffusion equations with the chemical reaction added as a source term. Such equations can be derived for the reagent B and the product C. The resulting system of such equations will characterize the behavior of polymer-surfactant complexation in microfluidic conditions:

$$\begin{cases} U \frac{\partial C_A}{\partial l} = D_A \frac{\partial^2 C_A}{\partial w^2} + D_A \frac{\partial^2 C_A}{\partial h^2} - k_1 C_A C_B + k_2 C_C \\ U \frac{\partial C_B}{\partial l} = D_B \frac{\partial^2 C_B}{\partial w^2} + D_A \frac{\partial^2 C_A}{\partial h^2} - k_1 C_A C_B + k_2 C_C \\ U \frac{\partial C_C}{\partial l} = D_C \frac{\partial^2 C_C}{\partial w^2} + D_A \frac{\partial^2 C_A}{\partial h^2} + k_1 C_A C_B - k_2 C_C \end{cases}$$
(5)

Where $U = f(w,h)U_{max}$ is the pressure-driven flow with parabolic profile.

Figure 2 demonstrates the results of 3D numerical simulations performed in Matlab software package for a polyelectrolyte-surfactant system. The association reaction occurs in the microchannel in the points where associating molecules meet by diffusion. The sandglass shape of the reaction front is the effect of the Hagen-Poiseuille flow profile in a rectangular microchannel: the flow velocity tends to zero near the walls.

4. Results and discussion

Figure 2 shows the results of 3D numerical simulations performed in Matlab PDE toolbox for a polyelectrolyte-surfactant system. The association reaction occurs in the microchannel in the points where associating molecules meet by diffusion. The sandglass shape of the reaction front is the effect of the Hagen-Poiseuille flow profile in a rectangular microchannel: the flow velocity tends to zero near the walls.

Polymer-surfactant systems demonstrate complex phase behavior depending on the ratio of components (the Z value). These ratios of surfactant and polymer concentrations Z were calculated by the ratio of the concentration of surfactant molecules in solution to the concentration of polyelectrolyte monomer units:

$$Z = \frac{c^{surfactant}}{c_{mon}^{Polymer}} \tag{6}$$



Figure 2. Formation of a polyelectrolyte-surfactant supramolecular system in a microchannel according to numerical 3D-simulation in Matlab PDE toolbox.

When the Z parameter reaches a certain value, the system undergoes phase separation and a line of precipitates emerge in a microchannel.

In bulk PAA-CTAB solutions with various ratios of components, formation of insoluble polymer-surfactant complexes and their precipitation occur at Z<<0.1. Further increase of surfactant-polyelectrolyte concentration ratio produces more turbid systems due to continuing phase separation. At Z>0.7-0.8, however, the turbidity of PAA-CTAB solutions decreases and precipitate dissolves at Z \approx 1 due to their solubilization be excessive CTAB additives.

In microfluidic devices supramolecular systems can precipitate even if no such precipitation occurs in a macroscopic solution. Figure 3 demonstrates precipitates of PAA-CTAB complexes synthesized in a microchannel at Z = 1.



Figure 3. Optical microscopy photo of insoluble polymer-surfactant particles precipitated in a microchannel.

Location of precipitated particles correspond to the maximum of the product concentration calculated by numerical simulations and shown in Fig. 2.

Among various advantages of microfluidic methods, an ability to control properties of supramolecular systems by varying microchannel geometry and flowrates is important for fabrication of smart soft matter materials. In this work, we managed to control the size of PAA-CTAB aggregates by varying flowrates of reagents and the solvent (Figure 4).

The solutions of PAA-CTAB complexes were taken at the output of the 3-input microfluidic chip. Solutions contain particles in the range of ~170-310 nm depending on the synthesis conditions (flowrates). The smallest aggregates form and the largest aggregates form if the solvent flowrate is reduced to zero. Such a behavior corresponds to the properties of macroscopic polymer-surfactant solutions characterized in our previous works [19,20] as well as for the behavior of PAA-CTAB solutions we synthesized in bulk conditions.



Figure 4. Hydrodynamic diameters of PAA-CTAB complexes synthesized in microfluidic experiments.

5. Conclusions

Microfluidics offers additional factors to control complexation of polyelectrolytes and surfactants. In addition to the ratio of components in bulk solutions, microfluidics offers such factors as flowrates of surfactant and polymer solutions and the solvent. The ratio of these flowrates contributes to association of polymer and surfactant molecules by diffusion and their subsequent aggregation.

Interaction of polymers and surfactants in microfluidic systems is governed by simultaneous convection, diffusion and kinetic processes. Numerical solutions of convection-diffusion-reaction equations provide a predictive model for association of polymers and surfactants in a microchannel. Parabolic profiles of pressure-driven microchannel flows are responsible for non-uniform distribution of the reaction product across the microchannel. Complexation reactions start at microchannel top and bottom sections and then proceed to other sections with the increase of microchannel length.

Complexation, aggregation and precipitation reactions occurring at microchannels with parallel flows of reacting supramolecular components such as polymers and surfactants contribute to fabrication of smart supramolecular structures that are sensitive to several factors. Their structural properties such as hydrodynamic size can be controlled by variation of flowrates od microchannel parameters in accordance with solution of the respective convection-diffusion-reaction equations.

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