



Triblock copolymers as versatile constituents of double stimuli-responsive ionic-liquid-based aqueous biphasic systems

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ABSTRACT

This work proposes the use of triblock copolymers as structurally versatile constituents to develop double stimuli-responsive aqueous biphasic systems (ABS) comprising ionic liquids (ILs). Phase diagrams of ABS comprising cholinium acetate ([Ch][C₂O₂]) and triblock copolymers composed of polyethylene oxide (PEO) and polypropylene oxide (PPO) with adjustable compositions of PEO, 20% (PE 6200) and 40% (PE 6400), were determined by the cloud point titration method at several temperatures (25–45 °C) and pH (5–7). These ABS present, for all the tested pH conditions, a Lower Critical Solution Temperature (LCST)-like behavior. However, only ABS with PE 6400 copolymer exhibit a simultaneous response to both stimuli. Compared to the homologous homopolymer polypropylene glycol (PPG), and despite their lower capacity to form ABS, copolymers with an adequate content of PEO provide a stronger response to the simultaneous action of pH and temperature. The results obtained highlight the value of an appropriate adjustment of the polymer structure/monomer composition in the development of ABS with double response to temperature and pH. The enhanced tailoring ability of the proposed systems is demonstrated with the simultaneous separation of two dyes by the application of the studied stimuli.

1. Introduction

Following the principles of Green Chemistry and Sustainability [1], chemical- and biotechnology-based industries strive to develop and apply safer and more environmentally sound processes and products. Within this framework, improving efficiency, decreasing the amount of generated waste, prioritizing recycling and reuse throughout the process, as well as integrating multiple unit operations, are examples of desirable goals [2]. To achieve these goals, the introduction of new equipment and techniques for process intensification is one of the measures currently applied [3,4]. Process intensification is defined as any development that makes technologies miniaturized, clean, safe, and energy-efficient, while integrating multiple process steps into smaller equipment or single/fewer unit operations [5].

Liquid-liquid systems comprising water and water-immiscible organic solvents are widely applied in processes of chemical and biotechnological relevance due to their technological simplicity, low cost, and high efficiency [6,7]. Currently, however, there is a paradigm shift in liquid-liquid systems by using more benign and water-rich approaches that better fulfill the Green Chemistry and Sustainability

standards [8,9]. Emerging in the 50s as an alternative to conventional liquid-liquid systems, aqueous biphasic systems (ABS) have been successfully used in several extraction, separation and integrated processes [10]. ABS are typically formed by polymer + polymer and polymer + salt combinations, with a third component, water [11]. These systems present a characteristic phase diagram and tailored properties, which depend on the chosen pair of phase-forming components and operating conditions (e.g., temperature and pH) [12,13]. Regardless of their potential, the poorly adjustable range of phases' polarities and modest customization degree of conventional ABS composed of polymer + polymer or polymer + salt restrict their potential as tailored extraction platforms [14]. To overcome the low efficiency or selectivity sometimes achieved by conventional ABS, several strategies have been proposed, including the use of structurally versatile and/or stimulus-responsive components [15,16].

Among the most versatile alternative ABS components are ionic liquids (ILs), but also copolymers (instead of the widely used homopolymers). Due to their tailor-made potential arising from the innumerable cation-anion possibilities available for their synthesis, ILs improve the hydrophobic-hydrophilic range and promote the design of

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high-performance ABS [15,17]. In turn, the advantage of using copolymers relates with the possibility of increasing the degree of manipulation of the properties of polymers. In addition to the length of the polymeric chain, it is also possible to control the ratio and organization of hydrophobic and hydrophilic monomers within copolymers [18]. Given the set of advantages of both type of compounds, the joint use of ILs and copolymers as phase-forming constituents has been adopted for the development of new ABS. Most reports available in the literature resort to cholinium-based ILs due to their enhanced ability to form ABS with polymers, combined with random or triblock copolymers composed of ethylene oxide and propylene oxide monomers [18–22]. These systems have led to high selectivity in the extraction and separation of miscellaneous molecules, ranging from drugs [20] to flavonoids [18] and proteins [21].

