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Fractionation of phenolic compounds from lignin depolymerisation using polymeric aqueous biphasic systems with ionic surfactants as electrolytes†

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Lignin-based materials and chemicals represent a large class of potential added-value compounds for biorefineries; however, the difficulty in fractionating heterogenous phenolic compounds that result from lignin depolymerisation still remains a challenge. Herein, a set of polymer-based aqueous biphasic systems (ABS) comprising sodium polyacrylate (NaPA 8000) and polyethylene glycol (PEG 8000), in which ionic surfactants and ionic liquids are used as electrolytes at concentrations below 1 wt%, is investigated for this purpose. Binodal curves were determined for three electrolyte concentrations, namely, 0.01, 0.1 and 1.0 wt%, and an intermediate electrolyte concentration was selected to investigate the partition of five phenolic compounds, caffeic acid, vanillic acid, gallic acid, vanillin and syringaldehyde, on these systems. The results show that the ABS allow the manipulation of the partition of the five phenolic compounds, which culminates with their selective isolation, with vanillin selectivities of $S_{VN/VA} = 23.75$, $S_{VN/GA} = 12.52$ and $S_{VN/CA} = 8.47$. The electrolyte nature seems to play an important role in the fractionation of the phenolic compounds, due to the difference in their hydrophobic nature and speciation. This study demonstrates the ability of polymeric-based ABS, using ionic surfactants or ionic liquids as electrolytes, to efficiently separate and isolate five structurally similar phenolic compounds using a low-cost and very eco-friendly integrated process.

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Introduction

Lignocellulosic biomass is composed of three major components: cellulose, hemicellulose and lignin.¹ Lignin is an amorphous and highly heterogeneous crosslinked biopolymer, which accounts for 25%–35% of the organic matrix of wood.² The pulp and paper industries produce large quantities of partially depolymerised and re-condensed lignin. For every tonne of pulp, 1.25 tonnes of black liquor solids are produced as by-product,³ which are presently considered of low economic value,⁴ and mainly burned for energy generation.

Among the large number of lignin depolymerisation and conversion methods,^{1,5} the alkaline oxidative⁶ and the hydrothermal processing⁷ of lignin have proven to be interesting platforms for the production of monomeric aromatic compounds. Different studies show that considerable yields of vanillic acid, vanillin and syringaldehyde can be obtained

from softwoods,^{8–10} hardwoods^{11–13} and lignocellulosic residues¹⁴ through the alkaline oxidative lignin depolymerisation process.⁶ More recently, the hydrothermal processing of lignin has emerged as a greener and more cost-effective platform, again for the production of a vast number of aromatic compounds such as syringaldehyde,¹⁵ vanillin,^{15–17} as well as vanillic,^{16,17} gallic,^{16,17} caffeic,¹⁷ ferulic,¹⁷ gentisic,¹⁷ *p*-coumaric,¹⁷ *p*-hydroxybenzoic,¹⁷ protocatechuic,¹⁷ sinapic,¹⁷ and syringic¹⁷ acids. Although there are a number of studies^{6–16} showing profitable ways to valorise lignin by the production of various monomeric phenolic compounds, they face difficulties regarding the fractionation/isolation of pure compounds from the complex mixtures resulting from lignin depolymerisation.^{18,19} Therefore, there is an urgent need to develop more efficient purification technologies, which preferentially operate at milder conditions, to selectively isolate the phenolic compounds resulting from these processes. Due to the fact that lignin hydrothermal processes are carried out in aqueous media, the use of aqueous biphasic systems (ABS) emerges as a promising approach in this context. These aqueous systems are formed by two immiscible aqueous-rich phases and are formed by the combination of different solutes (*e.g.* polymers,

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salts and others), which separate into two coexisting aqueous phases at a specific concentration, although both phase formers are water-miscible. ABS are very flexible systems due to the countless types of chemical compounds that can be combined for their formation. Moreover, because they are mainly composed of water,²⁰ they present an high biocompatibility and an environmentally friendly nature, thus finding wide applications in concentration, separation and purification processes. Evidence of their successful applications are well-documented for a large range of biocompounds, namely, proteins,^{21–24} enzymes,^{25,26} cells^{27,28} and antibiotics.^{29–31} Polyethylene glycol (PEG) is a non-ionic polymer commonly used in the ABS design. This polymer is recognized for its biodegradability, low toxicity and cost-effectiveness. To create polymeric ABS, combinations of PEG and other polymers, such as maltodextrin^{32,33} and specifically dextran,^{21,34} are the most common options. However, these are expensive and display high viscosities and opacities, and are characterized by aqueous phases with a limited range of polarities. Moreover, in spite of the large number of existing polymers some of these potential pairs do not form ABS, at least in adequate concentrations to be in contact with target biomolecules, thus consequently limiting very much the number of systems available. One of the proposed strategies to overcome this drawback is the addition of small amounts of salts (up to 5 wt%), which act as electrolytes³⁵ to induce phase separation more easily. PEG and NaPA are one of the most promising combinations reported in literature as ABS components using electrolytes. In previous studies, PEG–NaPA based ABS were used in the partition of clavulanic acid³⁶ and chloranilic acid,³⁷ and principally in the extraction of more complex biomolecules such as the green fluorescent protein (GFP),³⁸ hemoglobin,²⁴ lysozyme,²⁴ cytochrome c,³⁷ proteases,³⁹ and amyloglucosidase.⁴⁰ The fractionation of these biomolecules was successfully achieved due to the easier manipulation of the aqueous phases by the presence of different electrolytes. It was found that these systems have low polymeric contents, thus presenting low viscosity, and allowing fast phase separation. Behind their great capacity to concentrate, separate and purify diverse biomolecules, another important aspect of ABS is the possibility of recycling and reusing the polymers, PEG and NaPA, respectively, from the top and bottom-phases, which is a step taken into consideration in the integrated process proposed in this study. Considering the distinct hydrophobic/hydrophilic characteristics of monomeric phenolic compounds, the use of ionic surfactants as electrolytes seems to be appropriate and will be investigated here. It is noteworthy that cationic and anionic surfactants are ionic compounds with interesting characteristics, such as their amphiphilic nature, which is promoted by the presence of a hydrophobic tail and a hydrophilic head, with the capacity to promote the formation of aggregates in aqueous media.^{41,42} Moreover, most anionic surfactants are non-toxic and the cationic surfactants studied in this study show low toxicity towards mammal cells and aquatic organisms.⁴² In this sense, the application of these compounds as electrolytes seems to be a promising approach in the purifi-

