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Phase-Selective Gelation of the Water Phase in an Oil−Water Mixture: An Approach Based on Oil-Activated Nanoparticle Assembly in Water

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Cite This: *Langmuir* 2021, 37, 8107−8114

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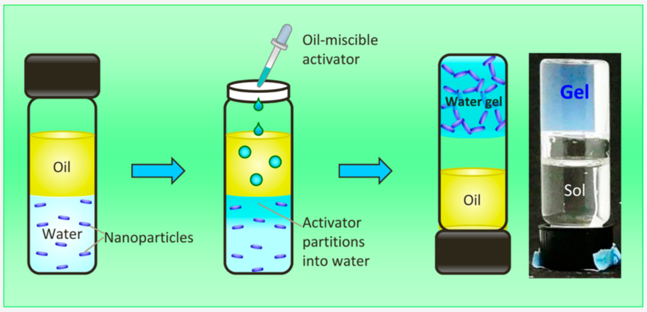
ABSTRACT: Phase-selective gelation refers to the selective gelation of one phase in an immiscible mixture. Thus far, all such examples have involved a molecular gelator forming nanofibers in (and thus gelling) the oil phase in an oil/water mixture. Here, for the first time, we report the counterpart to the above phenomenon, i.e., selective gelation of the *water phase* in an oil/water mixture (while leaving the oil undisturbed). This has been a challenging problem because moieties that gel water tend to be either amphiphilic or oil-soluble; thus, if combined with an oil/water mixture, they invariably form an emulsion. Our approach solves this problem by exploiting the tunable self-assembly of laponite (LAP) nanoparticles. Initially, LAP nanoparticles (25 nm disks) are dispersed in water, where they remain unaggregated due to the steric stabilization provided by a triblock copolymer (Pluronic P123) adsorbed on their surface. Thus, the dispersion is initially a low-viscosity sol. When an immiscible oil such as hexadecane is introduced above the sol, the mixture remains biphasic, and both phases remain unaffected. Next, an organic acid such as butanoic acid (BA) is added to the oil. The BA is oil-soluble but also has limited solubility in the water. Over about 30 min, some of the BA enters the water, whereupon it "*activates*" the self-assembly of LAP particles into a three-dimensional "house-of-cards" network. Ultimately, the water phase is converted into a homogeneous gel with a sufficient yield stress: the aqueous gel holds its weight in the inverted vial while the oil phase remains a thin liquid that can be poured out of the vial. On the whole, the concept advanced here is about activating nanoparticle assembly in water *through an adjacent, immiscible phase*. This concept could prove useful in conducting certain separations or reactions in the laboratory as well as in enhanced oil recovery.

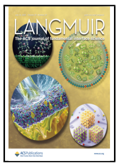


INTRODUCTION

The term "phase-selective gelation" has proven quite popular in the scientific literature over the last two decades.[1−6] It was first introduced in 2001 in a paper by Bhattacharya et al.[1] showing that the addition of *N*-lauroyl alanine to a biphasic oil−water mixture resulted in selective assembly of the molecules into a fibrous network within the oil phase. Thereby, the oil phase was converted into a gel (i.e., solidified) while the water was left undisturbed. The authors of this original paper[1] recognized that phase-selective gelation of oil could be used to immobilize an oil spill on the surface of the ocean. About a decade later, John et al.[3] synthesized a sugar-based molecular gelator that could selectively gel oil and dissolved this gelator in an oil-miscible solvent like ethanol. When the ethanol solution was added onto the oil phase, the gelator partitioned into the oil, and the gelled oil became sufficiently solidlike to be scooped off the surface of the water. Subsequently, there has been an explosion of interest in various phase-selective molecular gelators,[3−6] all of which work on the oil phase in an oil−water mixture. Numerous papers and reviews[7] have addressed the application of such gelators to eradicate oil spills, although, to our knowledge, the concept has not been applied in practice to a real oil spill. Nevertheless, this body of literature nicely illustrates how a concept that came out of academic research might eventually be applied to a real-world problem.

Why do some molecules function as phase-selective gelators of oil? To understand this, we have to delve into the fundamentals of molecular gelation in oil.[8−12] Organogelator molecules typically have both a hydrocarbon backbone and some additional polar groups that allow the gelator molecules to interact by weak, noncovalent interactions (such as polar or hydrogen-bonding interactions).[8,9] The gelator is typically soluble in oil at high temperatures, but if it is too soluble, it will not serve as an organogelator. When a solution of the gelator in

Received: March 8, 2021
Revised: May 14, 2021
Published: June 25, 2021



oil is cooled down, the gelator molecules will assemble through their noncovalent interactions into nanoscale fibers. The entanglement of these nanofibers results in the oil being gelled.[11] For an organogelator to be phase-selective, two further conditions should be met: (a) *it should be insoluble in water*, and (b) *it should not be strongly amphiphilic*. Most organogelators are water-insoluble, but some of them have polar groups on one end of the molecule, making them amphiphilic. If an amphiphilic organogelator is added to an oil—water mixture, it could result in an emulsion of the oil-in-water (or of the water-in-oil) rather than phase-selective gelation of the oil. In this scenario, the organogelator molecules will partition to the oil/water interface and coat the droplets of one phase in the other. Thus, if a gelator is intended to be phase-selective, it must *not* be strongly amphiphilic.

All examples of phase-selective gelation reported thus far in the literature have involved gelling the oil phase while leaving the water undisturbed. But what about the reverse? Is it possible to selectively gel the water phase in a biphasic mixture? In analogy with the reasoning mentioned above, a selective hydrogelator would have to be (a) *oil-insoluble* and (b) *non-amphiphilic*. This combination of properties is harder to achieve with hydrogelators for a variety of reasons. First, the number of hydrogelator molecules that are known to exist[13,14] is much smaller than the number of organogelators. Second, many of the hydrogelators work through *hydrophobic interactions*; i.e., when added to water, the molecules assemble into nanofibers due to attractions between the hydrophobic regions of the molecules.[13,14] When the same molecules are added to an oil/water mixture, their hydrophobic regions will associate with the oil, and thereby the tendency to assemble into nanofibers will be diminished. Apart from small-molecule gelators, there do exist polymeric thickeners (such as xanthan or guar gum),[15,16] which are long, hydrophilic chains that dissolve in water but not in oil. However, adding such a thickener to an oil/water mixture also invariably results in an emulsion. Moreover, dissolving a polymeric thickener in any liquid phase typically involves both heat and shear.[15] An ideal scheme for phase-selective gelation should instead be one that can be conducted ***under ambient conditions in the absence of shear***. As depicted in Figure 1A, this is possible in the case of oil. The figure shows an oil/water mixture in a vial, with the oil invariably on top due to its lower density. Initially, both the phases are thin liquids (panel 1). Upon adding a third liquid, i.e., a solution of the organogelator, through a pipet into the oil phase, phase-selective gelation of the oil is accomplished without heat or shear (panels 2, 3), while the water phase is unaltered. Can a similar process be done to selectively gel the water instead?