Another strategy to improve the customizability of ABS is the use of stimuli-responsive phase forming components, especially if these are also, or at least combined with, structurally versatile compounds such as ILs [21]. Due to their sensitivity to temperature and pH, polymers and salts are commonly used as the second, stimulus-responsive, phase-forming agent in the development of stimuli-responsive IL-based ABS [23,24]. The presence of these compounds allows changing between monophasic and biphasic systems by simply applying temperature or pH variations [23,24]. In the origin of temperature-responsive IL-based ABS is their ability to exhibit an upper critical solution temperature (UCST)-like behavior or a lower critical solution temperature (LCST)-like behavior. The former is characterized by a decreasing ABS formation ability upon increasing temperature, whereas the latter is described by an increasing ABS formation ability upon increasing temperature [25]. While IL + salt ABS most commonly follow an UCST-like behavior [26], the behavior of IL + polymer ABS is not as straightforward [25]. LCST-like phase behaviors are normally associated with polyethylene glycol (PEG) + cholinium-based ILs or polypropylene glycol (PPG) + imidazolium-based ILs [27,28]. In contrast, UCST-like behaviors are displayed by systems comprising PEG and imidazolium-based ILs [29]. These behaviors depend on the interactions/mutual solubility between the polymer and IL under appraisal and their affinity for water [25,27,28]. In turn, pH-responsive IL-based ABS are originated by the speciation ability of one the phase-forming components, usually the salt or the IL, as a function of pH [24,30]. Upon pH variations, the species in solution present different protonation degrees and, consequently, abilities for hydration. Overall, ions with higher valence have higher propensity for hydration and, thus, to form ABS [24,30]. Remarkably, these stimuli-induced phase transitions have led the development of integrated processes to success as shown with the integrated production-separation of hydroxymethylfurfural by fructose dehydration using pH-responsive IL + salt ABS [24].

Instead of a single stimulus, the use of multiple stimuli can add extra advantages regarding technological flexibility [16]. Despite the already reported advantages of using ILs, their use in double stimuli-responsive (temperature and pH) ABS was only recently proposed by us using cholinium-alkanoate-based ILs and a polymer as the pH- and thermo-responsive components, respectively [31]. Instead of the homopolymer PPG used in our previous work [31], herein we propose the use of copolymers as the thermo-responsive phase-forming agent. To achieve this goal, the phase diagrams of ABS composed of triblock copolymers composed of polyethylene oxide (PEO) and polypropylene oxide (PPO) with variable compositions of PEO, 20% (PE 6200) and 40% (PE 6400), and cholinium acetate ([Ch][C₂O₂]) were determined as a function of both temperature and pH and further benchmarked against PPG.

To attest their potential as customizable separation platforms, the simultaneous separation of two dyes as model compounds, namely Brilliant blue FCF (E133) and Sudan III, is here also demonstrated. It has been shown the adequacy of ABS to extract and separate dyes from industrial effluents, allowing to overcome environmental contamination caused by the incorrect disposal of synthetic dyes [32]. Nevertheless, in this type of application the cross-contamination by the ABS phase-

forming components cannot be disregarded. ABS are also propitious candidates to improve the processing or detection of natural pigments [33]. In this vein, several ABS have been reported using (co)polymer + salt [34–36], surfactant + surfactant [37], IL + salt [38,39], IL + polymer [27,40], IL + surfactant [41], IL + organic solvent [42] and eutectic solvent + salt [43] combinations. Conventional polymeric systems lead to an efficient separation of dyes, but the incorporation of adjuvants is commonly needed to improve the performance or selectivity of the process [34]. Although IL + salt ABS enable the efficient (complete) extraction of dyes [38], the combination of IL + polymer, such as PEG, is more adequate for the selective separation of dyes [27,40]. As compared to conventional polymeric systems, IL + polymer systems are simpler in terms of composition as the addition of an extra component to improve selectivity is not required [40]. In the separation of dyes using IL + polymer systems, PEG has been the most widely adopted homopolymer [27,40]. Alternatively, triblock copolymers based on PPO and PEO are here used to extend the currently available systems for the separation of dyes. Two stimuli are simultaneously applied to manipulate the behavior of the ABS, which together with the use of structurally versatile triblock copolymers and ILs (here represented by [Ch][C₂O₂]), contribute to a higher technological flexibility of ABS as separation techniques.

2. Experimental procedure

2.1. Materials

Cholinium acetate ([Ch][C₂O₂]) with a purity of 98% was obtained from IOLITEC (Ionic Liquids Technologies GmbH). The triblock copolymers of polypropylene oxide (PPO) and polyethylene oxide (PEO) used were PE 6200 with a molecular weight of 2450 g.mol⁻¹ and 20% PEO, and PE 6400 with a molecular weight of 2900 g.mol⁻¹ and 40% of PEO. The chemical structures and acronyms of the IL and copolymer are provided in Fig. 1. Acetic acid with a purity of 99% was obtained from Labsolve. The brilliant blue FCF (E133) (>98 % purity) was obtained from Vahine and Sudan III (>99 % purity) was acquired at Merck. Materials were used as received.