cation of phenolic compounds. In this study, the characterization of different polymer-based ABS comprising PEG 8000–NaPA 8000, using common tensioactive ILs (meaning with long alkyl side chains, and able to promote the formation of aggregates/micelles) and conventional ionic surfactants as electrolytes, will be performed. Moreover, these ABS will be applied in the purification of five phenolic compounds produced in alkaline oxidative and hydrothermal lignin depolymerisation processes, namely, caffeic acid, vanillic acid, gallic acid, vanillin and syringaldehyde. The phase diagrams of the different ABS will be detailed as well their ability to partition the five phenolic compounds between both polymeric phases. Moreover, the selectivity of this purification process will be characterized for the best systems, and the integrated process of purification and isolation of the five phenolic compounds will be proposed. The recycling of the main phase formers is also contemplated in this study.

Experimental

Materials

The polymer-based ABS (Fig. 1) are formed by two polymers, polyethylene glycol (PEG) and sodium polyacrylate (NaPA), both with an average molecular weight of 8000 g mol⁻¹, which were obtained from Sigma-Aldrich. The ionic surfactants used in this study as electrolytes are the anionic surfactants sodium dodecylbenzenesulfonate (SDBS) and sodium dodecyl sulphate (SDS); the cationic surfactants are tetradecyltrimethylammonium bromide (TTAB), hexadecyltrimethylammonium bromide (CTAB), hexadecylpyridinium chloride (CPC) and hexadecylpyridinium bromide (CPB) and the long alkyl chain imidazolium-based ionic liquids, namely, 1-dodecyl-3-methylimidazolium chloride ([C₁₂mim]Cl) and 1-tetradecyl-3-methylimidazolium chloride ([C₁₄mim]Cl). Pharmaceutical grade SDS was acquired from Alfa Aesar, and SDBS and the cationic surfactants were acquired from Sigma-Aldrich (purity ≥98 wt%). The ionic liquids were purchased from Iolitec, with a purity >97 wt%. Caffeic acid, vanillic acid, gallic acid, vanillin and syringaldehyde were acquired from Sigma-Aldrich (purity >98 wt%). Calcium chloride was also acquired from Sigma-Aldrich (purity >99 wt%).

Phase diagrams of the polymeric ABS using ionic surfactants as electrolytes

Binodal curves were gravimetrically determined within an uncertainty of ±10⁻⁴ g using the cloud point titration method⁴³ at (298 ± 1) K and atmospheric pressure. In brief, three stock aqueous solutions were prepared: 50 wt% of PEG 8000 + 1 wt% ionic surfactant, 18 wt% NaPA 8000 + 1 wt% ionic surfactant and water + 1 wt% ionic surfactant. A PEG 8000-containing aqueous solution was added dropwise to an aqueous solution of NaPA 8000 until a turbid phase was visually detected. Subsequently, dropwise addition of the electrolyte-containing solution was conducted until complete elimination of the turbid solution (monophasic region). This

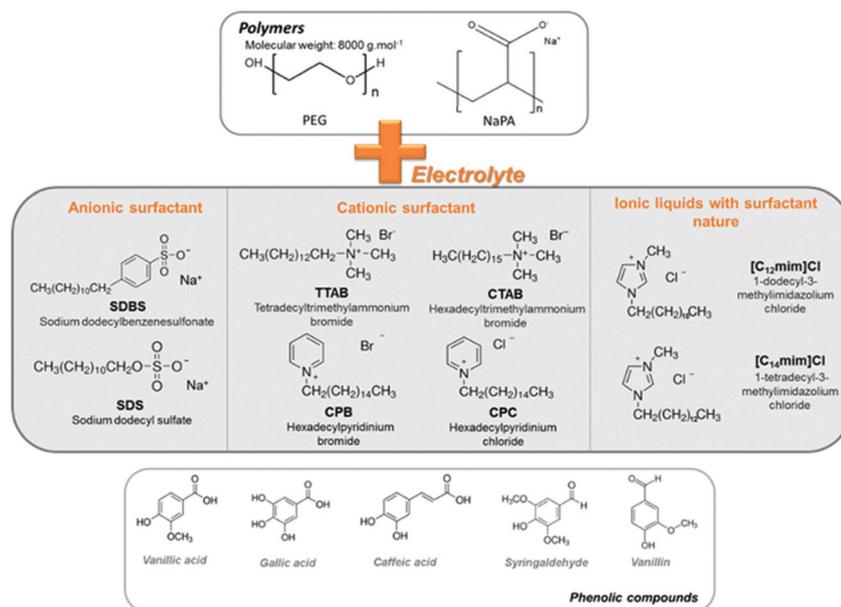


Fig. 1 Chemical structure of the polymers, electrolytes and phenolic compounds used in this work.

procedure was repeated several times to obtain the binodal curve, and the experimental procedure was performed under constant stirring. In addition, three distinct surfactant concentrations (used as electrolytes) were tested, namely, 1.0, 0.1 and 0.01 wt%. The experimental binodal curves were fitted using the Merchuk equation,⁴³ eqn (1):

$$[\text{NaPA } 8000] = A \exp[(B \times [\text{PEG } 8000]^{0.5}) - (C \times [\text{PEG } 8000]^3)] \quad (1)$$

where [PEG 8000] and [NaPA 8000] represent the weight percentages of PEG 8000 and NaPA 8000, respectively. *A*, *B* and *C* are constants obtained by the regression of the experimental data.

The pH (± 0.02) of the top and bottom phases was measured at (298 \pm 1) K using a Mettler Toledo pH meter.

The water content measurements of the top and bottom phases were performed by lyophilisation with the removal of water and the weight of the phases before and after lyophilisation was attained in order to quantify the water content in both phases.