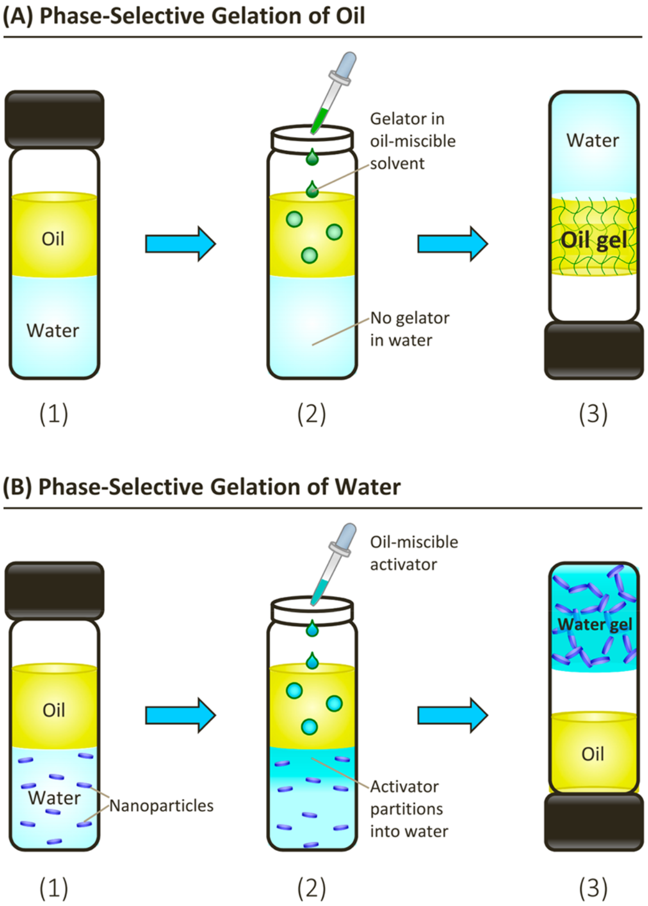


Figure 1. Phase-selective gelation of (A) the oil phase (previous work) and (B) the water phase (current work) from a two-phase mixture. (A) Adding a gelator in an oil-miscible solvent results in gelation of the oil without the need for heat or shear while leaving the water intact. The oil gel can hold its weight as well as that of the liquid water in the inverted vial. (B) Initially, disklike nanoparticles of laponite are stabilized in the water phase, which is then contacted with the oil. An oil-miscible activator (e.g., butanoic acid) is then added to the oil. Some of the activator partitions into the water, whereupon it activates nanoparticle assembly into a gel. The water is thereby transformed into a gel without the need for heat or shear while the oil is left intact.

Here, we introduce a way to accomplish the phase-selective gelation of water. The scheme is broadly depicted in Figure 1B. An oil/water mixture is shown in a vial, with the water at the bottom containing a suspension of nanoparticles. Because the nanoparticles are stabilized at the outset, the aqueous phase is a thin liquid, as is the oil phase (panel 1). Next, a liquid solute ("activator") is introduced into the oil phase atop the water. The solute dissolves in the oil, but it is also partially soluble in the water (panel 2). As a result, with time (over about 10—30 min), some of the solute partitions into the water phase, whereupon it activates the assembly of the nanoparticles into a three-dimensional network (panel 3). Ultimately, the water is converted from a sol to a gel, while the oil phase remains a sol (thin liquid). The mechanism by which the nanoparticles are activated to gel water is discussed further below. On the whole, the underlying idea here is to activate the assembly of nanoparticles in water *through an adjacent, immiscible phase*. Where could this concept be useful? One possibility is in conducting certain separations or reactions in the laboratory, such as those involving a transfer of reactants or products from one phase to another. One example is shown at the end of the paper. Gelling water across an oil interface could also potentially be useful in enhanced oil recovery.

■ RESULTS AND DISCUSSION

Typical Results. The components of our system are shown in Figure 2A. We use a type of inorganic (clay) nanoparticle called laponite (LAP).[17−20] As per the literature, LAP particles are nanoscale disks with a diameter of 25 nm and a thickness of 0.9 nm.[17,18] The faces of the disks are anionic while the edges of the disks are cationic or anionic depending on the pH of the water. When LAP (3 wt %) is added to water, the particles