2.2. Determination of ternary phase diagrams

The binodal curves of the ternary systems composed of IL + PE 6200/PE 6400 + water were determined by the cloud point titration method at various temperature (25–45 °C) and pH (5–7) under atmospheric pressure, as previously described [23,24]. To maintain the temperature, a window bath with a precision of ± 0.01 °C (ME-18 V Visco-Thermostat, Julabo) was used. The pH of the systems was adjusted by adding acetic acid (the IL anion parent acid) and controlled using a Metrohm 827 pH lab pH meter with an uncertainty of ± 0.1. IL and polymer aqueous solutions were prepared at initial concentrations of 60 wt%. Aqueous solutions of IL previously adjusted to the desired pH were added dropwise to the polymer solution placed at the desired temperature, up to the identification of a cloud point corresponding to the biphasic region. Under the same conditions, water was then added until the solution turns clear (monophasic point). After adding the IL solution or water, the ternary mixture compositions were determined by weight quantification within ± 10⁻⁴ g. A modified Merchuk et al. [44] equation was applied to fit the experimental binodal data, further enabling the determination of [Ch][C₂O₂] = [PE] and the extent of the ABS stimulus-responsive region. Equation used is presented in the [Supplementary Material](#).

2.3. Extent of the ABS stimulus-responsive region

The Euclidian distance between two mixture compositions of the binodal curves determined at the two extremes of temperature or pH was used to assess the extent of the stimulus-responsive regions. For these determinations, the mixture compositions used were acquired by

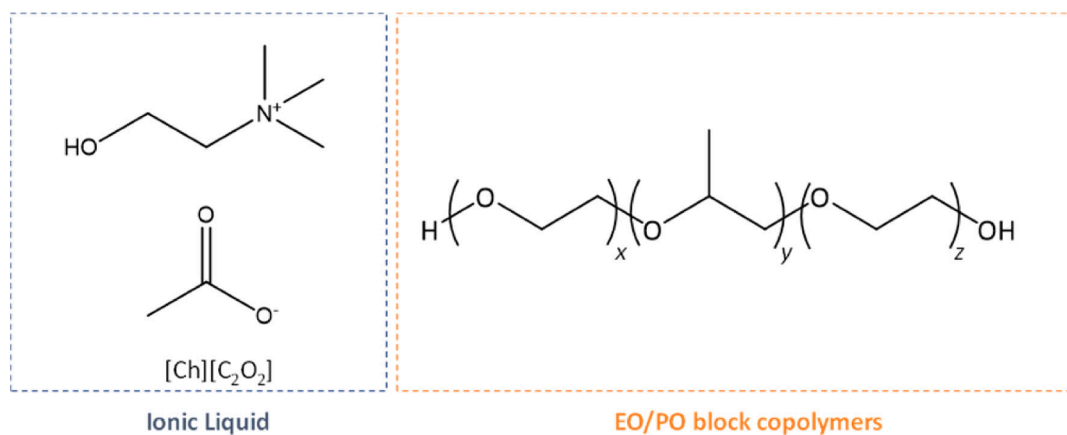


Fig. 1. Chemical structure and acronyms of the ABS phase-forming compounds used.

the intersection of a line crossing the graph origin, i.e., [Ch][C₂O₂] = [PE], with the respective binodal curve. For more details on these calculations please refer to the [Supplementary Material](#).

2.4. Dyes separation

Mixture points placed between the binodal curves at the two extremes of the conditions (temperature or pH) under consideration were prepared to study the separation of two dyes, Sudan III and E133, also allowing to verify the response of the systems to undergo phase separation by temperature and pH changes. These two dyes are here used as model compounds to demonstrate the versatility of the new responsive ABS as separation platforms. In the systems prepared to appraise the partition of Sudan III, the dye was dissolved before the system preparation in the copolymer solution. In the case of E133, the dye was introduced directly into the system.