Partition of surfactants and ionic liquids acting as electrolytes

The partition of the aromatic surfactants and ionic liquids used as electrolytes was determined. For this purpose, systems were prepared at the same extraction point adopted in the partition experiments and the phases carefully separated. The quantification of the electrolytes was conducted *via* several analytical techniques in both the bottom and top phases.

The aromatic surfactants and ionic liquids were quantified using UV spectroscopy on a Synergy HT spectrometer microplate reader at 261 nm for SDBS and 284 nm for [C₁₂mim]Cl and [C₁₄mim]Cl. The pyridinium cationic surfactant was

accessed at 256 nm with the Synergy HT spectrometer microplate reader. The trimethylammonium cationic surfactant partition was confirmed *via* ¹H NMR spectroscopy.

The terminal sulfate functional group of SDS was measured by ion-exchange chromatography, and the samples analysis was carried out on a Dionex 2000i/SP Ion Chromatograph with a conductivity detector. Anions were separated on an AS4A SC (25 cm \times 4 mm I.D) with an AG4A-SC ground column with a 4 mm I.D, and were detected using a suppressed conductivity detector on an Anion Micro-Membrane AMMS-I with the regenerant of 25 mN sulfuric acid. The injection volume was 10 μ L, and the flow rate was 2.0 mL min⁻¹. Chromatograms were recorded on a Chromjet integrator from Dionex.

The partition coefficient of the electrolyte was determined using eqn (2).

$$K_{\text{Elect}} = \frac{[\text{Elect}]_{\text{Top}}}{[\text{Elect}]_{\text{Bot}}} \quad (2)$$

where [Elect]_{Top} and [Elect]_{Bot} represent the electrolyte concentration in the top and bottom phases, respectively.

Partition of the phenolic compounds

The aqueous biphasic systems used in the partition studies of the phenolic compounds were prepared using graduated centrifuge tubes by weighing the appropriate amount of each phase component and phenolic-based aqueous solution. The extraction point adopted for the partition of the phenolic compounds was 20 wt% PEG 8000 + 5.0 wt% NaPA 8000 + 0.1 wt% of each surfactant + 74.9 wt% of the aqueous solution containing each phenolic compound, namely, caffeic acid (20.2 μ g mL⁻¹), vanillic acid (24.0 μ g mL⁻¹), gallic acid (44 μ g mL⁻¹), vanillin (21.1 μ g mL⁻¹) and syringaldehyde (20.9 μ g mL⁻¹).

Different phenolic compound concentrations were selected to assure maximum accuracy within the analytical technique employed. After the complete dissolution of all components in the mixture by the appropriate stirring of each mixture, they were left to equilibrate for 12 hours in an air oven at 298 ± 1 K, to achieve complete partitioning of each phenolic compound between the two aqueous phases. The phases were then carefully separated and the phenolic compounds were quantified in both the top and bottom phases by UV-Vis spectroscopy using a Synergy HT spectrometer microplate reader at the wavelengths of 252 nm (for vanillic acid), 263 nm (for gallic acid), 279 nm (for vanillin), 286 nm (for caffeic acid), and 306 nm (for syringaldehyde). Calibration curves for the determination of the concentration of each phenolic compound were established at the respective maximum absorption wavelengths. The quantification of each phenolic compound was performed in triplicate, where the final absorbance results are reported as the average of three independent assays with the respective standard deviations. Possible interferences of the polymers, surfactants and tensioactive ionic liquids investigated were taken into account through the use of blank controls (represented by the same mixture points but without the presence of the corresponding phenolic compound). Extraction parameters were determined to evaluate the partition performance of the different ABS, which are the partition coefficient of the phenolic compounds (K_{PC}), the recovery of the phenolic compounds in the top phase (R_{Top} %) and selectivity (S), as represented by eqn (3)–(5), respectively.

$$K_{PC} = \frac{[PC]_{Top}}{[PC]_{Bot}} \quad (3)$$

$$R_{Top} (\%) = \frac{100}{1 + \left(\frac{1}{K_{PC} \times R_v} \right)} \quad (4)$$

$$S = \frac{K_{PCi}}{K_{PCj}} \quad (5)$$

where $[PC]_{Top}$ and $[PC]_{Bot}$ represent the phenolic compound concentration in the top and bottom phases, respectively. The partition coefficient results are represented by specific abbreviations representative of each phenolic compound to help their analysis, namely, K_{CA} , K_{VA} , K_{GA} , K_{VN} and K_{SA} , for caffeic acid, vanillic acid, gallic acid, vanillin and syringaldehyde, respectively. R_v represents the volume ratio between the top and bottom phase volumes and K_{PCi} and K_{PCj} represent the partition coefficient of two different phenolic compounds, in which $K_{PCi} \geq K_{PCj}$ represent $S \geq 1$.

Optimization of phenolic compound fractionation

The optimization of the phenolic compound fractionation was carried out by studying electrolyte concentration using the most promising polymer-based ABS, in which the concentrations of 0.01, 0.1 and 1.0 wt% of SDS were tested for the extraction point of 20 wt% PEG 8000 + 5.0 wt% NaPA 8000. The preparation and separation conditions of the systems are

as described above. It should be highlighted that no gel formation was observed in these systems.

Isolation of the phenolic compounds

The isolation of the monomeric phenolic compounds from both the top and bottom phases was performed considering the ABS using SDS as the electrolyte (the most selective purification platform). The phenolic acids were isolated through dialysis. In this case, the top phase was dialyzed using a Spectra/Por membrane (cut-off: 1 kDa; diameter 24 mm) against a volume of 20 mL of ultra-pure water at room temperature. The dialysate was evaluated by UV-Vis spectroscopy to quantify the amount of phenolic acid present. When equilibrium was reached a new volume of water (20 mL) was added to recover the remaining phenolic compounds, whereas PEG 8000 remained in the retentate.

For the isolation of phenolic aldehydes, the bottom phase, which is rich in NaPA, was precipitated by the addition of $CaCl_2$, forming an insoluble polyacrylate/ Ca^{2+} complex. After the complex precipitation step, the bottom phase was centrifuged and the aqueous supernatant with the phenolic aldehydes was carefully separated and quantified *via* UV-Vis spectroscopy. 1H NMR was performed before and after the addition of $CaCl_2$ to confirm the selective precipitation of the polyacrylate/ Ca^{2+} complex.

