Application of Microgels for Switchable Phase Separation Behavior to Improve Extraction Processes

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Microgels are innovative deformable polymers. Their most outstanding properties are their switchable structural change and their surface activity. At interfaces microgels deform and act as surface active agents. Their surface activity combined with the switchability makes them promising candidates for the improvement of extraction processes, which suffer from high coalescence of drops. A new concept for the intensification of extraction processes by the application of microgels will be introduced. For the quantitative analysis of the switchable phase separation as response to a temperature shift, experiments in a standardized batch settling cell have been performed. Thereby, a large set of parameters has been tested, including microgel properties as well as process conditions such as ionic strength and pH value. Furthermore, a first investigation of mass transfer through microgel-covered interfaces has been performed. For the mass transfer experiments, a stirred two-phase cell has been utilized.

1. Introduction

The performance of many liquid-liquid extraction processes suffers from strong drop coalescence, leading to a broad drop size distribution. Thus, the drops have different sedimentation velocities and therefore different resident times. Furthermore, the specific mass transfer area varies. All these effects lead to a flat concentration profile and a reduced separation efficiency of the process.

A promising approach to tackle this challenge is the introduction of microgels to extraction processes. Microgels are soft and deformable crosslinked polymer particles with surface-active properties. Their most outstanding characteristic is the response to external triggers, e.g. temperature, by a structural change. Concomitant to the structure and size, the microgel properties change rapidly when exposed to a stimulus. [1, 2]

In this contribution, cross-linked poly(N-isopropylacrylamide) (PNIPAM) microgels are utilized. These microgels show a thermo-responsive behavior which is characterized by a volume phase transition temperature (VPTT) about 34°C which is typical for PNIPAM microgels. Below the VPTT the microgels are in a swollen state containing about 90 Vol-% solvent. Above the VPTT the polymer network collapses leading to a smaller radius and higher polymer content [1]. The interfacial properties of microgels have been investigated by many researchers. Microgels are known to stabilize oil-water [3] and water-air interfaces [4]. Their ability to generate switchable emulsions has been shown qualitatively [1, 3, 5]. Nevertheless, a quantitative investigation on stability and the impact of different parameters is still missing. Furthermore, the arrangement and packing of microgels at liquid interfaces has been studied intensively [3, 5–8]. Microscopic insights and compression isotherms indicate the formation of a microgel monolayer at the interface [3, 8]. In contrast to rigid particles, microgels have the ability to spread and deform at the interface, the magnitude of spreading is correlated to the degree of crosslinking within the gel and consequently has a big effect on the interfacial behavior [7].

In an extraction column, the switchable interfacial properties will be utilized as follows and illustrated in Figure **1**. Microgels will stabilize the drops suppressing coalescence while passing the active part of the column. At the top of the column, where coalescence is required and phase separation takes place, the microgel properties will be switched by a temperature shift to enable coalescence. Therefore, the switchability of the phase separation behavior by microgels are investigated quantitatively by batch settling experiments [9]. The other important aspect for the application in extraction processes is the impact of the microgel layer on the mass transfer, which is also part of this contribution. The mass transfer trough a flat interface is observed by experiments in a stirred two-phase convection cell [10, 11].