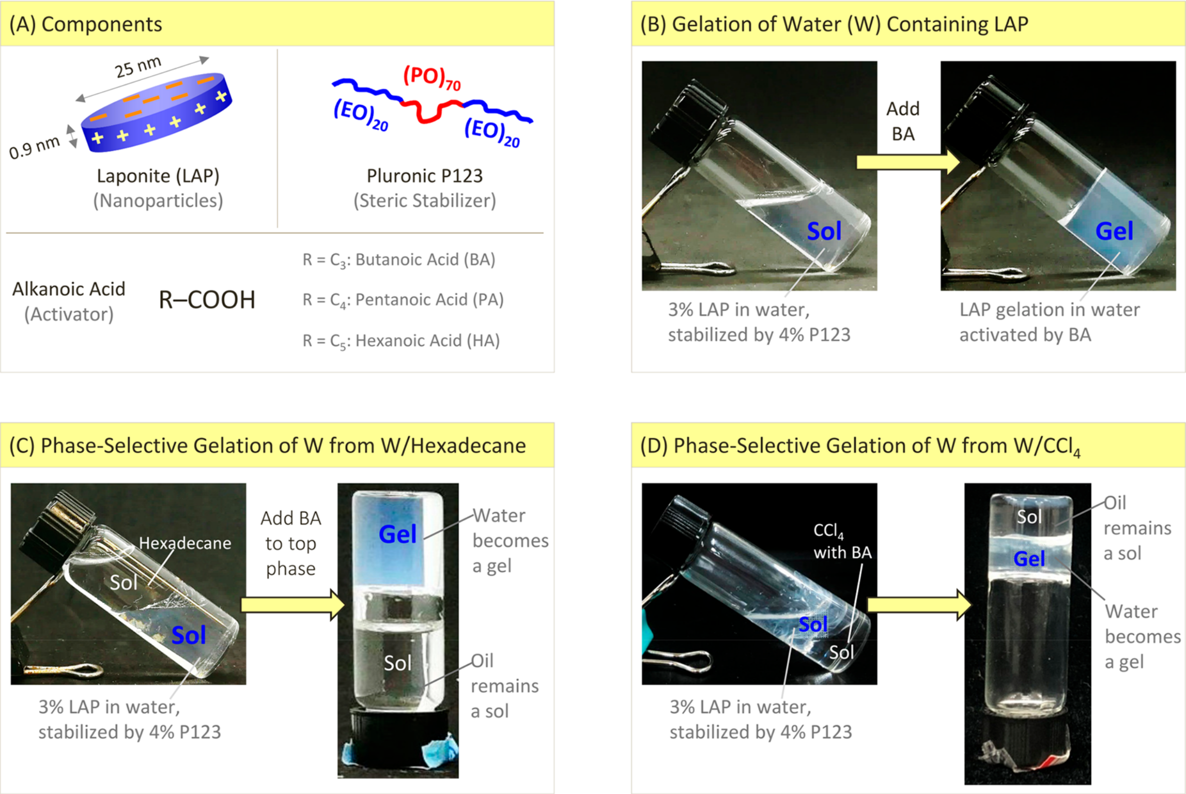


Figure 2. Components used in this study for phase-selective aqueous gelation and examples of the latter. (A) The components include the disklike nanoparticles of a synthetic clay called laponite (LAP), a triblock copolymer such as Pluronic P123 that acts as a steric stabilizer for the LAP particles in water, and an alkanoic acid such as butanoic acid (BA). (B) Photos showing that BA activates gelation of LAP in water. An initial aqueous sol (3% LAP + 4% P123) is converted into a gel by adding 26 mM BA. (C) Photos showing selective gelation of the water (bottom) phase in a two-phase mixture of water and a lighter oil (hexadecane, top). Upon adding 26 mM BA to the hexadecane phase, the water phase (sol of 3% LAP + 4% P123) is transformed into a gel within about 30 min; see the inverted vial. (D) Photos showing selective gelation of the water (top) phase in a two-phase mixture of water and a heavier oil (CCl_4, bottom). If 26 mM BA is present in the CCl_4 phase, the water phase (sol of 3% LAP + 4% P123) is transformed into a gel within about 30 min. The photo of the inverted vial shows the aqueous gel supporting its weight as well as that of the CCl_4 sol.

initially form a stable suspension (sol). Over time (around a day), the particles aggregate to form a three-dimensional network (gel) due to interactions between the edges and faces of the disks.[18,20,21] This type of network is termed a "house-of-cards" structure. If the water contains a "stabilizer", however, gel formation of LAP can be prevented.[22,23] Typical stabilizers for LAP are the triblock copolymers from the Pluronic family.[24] Here, we have selected Pluronic P123, which has an approximate formula of $(EO)_{20}(PO)_{70}(EO)_{20}$, where EO refers to ethylene oxide and PO to propylene oxide.[25] When 3% LAP is added to water along with 4% P123, a stable, low-viscosity sol is formed, and this remains stable for days. The stability arises because P123 molecules adsorb on the LAP disks, with the more hydrophobic PO midblock being anchored on the disks and the hydrophilic EO side-blocks extending into solution.[23,26] Thereby, the P123 sterically stabilizes the LAP; i.e., it imparts a repulsive interaction when two LAP particles encounter each other in the water.

The key to gelation in our experiments is the third component in Figure 2A, which is an organic acid. For our purpose, the organic acid has to be soluble both in nonpolar liquids (oils) as well as in water. Most of our studies have been conducted with butanoic acid (BA). Figure 2B shows the first result: BA (a liquid) is added to the aqueous LAP dispersion (sol) at a concentration of 1 vol % (26 mM). The liquids are miscible, and thus the BA mixes with the low-viscosity sol without any vigorous agitation. Within 10 min, the aqueous sol transforms into a gel, and this can be visually noted by the sample holding its weight in a tilted or inverted vial. Note that the pH of the LAP sol at the outset is around 10, while adding the BA reduces the pH to around 7. This drop in pH is the key to LAP gelation, as discussed later in the paper. Other common acids like hydrochloric acid (HCl) and acetic acid can be used (instead of BA) to induce aqueous gelation; however, these acids are insoluble in the oil phase. This is the reason it is necessary to use organic acids like BA for the phase-selective gelation studies.

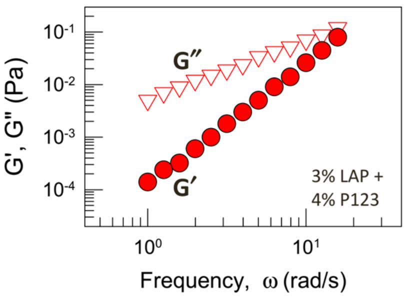
Figure 2C demonstrates phase-selective gelation of the aqueous LAP sol. Here, in the initial state, the vial contains two immiscible liquids: the LAP sol (same as in Figure 2B) as the bottom layer and hexadecane as the oil that forms the top layer. To this two-phase oil/water system, we add liquid BA from the top at a concentration of 26 mM in the oil. The BA mixes readily with the oil, but some of it will partition into the aqueous phase. The reported value of the octanol/water partition coefficient $K_{O/W}$ for BA is ~6, which means that about 1/6th of the BA molecules will partition into the water from an immiscible oil phase.[27] Within about 30 min, the LAP sol is transformed into a gel, and this can be seen from the photo in Figure 2C. Note from this photo that the aqueous gel supports its weight in the inverted vial whereas the oil flows to the bottom. Lastly, if the oil phase has a higher density, the

https://doi.org/10.1021/acs.langmuir.1c00647
Langmuir 2021, 37, 8107−8114

experiment can be conducted differently, as shown in Figure 2D. Here, the oil is carbon tetrachloride (CCl_4), which has a higher density (1.59 g/cm^3) than water. BA is dissolved in CCl_4 at a concentration of 26 mM, and this forms the bottom phase in the vial. We then introduce the aqueous LAP sol above the CCl_4 phase. The LAP sol again converts into a gel within about 30 min. From the photo, note that the aqueous gel supports both its weight as well as that of the liquid oil above it in the inverted vial.

Rheological studies confirm that the water phase in Figures 2B−2D is indeed converted to a gel upon contact with BA. Data from dynamic rheology for the elastic modulus G' and viscous modulus G'' as functions of frequency ω are shown in Figure 3 for samples before and after gelation. Initially (Figure 3a), the stable suspension of 3% LAP in water shows viscous rheology, i.e., $G'' > G'$, with both moduli being strong functions of ω. When 26 mM BA is added to this suspension, either directly or through an immiscible oil phase, the rheology becomes elastic or solidlike; i.e., G' and G'' become independent of ω with $G' \gg G''$.[28,29] Gels can be characterized by the value of G', which is the "gel modulus" and is a measure of the stiffness or rigidity of the gel.[28] We find that the G' of the LAP gel is about 10 000 Pa, and this is the same whether the BA is introduced directly into the aqueous phase or through the oil.