Results and discussion

Polymer-based ABS formation and characterization

The phase diagrams of the ABS based on the polymers PEG 8000 and NaPA 8000, using ionic surfactants and tensioactive ionic liquids as electrolytes were measured. Table 1 depicts the properties (hydrophilic–lipophilic balance^{44–46} and octanol water partition coefficient⁴⁷) and ability of the various electrolytes with a tensioactive nature to form polymer-based ABS, by the manipulation of their surfactant nature and concentration (0.01, 0.1 and 1.0 wt%). It was observed that some cationic surfactants such as CPB cannot promote the formation of two phases. The anionic surfactants present a higher ability to induce the formation of two phases, taking into account the electrolyte concentration, because they can promote ABS formation for the three concentrations studied. In the case of CTAB, CPC, TTAB and ionic liquids, the formation of biphasic systems is conditioned by the electrolyte concentration, *i.e.*, only the lower concentrations of surfactants studied are able to form ABS. Actually, ionic surfactants can promote the formation of biphasic systems at concentrations as low as 0.01 wt%, which is below the concentration of electrolyte applied in the formation of the polymer-based ABS previously reported,^{35,37} *circa* 0.1 wt%. The phenomenon behind the formation of ABS in PEG–NaPA systems, using electrolytes as phase promoters, is well described for conventional inorganic salts³⁵ and for $[C_2mim]$ -based ionic liquids.³⁷ The main driving-force for the formation of these NaPA-based ABS is the compartmentalization phenomenon, in which the partition of

Table 1 List of the common surfactants and tensioactive ionic liquids used in this work, considering their names, acronyms, critical micelle concentration (CMC) in water, logarithm of octanol–water partition coefficient ($\log K_{ow}$) and hydrophilic–lipophilic balance (HLB), where applicable. The ability of the various electrolytes at different concentrations to form ABS is identified

Surfactant family	Surfactant name	CMC (mM)	CMC (wt%)	$\log K_{ow}$	HLB	Surfactant concentration (wt%)		
						0.01	0.1	1.0
Anionic	Sodium dodecyl sulfate (SDS)	8.2 ⁵⁰	0.24	4.42 ⁴⁷	40.0 ⁴⁵	✓	✓	✓
	Sodium dodecylbenzenesulfonate (SDBS)	1.6 ⁵²	0.06	6.56 ⁴⁷	36.7 ⁴⁴	✓	✓	✓
Cationic	Hexadecyltrimethylammonium bromide (CTAB)	9 ^{50,51}	0.33	2.69 ⁴⁷	10 ⁴⁴	✓	✓	×
	Tetradecyltrimethylammonium bromide (TTAB)	3.6 ⁴⁹	0.12	1.80 ⁴⁷	—	✓	✓	×
	Hexadecylpyridinium chloride (CPC)	1.0 ⁵⁴	0.03	3.47 ⁴⁷	26 ⁴⁶	✓	✓	×
	Hexadecylpyridinium bromide (CPB)	1.5 ⁵³	0.06	3.47 ⁴⁷	—	×	×	×
Ionic liquids	1-Dodecyl-3-methylimidazolium chloride ([C ₁₂ mim]Cl)	15 ⁴⁹	0.43	1.41 ⁴⁷	—	✓	✓	×
	1-Tetradecyl-3-methylimidazolium chloride ([C ₁₄ mim]Cl)	4 ⁴⁹	0.13	2.30 ⁴⁷	—	✓	✓	×

the ionic electrolytes between the two aqueous phases is driven to promote the electroneutrality of the phases, through the formation of an entropically favourable electrochemical potential.^{35,48} The experimental binodal curves were fitted using the empirical relationship described by eqn (1), the Merchuk equation. The regression parameters were estimated by the least-square regression method and their values and corresponding standard deviations (σ) are provided in Tables S1 to S3 in the ESI,[†] along with all the experimental points used.

The compartmentalization phenomenon is clearly observed in Fig. 2, in which the influence of the electrolyte type and the respective concentration is shown for the three classes of compounds investigated, cationic and anionic surfactants and tensioactive ionic liquids. Fig. 2 shows the results of ABS formation considering one example from each class of electrolyte. Due to the similar behaviour found for the remaining electrolytes, their results are depicted in Fig. S1 in the ESI.[†] It is found that the ability of each ionic surfactant to form an ABS increases with the concentration of electrolyte, and this is in agreement with previous results³⁵ in which the electroneutrality of the system (compartmentalization phenomenon) is dominant. The electrolyte concentration effect is more noticeable in anionic surfactants, because it was possible to form two aqueous phases in higher concentrations of electrolyte. At lower concentrations of electrolyte (0.1 wt%), the ionic surfactants showed a better performance for phase separation than the inorganic salts (NaCl and Na₂SO₄)^{35,37} and [C₂mim]-based ionic liquids.³⁷ In this sense, lower amounts of each polymer are required to form the ABS, which is advantageous from an economic point of view for the purification process.

The effect of ionic surfactant nature (at a concentration of 0.1 wt%) on the ABS formation was further investigated (Fig. 3). The results depicted in Fig. 3 do not allow the definition of a clear tendency in terms of the capacity of each electrolyte to participate in the ABS formation. This behaviour is probably explained by their greater hydrophobic nature, which is shown by the logarithmic function of their octanol–water partition coefficient (Table 1). Moreover, both TTAB and CPC