To evaluate the response to temperature, a mixture composition composed of 18 wt% of [Ch][C₂O₂] and 20 wt% of PE 6400 at pH 7 was prepared. After ensuring the complete dissolution of all system components, the system was placed at 25 °C for 2 h to ensure a single-phase condition. Later, the same system was set at 45 °C for 48 h to check the temperature response through the formation of two phases. For the evaluation of the response to pH, a mixture composition composed of 25 wt% of [Ch][C₂O₂] and 12 wt% of PE 6400 at 35 °C was prepared at pH 5 (monophasic) and 7 (biphasic), using acetic acid to adjust the pH to the desired value. These systems were left at 35 °C for 48 h and centrifuged for 2 h at 5000 rpm to aid two-phase formation. UV-Visible spectroscopy was used for the quantification of the dyes in the top (IL-rich) and bottom (copolymer-rich) phases at wavelengths of 633 nm for E133 and 348 nm for Sudan III. A SYNERGY^{HT} microplate reader was used.

The extraction efficiencies of E133 (EE_{E133} , %) and Sudan III ($EE_{SudanIII}$, %) are defined according to Equations (1) and (2):

$$EE_{E133}, \% = \frac{Abs_{E133}^{IL} \times w_{IL}}{Abs_{E133}^{IL} \times w_{IL} + Abs_{E133}^{Copolymer} \times w_{Copolymer}} \times 100 \quad (1)$$

$$EE_{SudanIII}, \% = \frac{Abs_{SudanIII}^{Copolymer} \times w_{Copolymer}}{Abs_{SudanIII}^{Copolymer} \times w_{Copolymer} + Abs_{SudanIII}^{IL} \times w_{IL}} \times 100 \quad (2)$$

where $Abs_{E133/SudanIII}^{IL}$ and $Abs_{E133/SudanIII}^{Copolymer}$ are the absorbance of E133 or Sudan III in the IL-rich and copolymer-rich phase, respectively, taking into account the dilutions carried out. w_{IL} and $w_{Copolymer}$ are the weight of the IL-rich and the copolymer-rich phase, respectively.

3. Results and discussion

To develop ABS with simultaneous response to temperature and pH,

phase-forming components responsive to these stimuli were used, namely a pH responsive IL - [Ch][C₂O₂], and two thermo-responsive copolymers - PE 6200 and PE 6400. The two copolymers have 20% and 40% of PEO incorporated in their chemical structures, yielding polymers of distinct hydrophobic-hydrophilic nature. Compared to the homologous homopolymers, such as PPG, using copolymers in ABS allows obtaining an extra degree of flexibility in the development of ABS and response to stimuli by manipulating the PEO content. In turn, [Ch][C₂O₂], whose anion derives from acetic acid, allows manipulating the fraction of neutral versus negatively charged species in solution as a function of pH. It is thus expected to observe a temperature response due to the presence of copolymers and a pH response due to the pKa of the IL anion and consequent changes in its speciation. To evaluate the response to each stimulus, the binodal curves of [Ch][C₂O₂] + copolymer ABS were determined at temperatures between 25 and 45 °C and pH values ranging from 5 to 7. Above the binodal curve, mixture compositions undergo liquid-liquid demixing, i.e., binodal curves closer to the graph origin have an enhanced ability to form ABS. All experimental binodal data in weight percent as well as their fitting and correlation parameters are provided in [Supplementary Material](#), in Tables S1-12.

3.1. ABS response to temperature and pH

Fig. 2 shows the effect of temperature and pH in the liquid-liquid phase behavior of ABS composed of [Ch][C₂O₂] and the two copolymers under representative conditions of pH and temperature. According to Fig. 2a), an increase in temperature favors liquid-liquid demixing, i.e., less amounts of IL and copolymer are needed to accomplish biphasic systems. This trend is consistent under all conditions of pH applied, as demonstrated by the remaining binodal curves (cf. [Figures S1 and S2](#) in the [Supplementary Material](#)). The dependency of ABS formation with temperature follows a LCST-like behavior, similar to the copolymer + water binary mixture phase behavior in which a decrease in the solubility of the polymer with increasing temperature is observed [19]. Considering the interactions that occur between the three constituents of the system, it is possible to conclude that the copolymer-water interactions rule the temperature-responsive behavior. The observed LCST-like behavior is in agreement with data reported in the literature for other systems composed of cholinium-based ILs and homopolymers [19,27].

