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Multi-responsive ionic liquid emulsions stabilized by microgels.

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We present a complete toolbox to use responsive ionic liquid (IL) emulsions for extraction purposes. IL emulsions stabilized by responsive microgels are shown to allow rapid extraction and reversible breaking and re-emulsification. Moreover, by using a paramagnetic ionic liquid, droplets can be easily collected in low magnetic fields.

The use of ionic liquids (ILs) as green extraction solvents in chemical and biotechnological industries shows great promise, especially for the extraction of conformationally fragile and chemically sensitive compounds such as proteins, lipids, or other biomolecules. Nevertheless, their efficient use in small and large scale separation processes, especially of these biological products, imposes strict requirements on the design of the extraction system and procedure. To enhance the efficiency of extractions and minimize the time required to achieve good separation, the use of emulsions is highly favorable due to their inherently large surface area. These emulsions must be stable against coarsening due to coalescence or Ostwald ripening, yet simultaneously must be easy to collect and break to obtain the product-loaded ionic liquid phase. Moreover, the stabilizer used to create these emulsions should not interact in a detrimental way with the product to be extracted. Creating IL/water emulsions is a challenge by itself; the inherently large miscibility of the two phases, and resulting low interfacial tension, combined with the fact that, contrary to oil/water interfaces, IL-water interfaces are highly structured due to charge hydration and correlations, result in only partial relevance of the general rules of emulsion preparation and stability. While IL (micro)emulsions can be prepared using simple commercial surfactants, most of the desired requirements are not met. Due to the inherent water solubility of most ionic liquids, Ostwald ripening leads to fast coarsening and emulsion destabilization. Additionally, surfactants interact strongly with a variety of biomolecules, often amphiphilic themselves, which can lead to irreversible changes in the desired product such as denaturation of proteins. A universal strategy to prepare IL emulsions meeting these strict requirements is absent, precluding a more general application of IL-based green extraction processes.

In this paper, we demonstrate that microgel particles, which have been shown to efficiently stabilize oil-water interfaces, can also provide excellent stability to a wide variety of IL-water emulsions. The spontaneously formed and densely packed layer of microgels at the IL-water interface does not impart their use in extractions as the interface remains permeable to small biomolecules. Through ion exchange, the ionic liquid used for extraction can be rendered paramagnetic, which allows facile collection of the droplets from the extraction medium using a magnet. Utilizing the thermoresponsive nature of the microgel particles, the emulsion, which is stable for at least several days at room temperature, can almost instantaneously be de-emulsified using a small temperature trigger. Once the ionic liquid phase has been collected, the microgel particles, which remain in the aqueous phase, can be re-used for a new extraction. The combination of excellent stability and de-emulsification on-demand, the magnetoresponsivity of the droplets and the reusability of the emulsifier offers a complete and versatile toolbox for the sustainable application of IL emulsions in extraction processes.

A water-in-IL emulsion prepared from the water-immiscible [P4,6,6,14][NTf2] (see SI for details of the ILs used), stabilized by a commercial non-ionic surfactant shows rapid coarsening (see movie in SI); measured droplet diameters show an order of magnitude increase over 24 hours (see SI). Clearly, simple surfactants do not effectively stabilize these emulsions. Stability against Ostwald ripening can be improved by the formation of an elastic layer at the IL-water interface, for example by adsorption of colloidal particles rather than surfactants. However, preparing well-defined and stable Pickering emulsions almost always requires careful tuning of the wettability of the particles at the liquid-liquid interface. This is not the case when micron-sized gel particles are used as stabilizers. The microgel particles that we used in this study, contain a fluorescent polystyrene core embedded into a thermoresponsive microgel shell made of poly(N-isopropylacrylamide-co-methacrylic acid) (PNIPAm-co-MA). These particles are prepared in a two-step protocol: first, a fluorescent polystyrene core is synthesized through emulsion polymerization and then a fluorescent microgel shell is grown onto it through a precipitation copolymerization (see SI for detailed protocols). After synthesis, the microgel particles are repeatedly centrifuged and resuspended in deionized water to remove surface-active solutes remaining from the reaction. This design allows to visualize the particles at the interface while leaving the desired properties of the microgels, i.e their spontaneous
particles that remain in the aqueous phase. This indicates that the particles as stabilizers by preparing emulsions from a wide variety of pattern (Figures 1a,b). Clearly, microgel particles are able with the ionic liquid [BMIM][NTf\(_2\)] for only 30 s, a stable and well-dispersed emulsion is created (see details in the SI). We observe, using confocal microscopy, that almost all the interfaces are fully covered with particles, which have organized in a regular hexagonal pattern (Figures 1a,b). Clearly, microgel particles are able to effectively stabilize IL-water interfaces. This is corroborated by stability measurements that show no change in droplet size for several days (see SI). We therefore explore the universality of these particles as stabilizers by preparing emulsions from a wide variety of ILs: for different cations P\(_{6,6,14}\) and N\(_{1,8,8,8}\) while keeping the same anion NTf\(_2\); and for different anions Phos and DCA while keeping the same cation P\(_{6,6,14}\). For all of these, well-stabilized droplets of IL-in-water with hexagonally-packed interfaces result (Figures 1c-f). Remarkably, microgel particles can stabilize a wide variety of IL-water interfaces through their spontaneous adsorption at the liquid interface\(^{46}\). Although the exact mechanism with which microgels adsorb remains unclear, it has been established that it is significantly different from classical Pickering stabilization, and exhibits features of both particle- and polymer-adsorption\(^{35, 46}\). While we observe adsorption of our microgels at all IL-water interfaces explored, for solid colloid particles tuning of the chemistry is required, for example by changing the hydrophobicity\(^{40, 41}\) or the charge density and species\(^{42}\). This suggests that indeed microgel adsorption and that of solid particles do not occur with the same physical mechanism.