(a) LAP sol in water



(b) LAP gels activated by BA

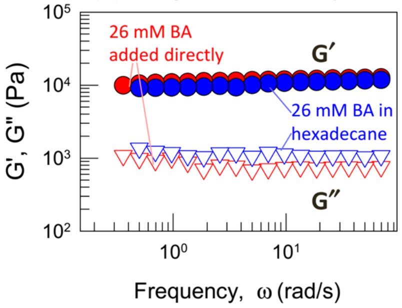
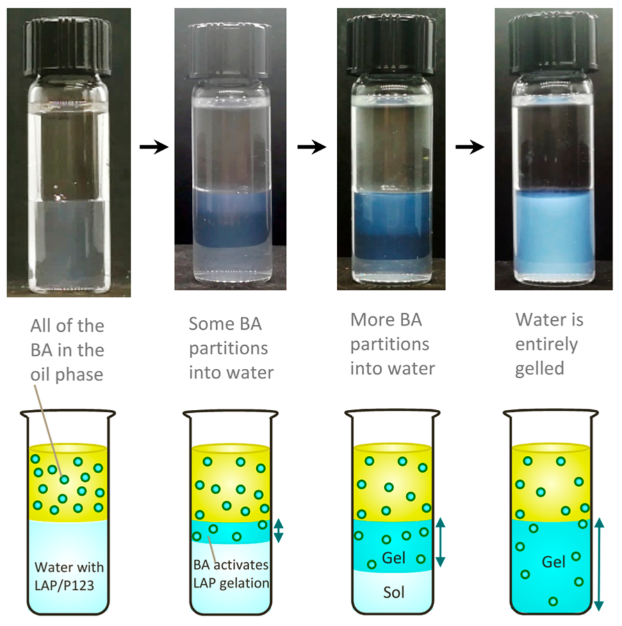


Figure 3. Dynamic rheological data showing BA-activated gelation of aqueous LAP sols. The plots show the elastic modulus G' (filled circles) and viscous modulus G'' (unfilled triangles) as functions of frequency ω. (a) Data for the initial LAP sol (3% LAP + 4% P123). (b) Data for the aqueous gels formed in two ways: (i) adding 26 mM BA directly to the LAP sol (red symbols) and (ii) bringing the LAP sol in contact with a solution of 26 mM BA in hexadecane. In both cases, the samples were allowed to stand for 4 h before measuring the rheology.

Kinetics. Phase-selective gelation can be accomplished using different amounts of BA. The greater the BA concentration in the oil phase, the quicker the water gets gelled. At a given concentration of BA, the kinetics of gelation can be studied visually, as shown in Figure 4A. Here, the oil phase (hexadecane) contains 26 mM of BA at $t = 0$. As the BA partitions into the water, it gels the top portion of the water phase (closest to the oil), which turns a blue color as a result. The blue color, which can also be seen in Figure 2, arises because the gel scatters light more strongly than the sol. By observing the height of the gel phase (h_{gel}) relative to that of the overall water phase (h_0), we can estimate the fraction of the water that has been gelled. This gel fraction (h_{gel}/h_0) increases from 0 to 1 over time, and it is plotted in Figure 4B. For the case of 26 mM BA, the gel fraction reaches 0.2 in about 30

(A) Kinetics of Phase-Selective Gelation: Photos



(B) Kinetics: Data for different BA conc

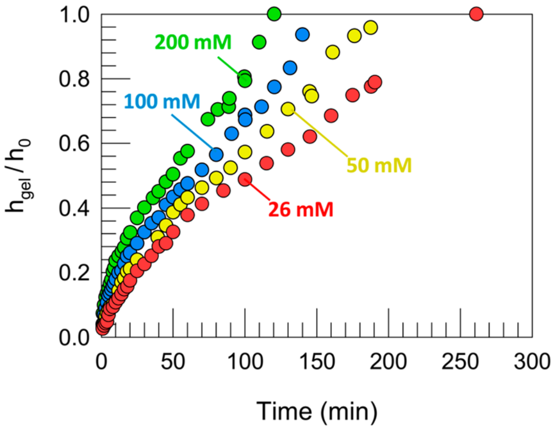


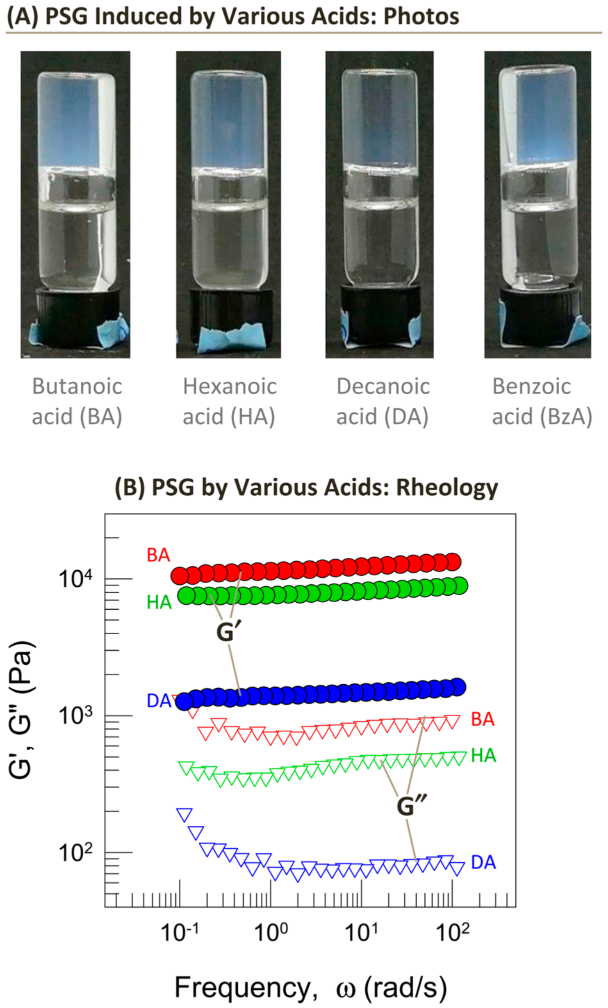
Figure 4. Kinetics of BA-induced phase-selective gelation of an aqueous LAP sol. (A) At $t = 0$, BA is introduced into the oil phase (hexadecane) above a LAP sol (3% LAP + 4% P123). With increasing t, BA diffuses from the oil into the water, and in the process the top portion of the water gets gelled (this exhibits a bluish tint). The height h_{gel} of the blue gel fraction (see arrows) increases with t, and this is normalized and plotted in (B). The plots in (B) are for different concentrations of BA in the oil phase.

min, 0.5 in about 2 h, and 1 in about 4 h. As the BA concentration is increased, the gel front moves more rapidly through the water causing the entire plot of h_{gel}/h_0 vs t to shift leftward, i.e., toward shorter times.