Considering Fig. 2b), the ability to form ABS as a function of pH is highly dependent on the copolymer composition. Irrespective of the temperature under appraisal, the same trend is observed (cf. [Figure S3-S4](#) in [Supplementary Material](#)). In the presence of PE 6200, the pH has low to no impact on the ABS formation, as demonstrated by the overlapping of the binodal curves. It seems that the hydrophobicity of this copolymer, which has 20% PEO in its composition, and temperature are

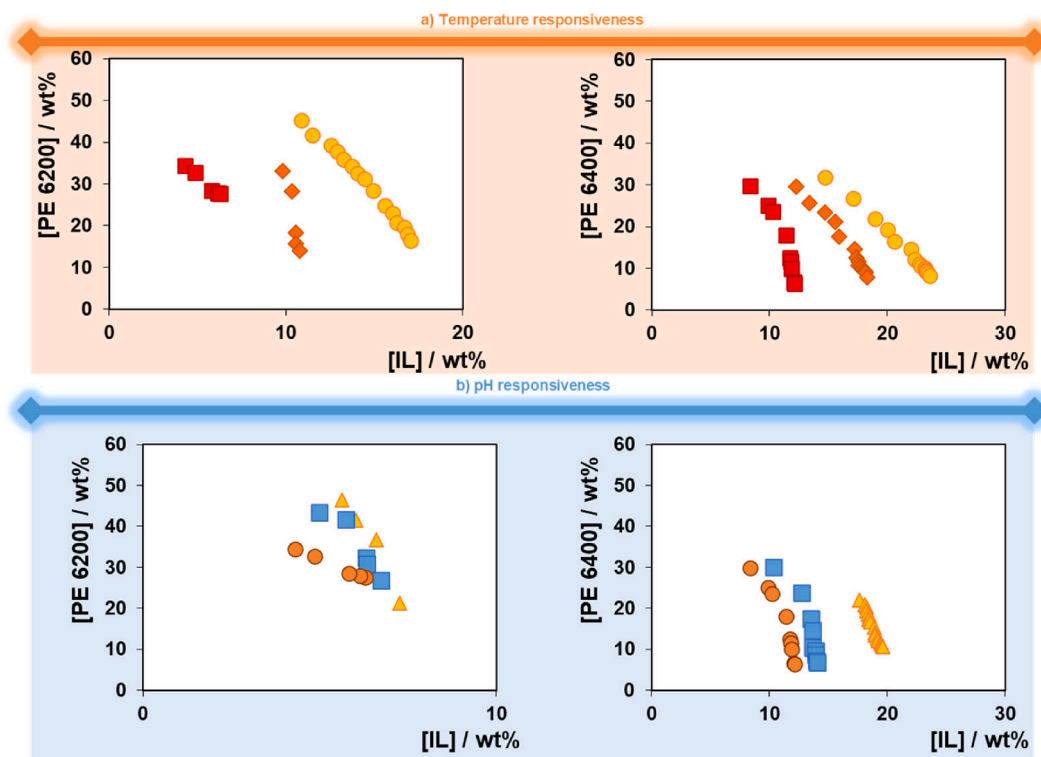


Fig. 2. Liquid-liquid phase diagrams shown in an orthogonal representation with the response to temperature or pH of ABS composed of $[\text{Ch}][\text{C}_2\text{O}_2]$ + copolymer + H_2O . Binodal curves presented are for variable temperatures of 25 °C (●), 35 °C (◆), and 45 °C (■) under pH 7 a) or variable pH values of 5 (▲), 6 (■) and 7 (●) under 45 °C b).

the preponderant factors in the formation of the respective ABS. By increasing the PEO content of the copolymer to 40% with PE 6400, the pH effect becomes notorious regardless of temperature. In this case, the ability to form ABS increases with increasing pH, as also reported for ABS composed of IL + salt [24] and polymer + salt [45].

The pH response of systems containing PE 6400 is due to the $[\text{Ch}][\text{C}_2\text{O}_2]$ anion, acetate, and its speciation as a function of pH. Negatively charged species are more prone to hydration than their neutral congeners, favoring the exclusion of the copolymer to a second aqueous phase [24]. Consequently, the ability to form ABS is enhanced. In conformity with the speciation curve of acetic acid as a function of pH provided in the Supplementary Material (Figure S5) [46], acetic acid has an acidity constant (pKa) set at 4.54. At values of $\text{pH} > \text{pKa}$, anionic species become increasingly more dominant in detriment of neutral molecules. Experimentally, at pH 7, the highest capacity to form ABS is observed due to the higher fraction of anionic species in solution (99.65%). At pH 6 (96.62%) and, especially at pH 5 (74.1%), the ability to form ABS is weakened following the continuous decrease in the anionic species.