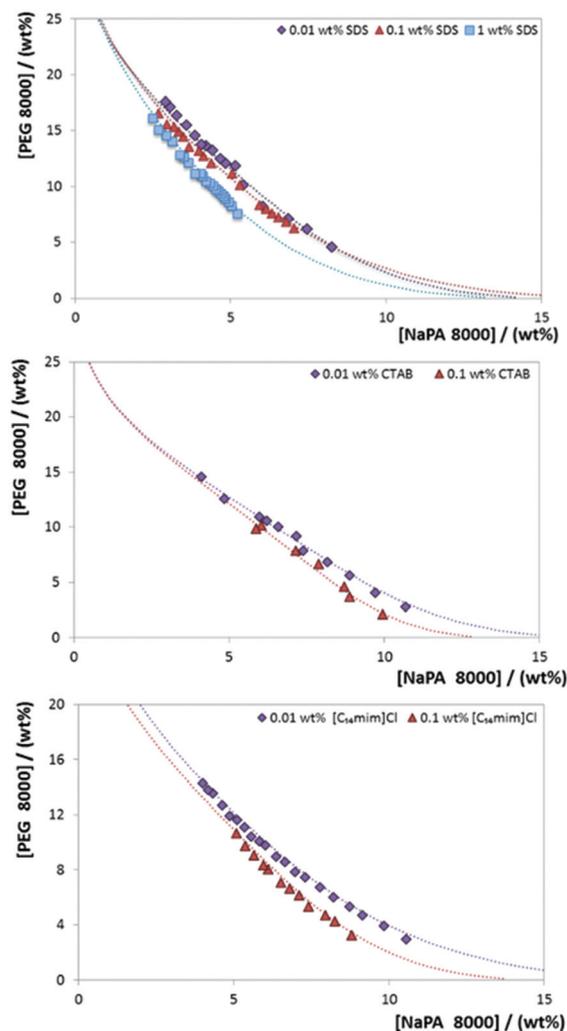


Fig. 2 Phase diagrams of the polymer-based ABS prepared considering each electrolyte class investigated, an example of the anionic and cationic surfactants and tensioactive ionic liquids, respectively, SDS, CTAB and [C₁₄mim]Cl at different concentrations. The binodal curves fitted using eqn (1) are represented by the dashed lines.

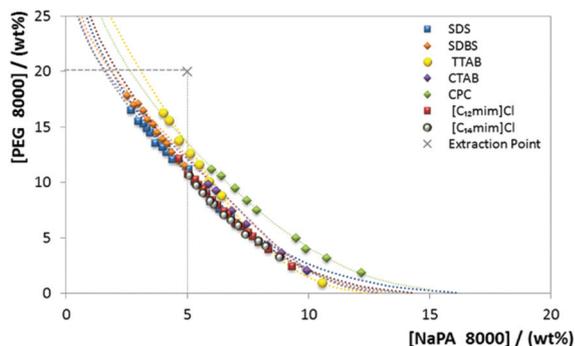


Fig. 3 Phase diagrams of the polymer-based ABS containing 0.1 wt% of each electrolyte: SDS, SDBS, TTAB, CTAB, CPC, [C₁₂mim]Cl and [C₁₄mim]Cl. The binodal curves fitted using eqn (1) are represented by the dashed lines as well as the extraction point selected to perform the extraction of the phenolic compounds.

are the surfactants that represent the systems with the lowest biphasic region (mainly in the region of higher amounts of PEG 8000), which is probably due to their cationic nature. Nevertheless, it is possible to conclude that the cationic electrolytes are the surfactants with the lowest capacity to induce ABS formation. If the NaPA 8000-rich region is analysed, the small electrolyte effects are suppressed because all the binodal curves converge, thus possessing similar biphasic regions. In summary, the effect of the surfactant nature does not seem to be very significant in the formation of polymer-based ABS, with the electrolyte concentration being a much more important parameter.

Regarding the proximity of all the binodal curves, the extraction point (Fig. 3) adopted in the fractionation of the phenolic compounds was selected considering the use of lower amounts of NaPA 8000 and a higher water content to enhance the ABS biocompatibility. The systems here studied were characterized in relation to the pH of both the top (PEG 8000) and bottom (NaPA 8000) phases (Table S4 in the ESI†) because this condition could have an important impact on the partition of phenolic compounds. The pH of both phases for the systems under study is close to neutrality ($7.06 \leq \text{pH} \leq 7.67$), independently of the electrolyte used, which is an important condition to guarantee the same chemical speciation of each phenolic compound during the partition studies.

The partition coefficient of the electrolytes (K_{Elect}) was measured (Table 2), indicating their preferential partition between the two aqueous phases. Different techniques were used to prove the electrolytes' partition, as indicated in Table 2 (¹H-NMR spectra are provided in Fig. S8 in the ESI†). These results show the preferential partition of anionic surfactants towards the top (PEG 8000-rich) phase, whereas the cationic surfactants and ionic liquids are concentrated in the bottom (NaPA 8000-rich) phase. Their partition is justified by the negative charge of NaPA 8000 at neutral pH, which promotes repulsive electrostatic interactions between the anionic surfactant and NaPA 8000, and favourable electrostatic interactions with

Table 2 Partition coefficient of the electrolytes (K_{Elect}), technique used to prove their partition and identification of the preferential phase in which they are concentrated

Surfactant	Instrumental method	K_{Elect}	Partition
SDS	Anionic chromatography	1.22 ± 0.02	PEG 8000-rich phase
SDBS	UV-Vis	1.92 ± 0.24	PEG 8000-rich phase
CTAB	¹ H NMR	Total	NaPA 8000-rich phase partition
TTAB	¹ H NMR	Total	NaPA 8000-rich phase partition
CPC	UV-Vis	0.14 ± 0.05	NaPA 8000-rich phase
[C ₁₂ mim]Cl	UV-Vis	0.29 ± 0.02	NaPA 8000-rich phase
[C ₁₄ mim]Cl	UV-Vis	0.32 ± 0.01	NaPA 8000-rich phase

the positive charges of the cationic surfactant and the ionic liquids' cation core.

Partition of phenolic compounds on polymer-based ABS

After the characterization of the polymer-based ABS, the partition of five phenolic compounds (caffeic acid, vanillic acid, gallic acid, vanillin and syringaldehyde), which are present in the complex matrices obtained from the lignin depolymerisation process, was studied. The partition measurements were carried out with systems composed of 20 wt% PEG 8000 + 5 wt% NaPA 8000 + 0.1 wt% of each electrolyte. Electrolyte concentrations below the critical micelle concentrations (CMC),^{49–54} as given in Table 1, were selected, thus allowing us to investigate their effect as electrolytes, and not as aggregates. The only exceptions were SDBS and CPC, which possess a CMC^{52,54} in water (at 25 °C), slightly lower than the concentration assumed. However, because SDBS is concentrated in the PEG 8000-rich phase, the CMC of the surfactant is increased,⁵⁵ allowing the maintenance of the same conditions in all the performed tests. Fig. 4A shows the results obtained for the top phase recovery (R_{Top} %) and Fig. 4B depicts the partition coefficients of the phenolic compounds (K_{PC}) considering the systems under study. The results suggest that the presence of ionic surfactants as electrolytes in the ABS promotes differences in the partition tendencies of the phenolic compounds. Actually, a large range of R_{Top} and K_{PC} was obtained, ranging from syringaldehyde ($R_{\text{Top SA}} = 18.6\% \pm 1.6\%$ and $K_{\text{SA}} = 0.055 \pm 0.005$) to vanillic acid ($R_{\text{Top VA}} = 95.6\% \pm 2.5\%$ and $K_{\text{VA}} = 3.4 \pm 1.3$; for more details see Tables S5 and S6 in ESI†).