Note that the various plots in Figure 4B merely reflect the fact that if BA is at a higher concentration, more BA molecules will diffuse from the oil to the water (i.e., there will be a higher diffusive flux due to a steeper concentration gradient). In all cases, the process underlying gel formation is the diffusion of the activator (BA) from the oil to the water. The diffusive nature of the process can be shown by replotting the h_{gel}/h_0 data in Figure 4B against $t^{0.5}$, as shown by Figure S1 in the Supporting Information.[30] At each BA concentration, the data follow approximately a straight line on this plot up to intermediate times. Such $t^{0.5}$ scaling is a signature of a diffusive process.[30] Thus, provided there are no convective currents generated by either heat or shear, phase-selective gelation occurs by diffusion of the small-molecule activator across the phase boundary. Note from Figure S1 that there is a deviation from purely diffusive behavior during the last stages of the gelation.

Variables That Affect Gel Stiffness. The properties of the aqueous gel formed by phase-selective gelation can be tuned by several variables, as shown by Figure S2 in the Supporting Information. First is the concentration of BA, which we discussed above with regard to the kinetics of gelation. Figure S2a presents the rheology of aqueous gels induced by 26 and 200 mM BA. The key parameter to note from these data is the value of the gel modulus G'—the higher the G', the stiffer the gel.[28] From Figure S2a, G' is threefold higher for the case of 200 mM BA compared to 26 mM BA. Next, Figure S2b describes the influence of the LAP concentration on the rheology. In all cases, LAP sols were made with 4% P123. Upon gelation by contact with 26 mM BA, the gel modulus shows a strong dependence on the LAP content: G' is about 10-fold higher for 4% LAP compared to that with 2% LAP. A third variable is the concentration of the stabilizer (P123). Figure S2c shows data for 1, 2, 3, and 4% P123, with the LAP fixed at 3%. Gelation was induced by 26 mM BA in all these samples. The data reveal a 10-fold higher G' for the lowest P123 content (1%) compared to the highest. This indicates that the triblock copolymer opposes LAP gelation. However, if only 1% P123 was used, we also observed that the LAP sol exhibited instability over time.[17,18] That is, the LAP particles would begin to cluster even without the addition of the activator (BA). This is why in the rest of our experiments we have used a higher concentration (4%) of P123 in conjunction with 3% LAP. Thereby, we could ensure that the LAP sol remained stable and did not exhibit any increase in viscosity until phase-selective gelation was induced.

Another factor is the nature of the organic acid itself. We have found that a variety of acids can activate the gelation of LAP sols. These include alkanoic acids with different lengths of the alkyl tail, such as hexanoic acid (HA) and decanoic acid (DA). In addition, aromatic acids like benzoic acid (BzA) are also able to induce gelation. Figure 5A shows inverted vials demonstrating that the aqueous phase (mixture of 3% LAP + 4% P123) gets gelled upon contact with a hexadecane phase bearing the above acids (each at 26 mM). Rheological data comparing the gels induced by BA, HA, and DA (Figure 5B) reveal that the highest G' is achieved with BA, followed by HA, and then DA. This order suggests that the key factor is the solubility of the acid in the oil phase compared to water. As noted earlier, the octanol/water partition coefficient $K_{O/W}$ for BA is 6, whereas it is 83 for HA and 12 300 for DA.[27] That is, as the alkyl tail gets longer, fewer of the acid molecules will partition from the oil into the aqueous phase. In turn, the stiffest gel is formed with BA, which has the lowest partition coefficient of the acids studied.


(A) PSG Induced by Various Acids: Photos

(B) PSG by Various Acids: Rheology

Figure 5. Phase-selective aqueous gelation induced by various organic acids. (A) Vials of aqueous sols (3% LAP + 4% P123) contacted with hexadecane containing different acids at a 26 mM concentration. In all cases, the aqueous phase gets gelled, and the gel sustains its weight in the inverted vial. (B) Rheological data for aqueous gels induced by BA, HA, and DA (acids with increasing length of their alkyl tail). The elastic modulus G' (filled circles) and viscous modulus G'' (unfilled triangles) are plotted as functions of frequency ω. All samples show gel-like rheology, with the gel modulus (value of G') being the highest for the case of BA.

Mechanism for Phase-Selective Gelation. Figure 6 is a schematic showing the gelation of the aqueous sol (LAP/P123) upon the addition of acids like BA, either directly or through the oil phase. In the initial state, LAP disks are covered by chains of P123, with the PO midblock being adsorbed on the disks and the EO side-blocks extending into solution. The P123 chains thus sterically stabilize the LAP disks and prevent their aggregation. In this state, the pH of the aqueous phase is about 10, and accordingly, the LAP disks have anionic faces and nonionic edges. When the BA enters the water, the acid-induced reduction in pH to about 7 imparts cationic charges to the edges of the LAP disks, while the faces retain their anionic

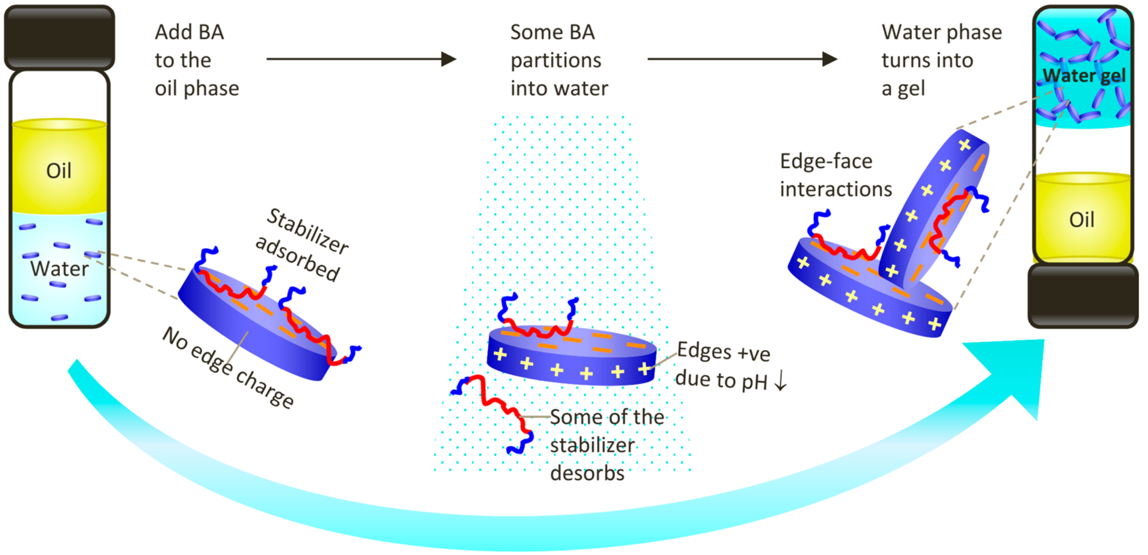


Figure 6. Schematics illustrating the mechanism for phase-selective aqueous gelation. Initially, LAP disks in the water bear no edge charge, and they form a stable dispersion due to the stabilizer (P123 triblock copolymer) adsorbed on them. Note that the hydrophobic segments of P123 in red are shown to lie on the LAP surface while the hydrophilic segments in blue extend into the water. When an acid like BA is added to the oil phase, some of it partitions into the water, whereupon the LAP edges acquire a cationic charge and some of the P123 desorbs from the particles. Thus, BA activates edge−face binding of the LAP disks to form a 3D "house-of-cards" network. The water thus gets gelled, and this gel has sufficient yield stress to bear its weight in the inverted vial. The oil is unaffected.