In our systems, we always observe an excess of microgel particles that remain in the aqueous phase. This indicates that the emulsions are not prepared in the limited coalescence regime. However, when we combine the hydrophobic cation P\(_{6,6,14}\) with an anion that prefers to partition into water, in this case Cl\(^-\), we observe the spontaneous and full migration of all microgels into the IL. We hypothesize this is partly due to ion-exchange\(^{37}\), in which transfer of the negatively charged microgel into the IL is accompanied by the migration of equal number of charges of the chloride ions into the aqueous phase, leading to a large increase in the counterion entropy.

In this specific case there is a preference for forming water-in-IL instead of IL-in-water emulsions (Figure 1g). This illustrates how in-situ ion exchange can be used to tailor the emulsion type. However, when we combine Cl\(^-\) with another hydrophobic cation N\(_{1,8,10,8,10,8,16}\), the microgels remain in the aqueous phase and the preferred emulsion type is IL-in-water (Figure 1h). This result suggests that not only entropic gain associated with counterion release is important but that also specific affinity between the microgels and the IL cation may play a role\(^{48}\).

An important prerequisite for extractions is that the interface between IL and water remains permeable. To test this, we add β-carotene as a powder to the continuous phase of an IL-in-water emulsion prepared with [P\(_{6,6,14}\)][DCA] and stabilized with microgel particles (Figure 2a). After only a few minutes, the pigment is found in the IL phase (Figure 2b). To more clearly visualize the uptake of small molecules across a microgel laden interface, we replace β-carotene by a hydrophobic fluorescent dye, pyromethene. We observe, with confocal microscopy, that all of the dye is located in the ionic liquid droplets and none remains in the water phase (Figures 2c,d). Despite the densely packed interface, small molecules easily permeate across the microgel layer.

To facilitate IL-emulsion based extractions, ideally the droplets should be collected with minimal energy input. To accomplish this, we render the IL magnetoresponsive by ion exchange of [P\(_{6,6,14}\)][Cl] to [P\(_{6,6,14}\)][FeCl\(_4\)]\(^\text{37, 48}\). The resulting paramagnetic IL is immiscible with water (Figure 3a). As a magnet approaches, the liquid is attracted toward the magnet as can be seen in Figure 3b. Also this IL can successfully be emulsified with microgel particles (Figures 3c-e). Interestingly, this results in a paramagnetic emulsion in which the droplets can be collected almost instantaneously and without energy input, with even a small magnet (Figure 3d).

Figure 1. Confocal microscopy images of IL droplets in water stabilized with hexagonally packed microgel particles (a-f). Confocal microscopy images of emulsions with ILs containing Cl\(^-\); the IL is colored red and the microgel particles green: (g) water-in-IL and (h) IL-in-water.

Figure 2. The top row shows photographs of: (a) [BMIM][NTf\(_2\)]-in-water emulsion stabilized with microgel particles, (b) same as (a) after adding β-carotene, the pigment diffused to the IL droplets. The bottom row shows confocal microscopy images of the successful extraction of pyromethene by the same IL; the IL is colored red and the microgel particles green.
becomes unstable and demixes into two macroscopic phases (Figures 3f-h, full movie in SI). While the exact mechanism of this temperature-induced emulsion breaking remains speculative, we hypothesize the following: upon increasing the temperature above the LCST of the microgels, they both deswell and become adhesive. As a result, the surface coverage rapidly decreases and the two interfaces, separated by a thin film of water, become attractive. This combination simultaneously removes both the thermodynamic and kinetic barriers preventing coalescence.

To arrive to a sustainable extraction toolbox based on the system we present, this process should allow re-using of the microgel emulsifiers. To check the feasibility of this idea, we prepare an IL-in-water emulsion and break it by centrifugation at 35°C and 200 g. The IL phase is then removed and using the same aqueous phase still containing the microgels, a new emulsion can be prepared.

These results provide a comprehensive toolbox for the efficient sustainable application of ionic liquids in (bio)molecule extraction. Using the unique properties of the responsive microgel particles and through tuning the IL composition, we can prepare stable emulsions of both IL-in-water and water-in-IL type, that can be easily concentrated using a magnetic field, that can be broken on-demand with a small temperature trigger and in which the emulsifier can be re-used for subsequent extractions. This opens up new and directly applicable avenues for the transition towards a greener (bio)chemical industry.

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Notes and references