Two distinct profiles were observed for the phenolic compounds partition: the non-dependent electrolyte partition and the dependent-electrolyte partition. The syringaldehyde and vanillin partition is non-dependent of the electrolyte, because by the manipulation of the electrolyte, even from different families (ammonium, imidazolium and pyridinium), the partition pattern is maintained, and for both, their partition is preferential towards the NaPA 8000-rich phase. Herein, the main driving-force acting is the hydrophobicity of the phases. In fact, the phenolic compounds (in their neutral form at

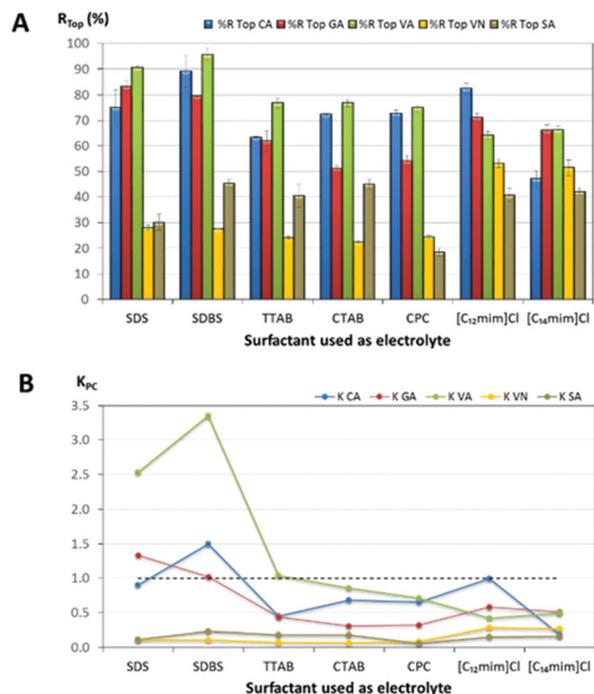


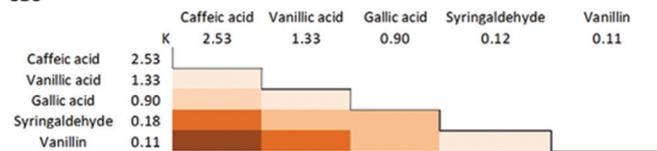
Fig. 4 (A) Top-phase recovery (R_{Top}) and (B) partition coefficients (K_{PC}) of the phenolic compounds obtained by the application of the ABS employing common surfactants and tensioactive ionic liquids as electrolytes. The lines represent K_{PC} and bars correspond to R_{Top} (%).

pH \sim 7) partition towards the less aqueous phase (with a lower amount of water, Table S7 in the ESI†). Actually, for the systems with lower water contents in the NaPA-rich phase, namely, those using SDS and CPC as electrolytes, a more pronounced effect in the preferential partition of syringaldehyde and vanillin to the hydrophobic phase (for SDS $K_{SA} = 0.12 \pm 0.01$; $K_{VN} = 0.11 \pm 0.01$ and for CPC $K_{SA} = 0.055 \pm 0.005$; $K_{VN} = 0.08 \pm 0.01$) was observed. This means that the partition of these two phenolic compounds is probably more related with hydrophobic interactions with the charged polymer NaPA 8000, than with electrostatic interactions.

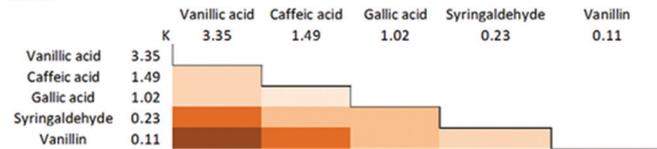
On the other hand, the partition of the phenolic acids, specifically caffeic, gallic and vanillic acids, represents an electrolyte dependent partition behaviour. The manipulation of the electrolyte is so pronounced that it strongly affects the partition of the phenolic compounds from one phase to the other. In general, we observed that the partition of the phenolic acids is dependent on the electrolyte nature. In this sense, the anionic surfactants boost the partition towards the upper phase, whereas the cationic surfactants and ionic liquids favour the bottom (NaPA 8000-rich) phase. Therefore, specific electrostatic interactions between the anionic form of the phenolic acids, which are predominant at the system pH (their speciation is depicted in Fig. S2–S6 in ESI†), and the electrolytes are suggested to be the main driving force present, thus electrolyte dependent partition behaviour is exhibited, which