charges.[20,21] Further, we speculate that some of the P123 desorbs from the faces of the LAP disks, which is consistent with previous reports showing that the interaction of polymers with laponite is pH-dependent.[31−33] At this point, the cationic edges of LAP disks bind to the anionic faces of adjacent disks (Figure 6). This leads to a "house-of-cards" network, thereby converting the sol to a gel. The oil is not affected during this process.

Several aspects of the above mechanism need discussion. First, as noted earlier, instead of BA, acids like HCl or acetic acid can also induce gelation of LAP/P123 aqueous sols, provided they are added in sufficient quantity to lower the pH from 10 to 7. Thus, lowering the pH is what induces gelation, and the converse of this statement is also true—increasing the pH reverts the gel to a sol. For example, Figure S3 shows an aqueous gel obtained by combining 3% LAP, 4% P123, and 26 mM BA. If sodium hydroxide (NaOH) is added to increase the pH (thereby removing the edge charges), the gel is transformed into a milky-white sol. Figure S3 also shows that if excess P123 (equivalent to >10%) is added to the above gel, it is again converted to a cloudy sol. This result suggests a *competition between polymer-provided stabilization and acid-induced gelation*. If there is a high-enough concentration of P123, then despite the pH being favorable to induce edge−face binding of LAP, no gel forms. Conversely, if there is no P123, then the particles bind and a gel forms even at pH 10. From the literature, it is known that P123 is one of the more hydrophobic Pluronics, and its hydrophilic−lipophilic balance (HLB) is between 7 and 12.[24,25] We have found that other Pluronics with comparable HLBs such as P103, P104, and P105 can be substituted for the P123 in our system and provide similar results (data not shown). The ability to reverse the gelation also confirms that the entire process is mediated via self-assembly, i.e., that it involves weak, noncovalent bonds between the particles.

Phase-Selective Gelation Can Facilitate Separations. As noted in the Introduction, the ability to selectively gel the aqueous phase could simplify certain separations or extractions involving two phases. One example, shown in Figure S4, involves the separation of iodine from aqueous solutions. It is well-known that iodine is sparingly soluble in water but much more soluble in organic liquids like cyclohexane. When water containing iodine is contacted with cyclohexane, most of the iodine partitions from the water to the cyclohexane (oil) phase. The partition coefficient for iodine between cyclohexane (C) and water (W), $K = C_C/C_W$, is reported to be around 66.[34] Such partitioning can be visually discerned from the photos in Figure S4. Iodine in water has a yellow color due to the formation of a complex between iodine and water (photo A),[35] but when contacted with cyclohexane, most of the iodine moves to the cyclohexane phase, where the iodine has the familiar violet color (photo B).

Consider a scenario where the oil phase (cyclohexane) in the above experiment has to be carefully removed from the water. This would be important if the iodine, representing a solute of interest, has to be purified from the oil. If the vial is tilted, both liquids would flow down. To cleanly separate the two phases, we can use the phase-selective gelation concept described in this paper. For this, we add LAP powder (equivalent to 3% in the water) to the oil/water mixture and mix the system using a vortex mixer. Initially, some of the LAP particles are incorporated into the oil (photo C), but when left to stand for an hour, the LAP completely moves into the water (photo D). At this stage, the aqueous phase is still a flowing liquid because the suspended LAP particles are discrete and unaggregated. We then add BA to the oil phase, and this induces gelation (i.e., network formation) of the LAP particles in the water, as discussed in Figures 2−6. Within 30 min, the aqueous gel at the bottom develops a sufficient yield stress such that the vial can be overturned to allow all of the oil phase to flow down (photo E). The aqueous gel remains at the top of this inverted vial while the violet cyclohexane phase has flowed to the bottom. This permits convenient separation of the oil from the aqueous phase. Note that, in this entire experiment, we omitted the P123 stabilizer because there was no need to keep the LAP particles stable in the water over long times.

CONCLUSIONS

In summary, we have demonstrated the first example of phase-selective aqueous gelation, where an aqueous phase is gelled by adding a component to a coexisting oil phase. The aqueous phase in our studies contains a mixture of LAP particles and a steric stabilizer (P123). This aqueous sol is brought into contact with an oil phase such as hexadecane, and a hydrophobic acid such as BA is then added to the oil. The BA partitions into the aqueous phase, and it causes the LAP edges to acquire cationic charges. The result is the aggregation of the particles (cationic edges meeting anionic faces) into a house-of-cards network, which converts the sol to a gel. A variety of hydrophobic acids added to the oil are capable of activating aqueous gelation, and the gel modulus depends on the oil/water partition coefficient. The aqueous gel can be ungelled by either adding excess P123 or by increasing the pH. In the future, the concept of phase-selective aqueous gelation could find application in many areas, including enhanced oil recovery.

EXPERIMENTAL SECTION

Materials. Laponite RD (LAP) was a gift from Southern Clay Products. All other chemicals were purchased from Sigma-Aldrich, including P123, the various organic acids (BA, HA, DA, BzA), and the oil phases (hexadecane, chloroform). Deionized (DI) water was used in all experiments.

Sample Preparation and Experimental Protocols. Dispersions of LAP were prepared by adding the particles to DI water, followed by vortex mixing for 5 min. Weighted quantities of P123 were then added to the dispersions, and the mixture was stirred for 1 h using a magnetic stirrer bar. For the kinetic studies, the LAP dispersion was contacted with hexadecane in a vial as shown in Figure 4. At $t = 0$, a given amount of BA was added to the hexadecane, and the vial was monitored by a camera (IPhone 7). From images at various t, the height of the gel phase was measured as a function of t.

Rheological Studies. Experiments were run on an AR 2000 stress-controlled rheometer (TA Instruments) at 25 °C using a cone-and-plate geometry (20 mm diameter, 1° cone angle). Dynamic frequency spectra were obtained in the linear viscoelastic regime of each sample, as determined by dynamic strain−sweep experiments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.1c00647.