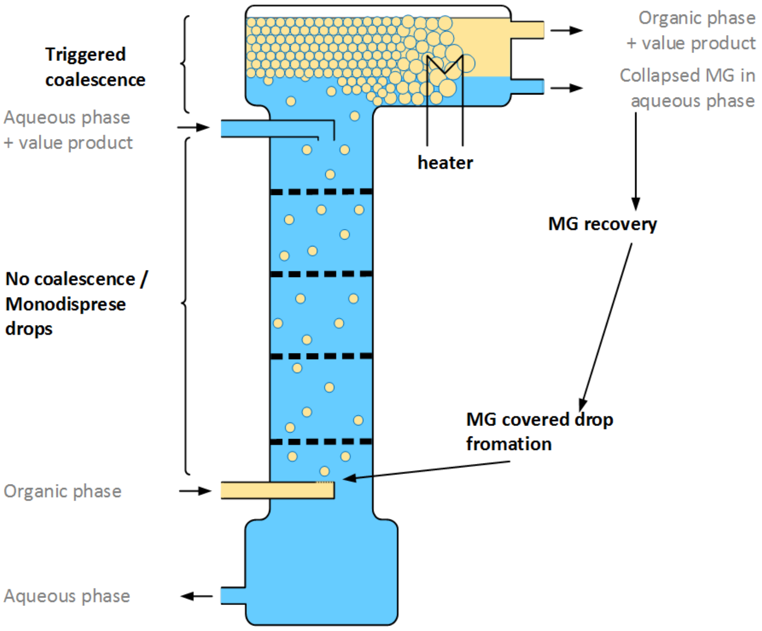

Figure 1. Process concept for an improved extraction process utilizing microgels

2. Experimental work and Simulation

2.1 **Temperature responsive phase separation**

For the investigation of phase separation and mass transfer through microgel-covered interfaces the standard test system Toluene-Water-Acetone is utilized as recommended by the EFCE [12]. Experiments for the investigation of the phase separation regarding coalescence and sedimentation were performed in a standardized batch settling cell [9]. The experiment is based on the optical evaluation of the settling process over time. Therefore, sedimentation and coalescence of the dispersed drops are observed by means of the heights of the droplet free phases in the cell. In order to investigate the transfer of the temperature-responsive properties of the microgels on the phase separation process temperatures below and above the volume phase transition temperature (VPTT) were tested. Since the VPTT of the PNIPAM microgels is app. 34°C, experiments are performed at 25°C and 40°C respectively. As the microgel properties are part of this investigation, microgels with different crosslinker content have been utilized, 2.5 and 5 mol% BIS respectively, while size and VPTT of the microgels are not affected as can be seen in Figure 2.

Furthermore, the impact of different process parameters such as ionic strength and pH value is studied. For the adjustment of the ionic strength and the pH value sodium chloride and sodium hydroxide are used. Since the amount of parameters leads to a large number of experiments, a statistical experiment planning (DOE) has been utilized in order to determine the most significant single parameter and interaction effects. Every experiment was repeated at least for four times.

The experiments have been evaluated regarding the overall separation time, which is taken directly from the experiment. Furthermore, the Sauter mean diameter and the coalescence are evaluated utilizing the Henschke model approach [9]. The Sauter mean diameter is determined via a force balance from the slope of the linear part of the sedimentation line. The coalescence parameter is derived from the coalescence line utilizing the settler model approach [9].

2.2 Mass transfer through microgel-covered interface

For the investigation of mass transfer through a microgel-covered interface a stirred two-phase cell is utilized. The total volume of the cell is 500 ml [11]. To ensure the coverage of the interface with microgels preliminary experiments were performed. First, the flow conditions at the interface have been observed with sand particles as a visible model system (mean diameter 148.5 ± 43 µm). Furthermore, the time necessary to cover the interface has been evaluated by variation between 30 minutes and 24 hours. According to the results from the preliminary experiments, the microgel containing solvent system is filled into the cell and stirred slowly for 2 hours allowing the microgels to cover the interface. At the beginning of the measurement acetone is injected to the aqueous phase leading to an initial concentration of about 1.5 w%. The mass transfer is tracked by concentration measurement in the organic phase. The Acetone concentration in the organic phase is determined by gas chromatography.

3. Results and Discussion

3.1 Temperature responsive phase separation

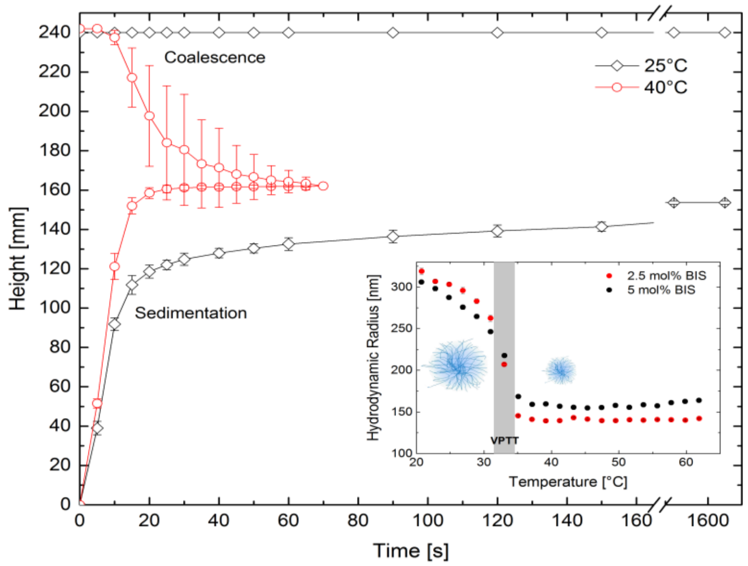

Figure 2. Settling process with microgels at different states (swollen microgels at 25°C, collapsed microgels at 40°C, indicated by the radius measured by DLS at IPC RWTH Aachen) utilized microgels with 2.5 mol% BIS, ionic strength 100 mmol/L, pH 11.