Anionic surfactants

SDS

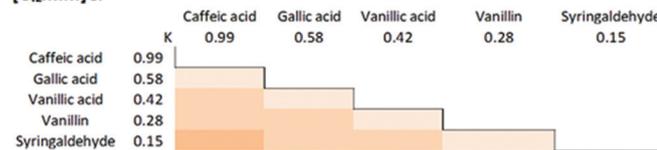


SDBS

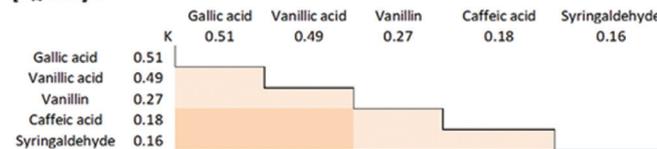


Ionic liquids

[C₁₂mim]Cl

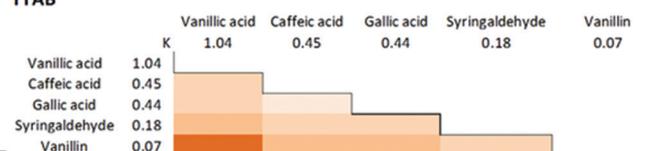


[C₁₄mim]Cl

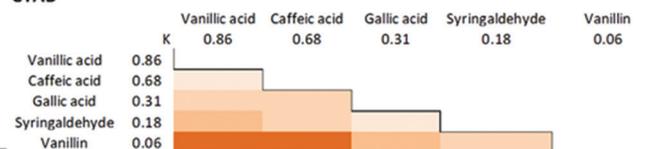


Cationic surfactants

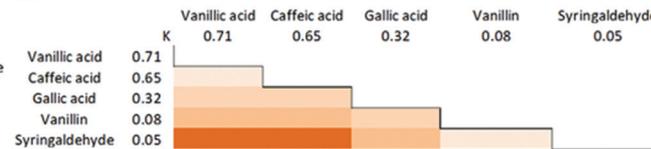
TTAB



CTAB



CPC



Selectivity values

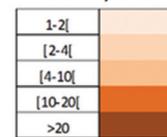


Fig. 5 Selectivity determined for the various phenolic compounds studied by the application of the distinct polymer-based ABS under study, employing common surfactants and tensioactive ionic liquids as electrolytes.

is very pronounced for gallic acid. If the anionic surfactants enhance the partition of gallic acid to the upper phase ($K_{GA} > 1$), both the ionic liquids and mainly cation surfactants favour its partition to the bottom (NaPA 8000-rich) phase ($K_{GA} < 1$). The same partition pattern was displayed for vanillic acid (towards the bottom phase) with the use of cationic surfactants; however, in this case, mainly for ionic liquids. It should be stressed that for TTAB similar partition between the two phases was observed ($K_{GA} = 1$). Regarding the caffeic acid partition, the use of anionic surfactants, particularly SDBS, favours the partition towards the upper phase. Differently, an equal partition between both phases was observed for SDS and $[C_{12}mim]Cl$ ($K_{CA} = 1$). The other cationic surfactants and ionic liquids studied concentrate caffeic acid in the bottom phase ($K_{CA} < 1$), because this partition is dependent on the electrolyte nature.

Selectivity of the phenolic compounds partition

In this study, the selectivity of each compound on the ABS studied was determined, as depicted in Fig. 5 (detailed selectivity data presented in Fig. S9 and S10 in the ESI†). From the analysis of the selectivity diagram (Fig. 5), it is evident that the ability of the ABS to separate each phenolic compound from the others comes from the manipulation of the electrolyte nature. Their capability to separate the phenolic compounds is as follows: ionic liquids < cationic surfactants < anionic surfactants, meaning that the anionic surfactants seem to be the most selective. The results demonstrate that vanillin can be easily isolated from the other phenolic compounds using the anionic surfactant SDS ($S_{VN/VA} = 23.75$; $S_{VN/GA} = 12.52$; $S_{VN/CA} = 8.47$; $S_{VN/SA} = 1.08$).

These results are greater than those previously obtained for the separation of gallic acid and vanillin using ABS based on PEG- Na_2SO_4 ⁵⁶ and PEG- Na_2SO_4 -IL⁵⁶ (with ionic liquids as adjuvants) combinations, in which no selectivity was achieved.

Optimization of phenolic compound fractionation

To fully optimize the fractionation process, a set of extractions of all the studied phenolic compounds was performed for three electrolyte concentrations: 0.01, 0.1 and 1 wt% of SDS. Fig. 6A and B show similar partition behaviour with the manipulation of the electrolyte concentration, because this parameter is less relevant to the fractionation of the phenolic compounds when compared with the electrolyte nature. Nevertheless, small changes were observed, namely, an increase in the K parameter with electrolyte concentration for gallic acid and vanillic acid (phenolic compounds with electrolyte dependent partition behaviour). Less significant changes were observed for caffeic acid, syringaldehyde and vanillin. Looking the effect of concentration on the selectivity data (Fig. 7), a slight increase in this parameter was observed for both vanillic and gallic acids towards syringaldehyde (parameters $S_{SA/VA}$ and $S_{SA/GA}$); because the system with the lower electrolyte content (0.01 wt%) was the most selective.

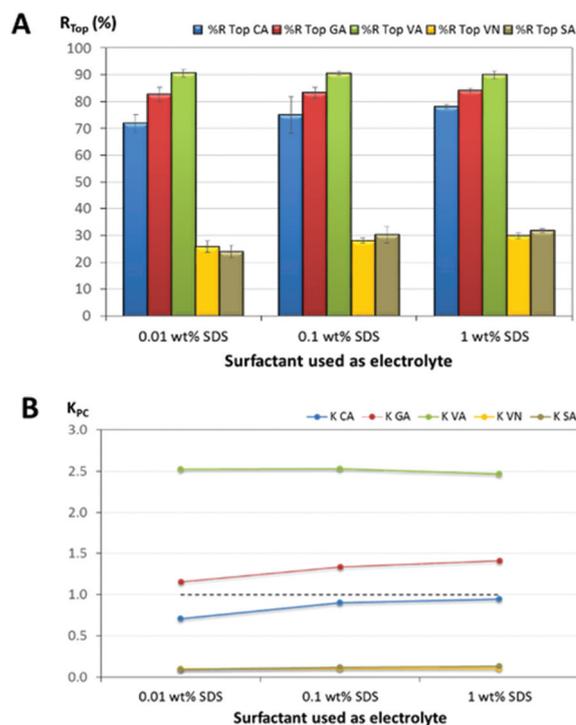


Fig. 6 (A) Top-phase recovery (R_{Top}) and (B) partition coefficients (K_{PC}) of the phenolic compounds obtained by the application of distinct concentrations of polymer-based ABS using SDS as the electrolyte. The lines represent K_{PC} and the bars correspond to R_{Top} (%).