3.2. Impact of the (co)polymer in ABS formation

To attest the usefulness of the copolymer structural versatility, the impact of the polymer PEO content (from 0 to 40%) on the ability to form ABS with $[\text{Ch}][\text{C}_2\text{O}_2]$ was evaluated. The binodal curves of ABS comprising $[\text{Ch}][\text{C}_2\text{O}_2]$ and the homopolymer PPG 400 previously reported by us are also considered for comparison purposes [31].

Fig. 3 shows that the ability of polymers to form ABS with $[\text{Ch}][\text{C}_2\text{O}_2]$ follows the order PPG 400 > PE 6200 > PE 6400, this being maintained for all conditions of temperature and pH values tested (cf. Figures S6 to S8 in the Supplementary Material). Therefore, less amount of PPG 400 is required to create ABS in the presence of $[\text{Ch}][\text{C}_2\text{O}_2]$ when compared to the copolymers. PPO is more hydrophobic than PEO due to the extra methyl group incorporated in its structure. As the percentage of PEO decreases, the hydrophobicity of polymers increases. More

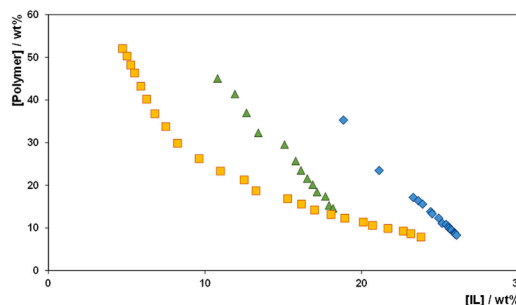


Fig. 3. Effect of the polymer in the binodal curves of the systems composed of polymer + $[\text{Ch}][\text{C}_2\text{O}_2]$ + H_2O at pH 6 and 25 °C: PE 6200 (▲); PE 6400 (◆); PPG 400 (■). Binodal data for the $[\text{Ch}][\text{C}_2\text{O}_2]$ + PPG 400 + H_2O system is obtained from reference [31].

hydrophobic polymers have lower water affinity and, thus, enhanced aptitude for ABS formation in the presence of $[\text{Ch}][\text{C}_2\text{O}_2]$. This justifies the higher capacity of PPG 400 (0% PEO) to form ABS than the copolymers PE 6200 (20% PEO) and PE 6400 (40% PEO). The same pattern is found in the literature, where the capacity of copolymers to undergo phase separation in the presence of salts correlates well with their solubility in water (an indirect measure of their hydrophobicity-hydrophilicity) [47].

3.3. Double stimuli-responsive behavior

Fig. 4 shows the double responsiveness of $[\text{Ch}][\text{C}_2\text{O}_2]$ + copolymer ABS and how this compares with the system comprising PPG 400. For a better understanding of the double stimuli response, the distances between the binodal curves for the extreme values of each condition studied, i.e., between 45 °C and 25 °C at a given pH value (temperature-

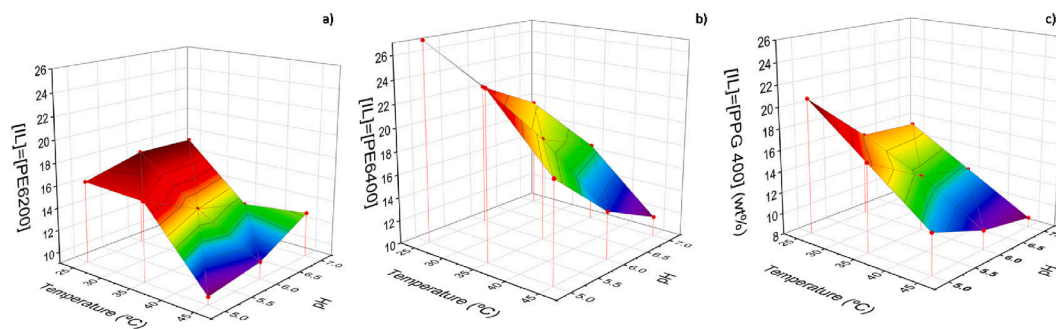


Fig. 4. Double responsiveness to temperature and pH of ABS composed of [Ch][C₂O₂] + PE 6200 a), PE 6400 b) and PPG 400 c) + H₂O. Red dots correspond to the mixture compositions in which [Ch][C₂O₂] = [Polymer]. Data for the [Ch][C₂O₂] + PPG 400 + H₂O system is obtained from reference [31]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

responsive region) and between pH 7 and pH 5 at a given temperature condition (pH-responsive region), were also considered. The distances between the binodal curves are shown in Table 1. For comparison purposes, data for the PPG 400 is also presented [31].