The experimental results obtained at constant temperature show that below the VPTT the microgels stabilize the disperse system extremely well as depicted in Figure 2. While above the VPTT complete separation of the phases was observed for all tested parameters. As an example the experimental results for a system with a low microgel concentration of 0.1 g/L, low crosslinking 2,5 mol% BIS, high ionic strenght 100 mmol/L and low pH value are shown in Figure 2. At 25°C no coalescence can be observed, the drops sediment to a dense packed zone. The minor slope of the sedimentation is due to the drainage of continuous aqueous phase from the packed zone. The hold-up of continuous phase in the dense packing decrease from approximately 30 vol-% at 60 s to 11 vol-% after the end of the experiment after 20 min.

For the evaluation of the separation time only the experiments at evaluated temperature are considered. For all tested parameters a complete separation of the phases was observed at 40°C. Nevertheless, the settling time varied in a wide range from 29 s to 91 s depending on the process parameters. For each parameter the averaged settling times for all experiments are determined, whereby it is only distinguished between the state of the regarded parameter. The microgel cross-linking and the pH value were identified to have the most significant impact on the separation time (Figure 3, top). The ionic strength has a minor effect, nevertheless it shows strong interactive effects with crosslinking as well as with the pH value. The coalescence parameter is also predominately affected by the degree of crosslinking (Figure 3, middle). Thereby the magnitude of this single effect is bigger compared to all interaction effects. The Sauter mean diameter (Figure 3, bottom) and subsequently the sedimentation velocity is not substantially affected by any of the investigated parameters. The scattering of the average values is about 10 %. The magnitude of the interaction effects is even minor.

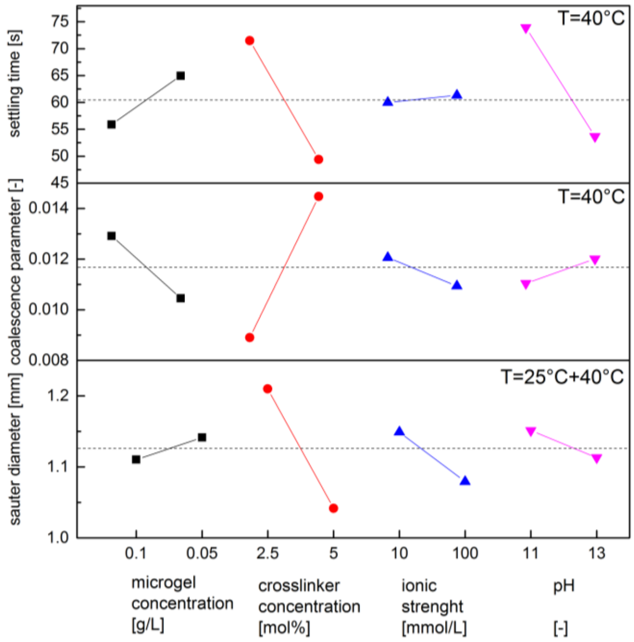

Figure 3. Effects of microgel concentration, crosslinker content, ionic strength and pH on settling time (top), coalescence parameter (middle) and Sauter mean diameter (bottom)

The transfer from the experiments at constant temperature to an operation with temperature-shift, as it would be applied in a future process, is shown in Figure 4. At the beginning of the experiment the microgels form the dens droplet packing, which is stable for 20 min until the heating begins. The coalescence is delayed and approximately 5 times slower as in the experiments at constant temperature. Whereby, the magnitude of time for the microgel collapse is much faster as the observed time range. Thus, a possible