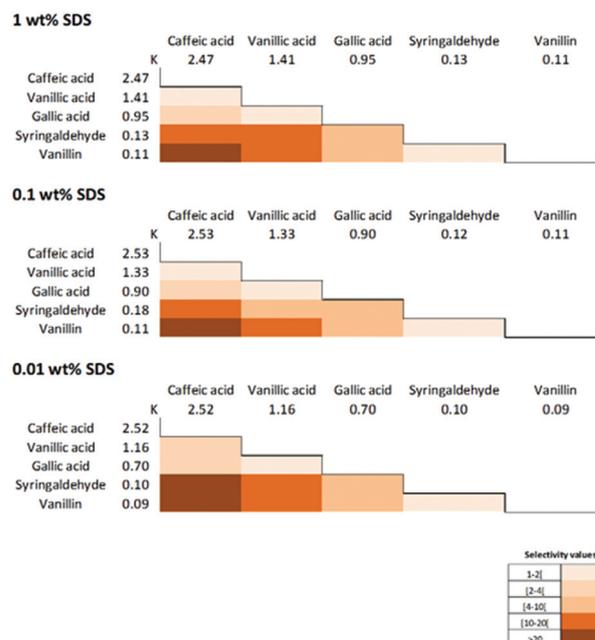


Fig. 7 Selectivity of the various phenolic compounds studied by the application of distinct concentrations of polymer-based ABS using SDS as the electrolyte.

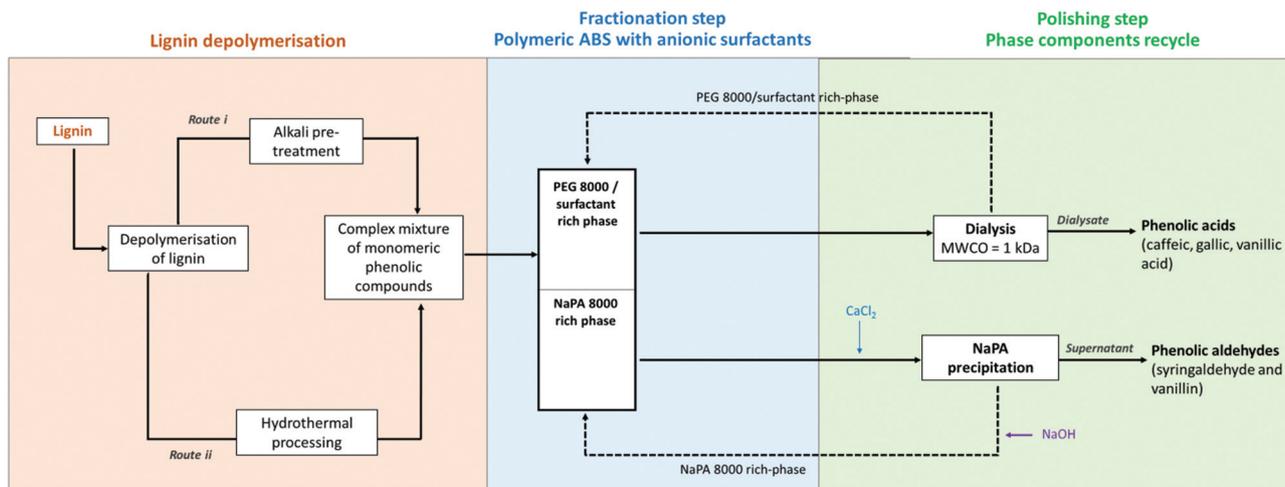


Fig. 8 Schematic of the integrated process of purification (using a polymer-based ABS with an anionic surfactant as the electrolyte), isolation and recovery of the phenolic compounds and recycling of the main phase formers.

Isolation of phenolic compounds and phase former recycling

To support the potential industrial application of this approach, an integrated process (Fig. 8) was designed regarding (i) the fractionation of various phenolic compounds produced through lignin depolymerisation by applying two distinct treatments, and (ii) the necessary strategies to isolate phenolic compounds from the phase formers, thus allowing (iii) their recycling.

Regarding steps (ii) and (iii), the isolation of vanillin and vanillic acid was performed for the polymer-based ABS with SDS as the electrolyte. Dialysis of the PEG 8000-rich phase was conducted with the use of a dialysis membrane with MWCO = 1 kDa, to retain the polymer inside the membrane and recover the vanillic acid in the dialysate. Around 93% of the initial mass of vanillic acid was recovered by two washing steps with water (63% and 31% of the phenolic acids were isolated in the first and second step of dialysis, respectively). For the isolation of the phenolic aldehydes, the precipitation of NaPA 8000 using calcium chloride was conducted. Precipitation is conducted by the formation of a water insoluble polyacrylate/Ca²⁺ complex,⁵⁷ which was checked using ¹H NMR (Fig. S11 at ESI†).

The precipitated polyacrylate/Ca²⁺ complex can be regenerated and re-introduced in the purification step by the addition of a strong base (*e.g.* NaOH). After the isolation and removal of the phenolic compounds from both phases, the phase former components could be directly reintroduced in the ABS formation after a simple pre-treatment: for the PEG-rich phase some water needs to be evaporated to allow the preparation of the ABS in the same conditions. The NaPA-rich phase is regenerated by the addition of NaOH, followed by successive washing steps until its neutralization. Excess water may be removed by evaporation if needed. With the regeneration and reuse of the phase formers, no significant loss of polymers or surfactants to the environment is expected.

In summary, this study demonstrates the capacity to purify and isolate five structurally similar phenolic compounds found after lignin depolymerisation by applying a low-cost (low polymer content) and eco-friendly (mild conditions) polymeric-based ABS using surfactants and ionic liquids as electrolytes.

Conclusions

Polymer-based ABS with ionic surfactants and ionic liquids as electrolytes are shown to present good selectivity for phenolic compounds, and thus have good potential for use as an efficient process for the fractionation of phenolic compounds from complex matrices obtained from the depolymerisation of lignin. The ability of electrolytes to promote ABS formation was assessed, with electrolyte concentration and nature the conditions with the major effects. The partition results show two distinct behaviours of the phenolic compounds, those that are non-dependent of the electrolyte partition and those that are dependent of the electrolyte partition. These profiles are justified by the surface charge of the phenolic compounds at a pH of around 7, and their higher affinity for water or their hydrophobic nature. Systems with high selectivity were obtained, which were then used to design an integrated process comprising the fractionation of selected phenolic compounds into different phases, their isolation and consequent recycling of the phase formers.

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