> Kinetics of phase-selective gelation (Figure S1); effects of different variables on the rheology of the gels (Figure S2); experiments supporting the mechanism for gelation (Figure S3); experiments showing that phase-selective gelation can facilitate separations (Figure S4) (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

X.Y. was supported by a fellowship from the China Scholarship Council (CSC). Fruitful discussions related to this work with Dr. Kunshan Sun, Dr. Vishal Javvaji, and Dr. Hyuntaek Oh (former members of our lab) are acknowledged.

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<u>**Supporting Information for:**</u>

Phase-Selective Gelation of the Water Phase in an Oil-Water Mixture: An Approach Based on Oil-Activated Nanoparticle Assembly in Water

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Contents

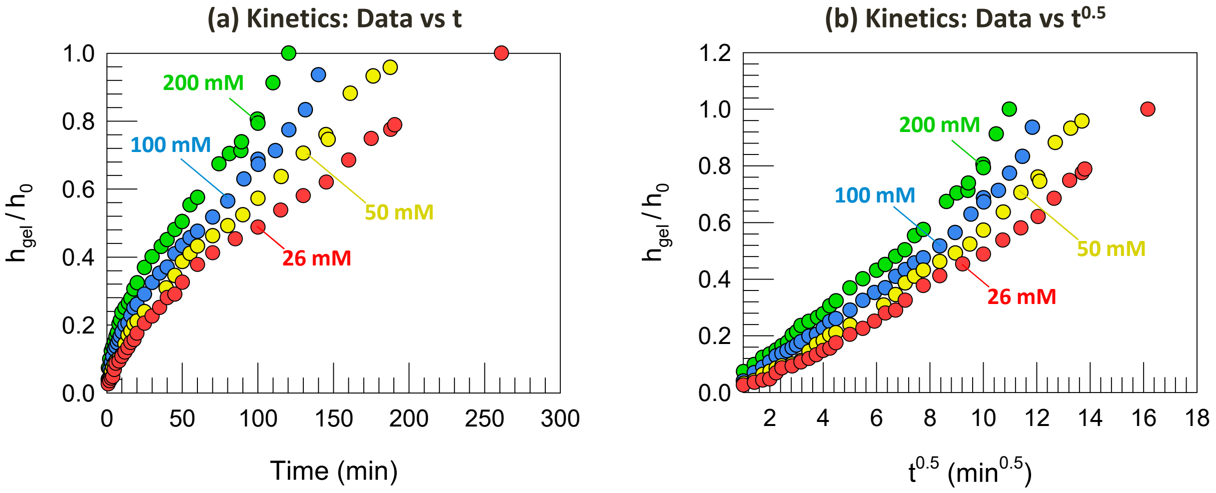
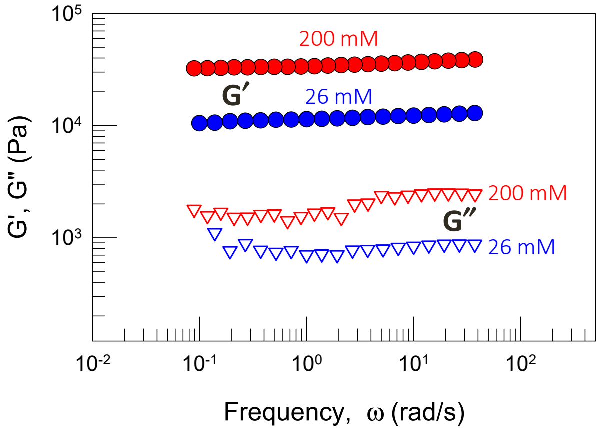


Figure S1. Kinetics of BA-induced phase-selective gelation of an aqueous LAP sol. The plot from Figure 4B is reproduced in (a). The data are for different concentrations of BA added to the oil (hexadecane) phase above a LAP sol (3% LAP + 4% P123). The parameter plotted on the y-axis is the height h_{gel} of the blue gel fraction normalized by the height of the overall aqueous phase h_0, and this is plotted against time t. In (b), the same data is replotted against $t^{0.5}$. The straight lines in (b) up to intermediate times are characteristic of a diffusive process, which indicates that the diffusion of BA from the oil to the aqueous phase controls the gelation. In each case, towards the end, there is a deviation from diffusive behavior, i.e., the lines curve upward.

(a) Varying BA Concentration



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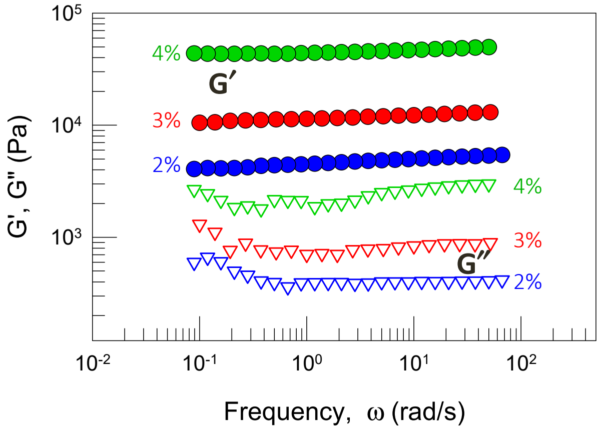

(c) Varying P123 Concentration

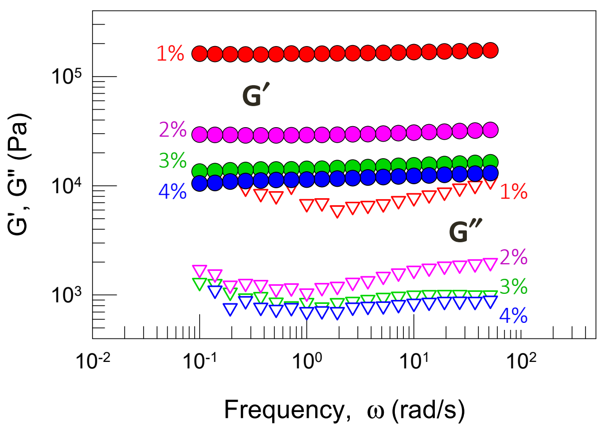

Figure S2. Rheology of aqueous gels formed by phase-selective gelation: Effects of different variables. In all cases, the elastic modulus *G′* (filled circles) and the viscous modulus *G″* (unfilled triangles) are plotted as functions of frequency *ω*. All samples show gel-like rheology, with the gel modulus (value of *G′*) being the key parameter as it reflects the stiffness of the gel. (a) Varying the BA concentration, with the LAP at 3% and the P123 at 4%. (b) Varying the LAP concentration, with the P123 at 4% and the gels induced by 26 mM BA. (c) Varying the P123 concentration, with the LAP at 3% and the gels induced by 26 mM BA.