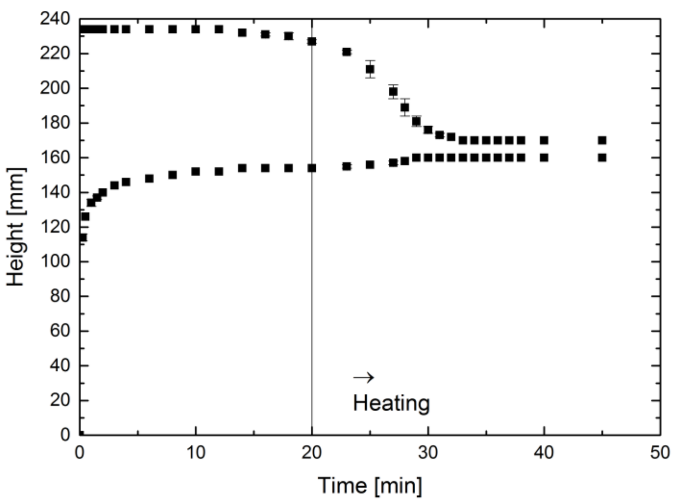

Figure 4. Settling process with subsequent heating, microgel concentration 0.1 g/L with 2.5 mol% BIS ,pH 10.92

explanation for the delay is the heat transfer from the water bath to the solution. Therefore, the heat transfer is the crucial design factor for a future settling unit.

3.2 Mass transfer through microgel-covered interface

As mentioned, besides phase separation also mass transfer could be a critical factor for the applicability of microgel in extraction processes. The partition coefficient determined from liquid-liquid equilibrium experiments at 25°C and 40°C is not affected by the presence of microgels. It was determined to 0.635 $w\%_{org}/w\%_{aq}$ for the pure system and 0.648 $w\%_{org}/w\%_{aq}$ with a microgel content of 1 g/L. The deviation is still within the range of the maximum error of 2 %. The microgels do not affect the partition coefficient, as the particles are suspended but not solved in water and therefore do not contribute to the molar composition of the solvent phase. The dynamic of the mass transfer through the microgel-covered interface was observed by means of a time dependent concentration profile for the organic phase as shown in Figure 5. The calculated mass transfer coefficient obtained from the integral view of the concentration profile is $1.99*10^{-4} \pm 0.4*10^{-4}$ m/s for the pure system and $1.77*10^{-4} \pm 0.9*10^{-4}$ m/s for the microgel containing system (0.25 g/L). Due to the small deviation of the mass transfer coefficients no significant impact of the microgel layer can be detected. Therefore, the microgels do not impede the mass transfer through the interface for the selected test system. It should be noted, that acetone is a very small molecule compared to the microgels. As the gels have a porous structure and a high water content it is assumed, that the transport of small molecules is not hindered.

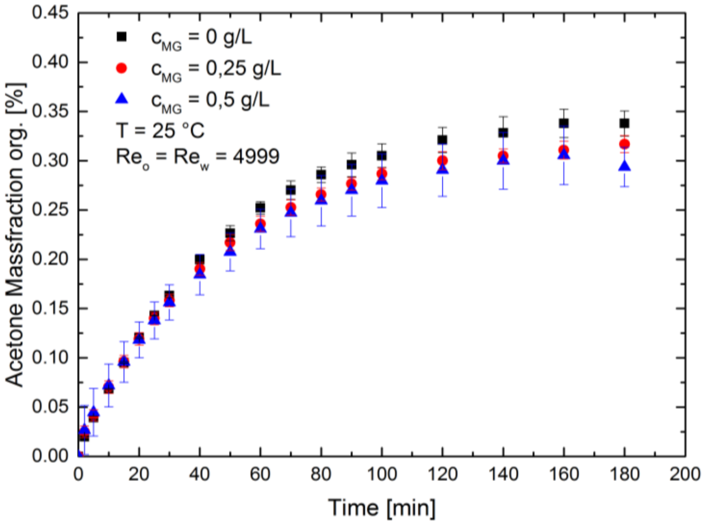

Figure 5. Measured acetone concentration in the organic phase over time, the initial acetone concentration in the aqueous phase was 1.5 w-%, microgels with 5mol% BIS .

4. Conclusion

It has been demonstrated, that microgels allow to switch phase separation by temperature shift. The degree of crosslinking was determined as most effectful parameter. Furthermore it has been shown, that micorgels do not affect the partition coefficient of acetone between water and toluene. The mass transfer experiments indicate that mass transfer of small molecules is not hindered by the interfacial micorgel layer. Nevertheless, more detailed investigation of mass transfer also for larger molecules need to be done to generate a better understanding of mass transfer through the microgel layer at liquid-liquid interfaces.

Acknowledgement

This work was performed as part of the collaborative research center (Sonderforschungsbereich) “SFB 985 – functional microgels and microgel systems”, which is funded by the DFG. Thanks to our project partners Dominik Wöll and Eric Siemes from the IPC RWTH Aachen.

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