According to Fig. 4 and Table 1, there is a response to temperature for all systems due to the thermo-responsiveness of the polymer, which decreases following an increase in pH. PE 6400 has a similar to slightly superior response to temperature as compared to PPG 400 and PE 6200, especially at pH 6 and 7, respectively. A simultaneous and well-defined response to temperature and pH is exhibited by the ABS comprising the copolymer PE 6400 and PPG 400, where the pH-responsive region decreases with increasing temperature. The PE 6400 additionally provides larger extents of the pH-responsive region than PPG 400 within the entire temperature range. Due to its higher PEO content (thus, higher hydrophilic character), a more delicate response to the action of pH is allowed, without overwhelming effects of the temperature or the polymer hydrophobicity. Based on these results, the adequate adjustment of the polymer structure/properties allows obtaining stronger responses to the simultaneous action of temperature and pH, as shown with PE 6400.

3.4. Application of double stimuli-responsive ABS as separation platforms

The concept of double stimuli-responsive ABS is depicted in Fig. 5, highlighting the main aspects to consider while projecting their application. Accordingly, mixture points to be adopted must be selected considering the stimuli-responsive region, which is localized between the binodal curves at two desired values of temperature or pH. Upon varying the desired condition, the selected mixtures switch from mono to biphasic and vice versa without the need to significantly change their original composition.

In this work, two dyes, namely Sudan III and E133, were used as model compounds to demonstrate that the proposed stimuli-responsive systems can be used as separation platforms. To evaluate the response to temperature between 25 (monophasic) and 45 °C (biphasic), a mixture composition bearing 18 wt% of [Ch][C₂O₂] and 20 wt% of PE 6400 at pH 7 was used. To evaluate the response to pH between 5 (monophasic) and 7 (biphasic), a mixture point formed by 25 wt% of [Ch][C₂O₂] and 12 wt% of PE 6400 at 35 °C was adopted. In these systems, the top phase

Table 1

pH- and temperature-responsive regions accounting for the distance between the binodal curves for the [Ch][C₂O₂] + polymers + H₂O systems. Distances for the [Ch][C₂O₂] + PPG 400 + H₂O system are obtained from reference [31].

Fixed condition	pH-responsive region			Temperature-responsive region		
	25 °C	35 °C	45 °C	5	6	7
PE 6200	1.13	2.12	4.67	11.46	10.18	5.66
PE 6400	11.60	11.88	9.33	12.45	12.02	10.18
PPG 400	7.49	5.51	4.24	12.31	8.91	9.06

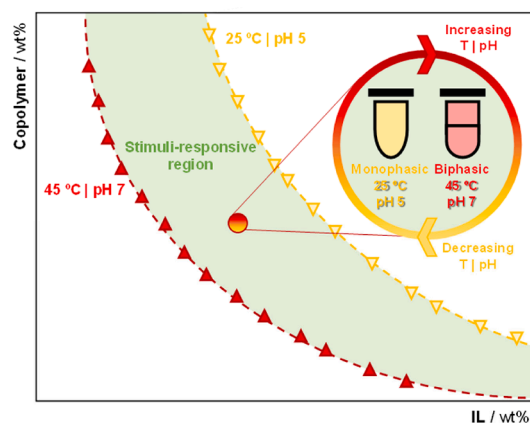


Fig. 5. Double stimuli-responsive IL-based ABS concept and application development.

is IL-rich and the bottom phase is copolymer-rich. PE 6400 was used due to the double stimuli-responsiveness exhibited by the respective ABS.

Fig. 6 shows the extraction efficiencies of the two model dyes using ABS composed of [Ch][C₂O₂] and PE 6400 compared with data previously obtained with systems containing PPG 400 [31]. The numerical values of the extraction efficiencies are presented in detail in Table S13 in the Supplementary Material. Overall, different partition patterns are obtained depending on the type of polymer (homopolymer versus copolymer), mixture composition and stimulus applied.