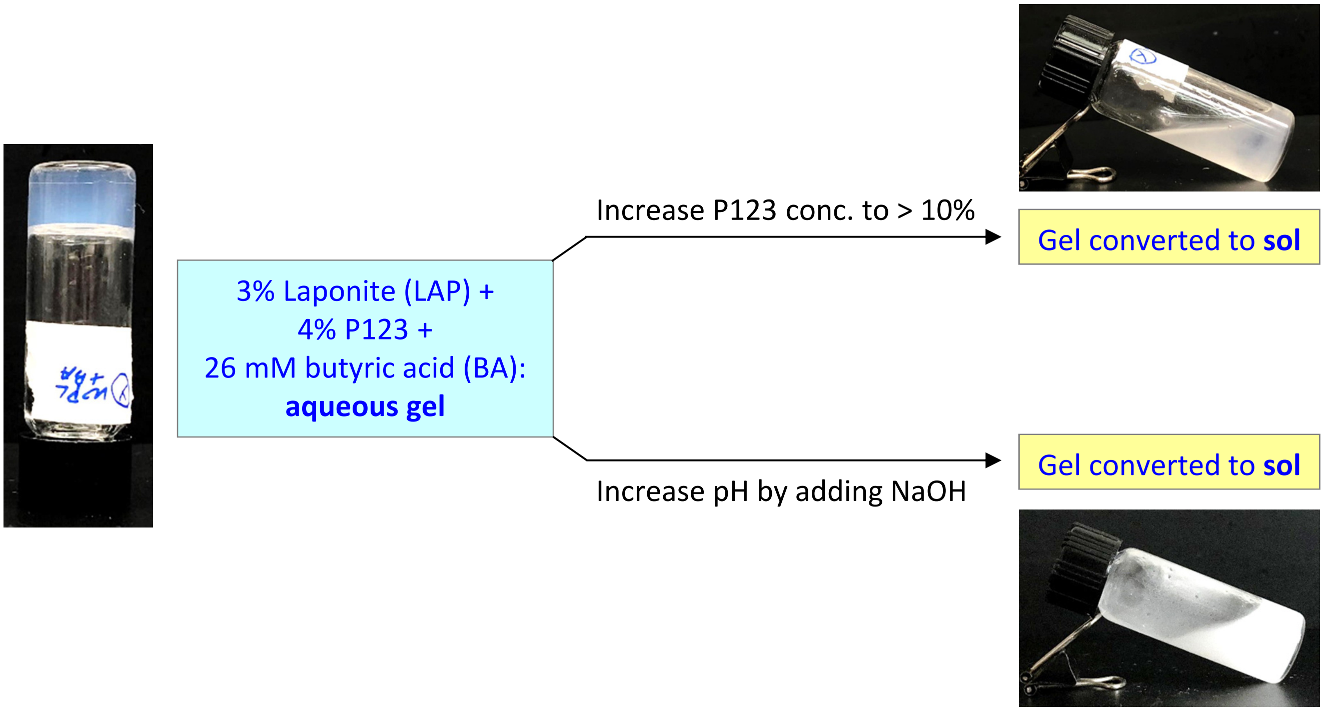

Figure S3. Experiments supporting the mechanism described in Figure 6 for phase-selective aqueous gelation. A gel formed by combining 3% LAP, 4% P123, and 26 mM BA is shown in the inverted vial. (Top) When excess (> 10%) P123 is added to this gel, it is converted to a turbid sol — note the sample in the tilted vial. When NaOH (> 10 mM) is added, the gel is transformed into a highly turbid (milky white) sol — again, this can be seen from the tilted vial.

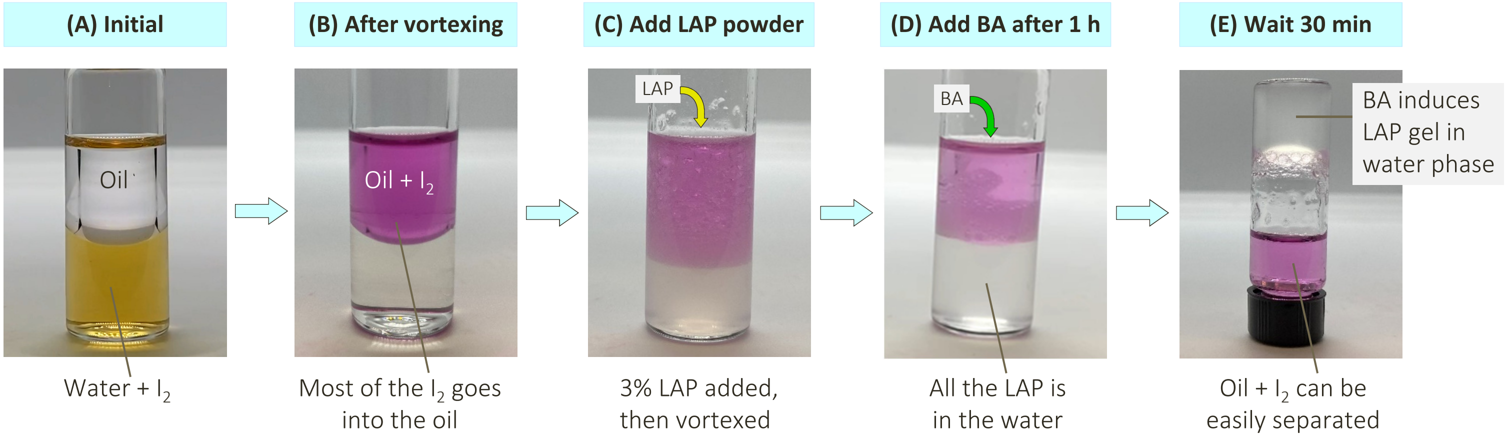

Figure S4. Phase-selective gelation can facilitate separations. The photos illustrate the extraction of iodine (I_2) from water using an immiscible oil (i.e., cyclohexane) phase, followed by a clean separation of the phases once the water is gelled. (A) The oil is brought into contact with water containing I_2. Note that the solution has a yellow color because the I_2 forms a complex with the water. (B) Upon vortex-mixing, most of the I_2 transfers to the oil phase due to the high partition coefficient of I_2 between cyclohexane and water. In the oil, the I_2 has a violet color. (C) LAP powder is added to the above oil/water mixture and vortex-mixed. (D) Within 1 h, all the LAP nanoparticles are in the water (at a concentration corresponding to 3% LAP). At this point, BA (26 mM) is added to the oil. (E) Within 30 min, the BA partitions into the water and activates LAP gelation. The gel is now strong enough to hold its weight in the inverted vial. The oil (with I_2 in it) is left undisturbed and can be readily poured out of this vial.