In all systems, Sudan III preferentially migrates to the more hydrophobic polymer-rich phase, which is due to its enhanced hydrophobicity (octanol/water partition coefficient, log $K_{o/w}$ of 7.63 [48]), regardless of the stimulus and mixture composition applied. Despite the hydrophilic nature of E133 (log $K_{o/w}$ of -4.94 [49]), different partition behaviors are obtained, depending on the stimulus applied and mixture composition. In the ABS composed of PE 6400 and [Ch][C₂O₂], the action of temperature allows to completely partition Sudan III into the copolymer-rich phase, but only 28% of E133 in the IL-rich phase (contrarily to the expected behavior based on the log $K_{o/w}$). Since complete partition to opposite phases is obtained using PPG 400 for the same dyes in conformity with their log $K_{o/w}$, it can be anticipated that the lower hydrophobicity of PE 6400 seems insufficient for the selective partition or complete separation of the two dyes. These results indicate that copolymers allow a more delicate balance between the ABS phases' properties than their parent homopolymers. This feature can be however used to selectively separate structurally similar compounds, as previously reported with naringin and rutin [18]. On the other hand, by the action of the pH, the extraction efficiency of E133 could be enhanced to 91%, while keeping the ability to partition Sudan III (73%) mostly to the copolymer-rich phase. Thereby, the different partition trends obtained

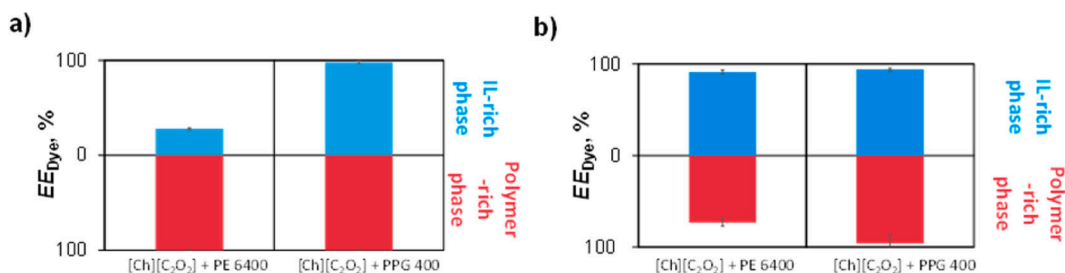


Fig. 6. Extraction efficiencies of both dyes (EE_{Dye} , %) obtained using $[Ch][C_2O_2]$ + polymers + H_2O systems with the application of temperature a) and pH b). Blue bars represent the EE_{E133} to the IL-rich phase, while red bars represent the $EE_{E\text{ Sudan III}}$ to the polymer-rich phase. Data for the $[Ch][C_2O_2]$ + PPG 400 + H_2O system is obtained from reference [31]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as a function of the stimulus and mixture composition applied suggest that the double stimuli response can be used to further enhance the tailoring ability of ABS as separation platforms.

4. Conclusions

In this work, the customization degree of double stimuli-responsive IL-based ABS was successfully amplified by using copolymers as phase-forming agents. The ternary phase diagrams were determined at pH 5 to 7 and between 25 and 45 °C using water, the pH-responsive IL $[Ch][C_2O_2]$ and each one of the two studied thermo-responsive triblock copolymers of PEO and PPO as phase-forming agents. All ABS present a similar response to temperature regardless of the copolymer, exhibiting a LCST-like behavior. A double response to temperature and pH is only achieved by the system composed of PE 6400, where the increase in pH favors ABS formation due to changes in the speciation of the IL anion. Comparing the use of copolymers with that of a homologous homopolymer, i.e., PPG 400, the latter shows a better aptitude to form ABS with $[Ch][C_2O_2]$. Despite this fact, PE 6400 offers a stronger simultaneous response to temperature and pH, especially by providing improved pH-responsive regions. As potential separation platforms, the use of PE 6400 versus PPG 400 and stimulus applied lead to different partition behaviors of two dyes, showing the tailoring ability of copolymers as phase-forming components of double stimuli-responsive IL-based ABS. Overall, if properly designed, copolymers provide not only a higher degree of customization, but also a stronger simultaneous response to temperature and pH than PPG 400. Copolymers are thus expected to contribute to the development of new and more tailored separation platforms based on double stimuli responsive IL-based ABS.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Ana F.C.S. Rufino: Investigation, Formal analysis, Writing – original draft. **Sara C. Ribeiro:** Investigation. **João A.P. Coutinho:** Supervision, Writing – review & editing. **Francisca A. e Silva:** Conceptualization, Visualization, Supervision, Writing – review & editing, Funding acquisition, Project administration. **Mara G. Freire:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2023.123852>.

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