Electronic Supplementary Information

Enhanced Separation Performance of Aqueous Biphasic Systems formed by Carbohydrates and Tetralkylphosphonium- or Tetralkylammonium-based Ionic Liquids

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Materials

The carbohydrates used were D-(-)-fructose (>98.0 wt.% pure from Panreac), D-(+)-glucose (>99.5 wt.% pure from Scharlau), D-(+)-mannose (>99.0 wt.% pure from Aldrich), D-(+)-maltose (>98.0 wt.% pure from Sigma), sucrose (>99.5 wt.% pure from Himedia), maltitol (>95.0 wt.% pure from Acros Organics), xylitol (>99.0 wt.% pure from Sigma), D-(+)-xylose (≥ 99.0 wt% pure, from Carlo Erba) and D-sorbitol (>99.0 wt.% pure from Fluka). Gallic acid (>99.5 wt% pure), syringic acid (>98 wt% pure) and vanillic acid (>97 wt% pure) were acquired from Merck, Sigma–Aldrich and Alfa Aesar, respectively. Phosphonium-based ILs, namely tributylmethylphosphonium methylsulphate ($[P_{4441}][MeSO_4]$, > 99 wt % pure), tetrabutylphosphonium bromide ($[P_{4444}]Br$, > 96 wt % pure), and tetrabutylphosphonium chloride ($[P_{4444}]Cl$, > 96% wt % pure), were kindly provided by Cytec Industries, Inc. The tetrabutylphosphonium bromide ($[N_{4444}]Br$, > 98 wt % pure) was acquired from Fluka. The ILs tri(n-butyl)[2-ethoxy-2-oxoethyl]phosphonium bromide ($[P_{444}(OC_2)]Br$) and tri(n-butyl)[2-ethoxy-2-oxoethyl]ammonium bromide ($[N_{444}(OC_2)]Br$) were synthesized and characterized according to protocols described in the literature.[1] Tetrabutylphosphonium butanoate ($[P_{4444}][But]$), tetrabutylphosphonium hexanoate ($[P_{4444}][Hex]$) and tetrabutylphosphonium octanoate ($[P_{4444}][Oct]$) were synthetized according to the literature.[2] Briefly, an aqueous solution of each carboxylic acid was added drop-wise to $[P_{4444}][OH]$ solution with a slight equimolar excess. The solution was stirred at room temperature during 12 h; then, the reaction mixture obtained was evaporated at 60 °C under vacuum. A mixture of acetonitrile and methanol (1:1) was added to the viscous liquid previously obtained, stirred vigorously at room temperature until the precipitation of the unreacted buffer, which was posteriorly removed by filtration. The solvent (acetonitrile + methanol) was evaporated and the ILs were dried under vacuum for 4 days at room temperature (40 °C).[2]

The materials used in these ILs synthesis were 2-bromoacetic acid ethyl ester, ethyl acetate, tri(*n*-butyl)phosphine, tri(*n*-butyl)amine, and tetrabutylphosphonium hydroxide (> 40 wt%) purchased from Sigma-Aldrich. Butyric acid (> 99.9 wt%, from Riedel de Haen), hexanoic acid (> 99.0 wt%, from Aldrich) and octanoic acid (> 98.0 wt%, from Sigma-Aldrich) were used. The organic salt potassium citrate tribasic monohydrate ($C_6H_5K_3O_7 \cdot H_2O$ ≥ 99 wt% pure) was acquired from Sigma–Aldrich.

The ABS studied at higher pH values were established using aqueous solutions of sodium hydroxide (NaOH) (≥ 99.5 wt % pure), purchased from José Manuel Gomes dos Santos. The water employed was double distilled, passed across a reverse osmosis system and further treated with a Milli-Q plus 185 water purification apparatus.

The SPE cartridge used in the solid-phase extractions to recover phenolic acids was Oasis HLB (200 mg) from Waters. Methanol used was of HPLC grade, acquired from Sigma-Aldrich.

Experimental Procedure

Two methods were used to evaluate the possibility of creating ABS by combining ILs and carbohydrates in aqueous media: cloud point titration and turbidimetric titration at 15, 25, 35 and 45 (±1) °C, and at atmospheric pressure. The cloud point titration method was used to determine the ternary phase diagrams with the ILs [P_{4441}][$MeSO_4$], [P_{444}(OC_2)]Br and [P_{4444}]Br combined with D-(-)-fructose. The experimental procedure adopted has been validated in previous works.[3,4] Aqueous solutions of D-(-)-fructose at ≈ 75 wt% and aqueous solutions of the different ILs at ≈ 90 wt% were gravimetrically prepared and used for the determination of the binodal curves. The dropwise addition of the aqueous IL solution to each carbohydrate aqueous solution was carried out until the detection of a cloudy (biphasic) solution, followed by the dropwise addition of water until the formation of a clear and limpid solution. Dropwise additions were carried out under constant stirring and atmospheric pressure. The ternary systems compositions were determined by weight quantification of all components ($\pm 10^{-4}$ g), using an analytical balance, Mettler Toledo Excellence XS205 DualRange. The turbidimetric titration method was used to determine the ternary phase diagrams with the IL [P_{4444}]Br combined with sucrose, maltitol, and xylitol at 25 °C, and for [P_{444}(OC_2)]Br with D-(-)-fructose at 25 °C. This method was also used for the determination of the binodal cruves of the ABS formed by [P_{4444}]Br + D-(-)-fructose at 15, 35 and 45 °C. Various mixtures of carbohydrate, IL and water were gravimetrically prepared within the biphasic region, in glass tubes up to 1 g and thoroughly mixed. Water was added until a clear solution was identified. With the knowledge of the initial mixture composition and of the added water amount, the system composition was determined and a new point on the binodal curve identified. These mixture compositions were gravimetrically determined ($\pm 10^{-4}$ g). In the systems composed of [P_{4444}][Oct], [P_{4444}][Hex] and [P_{4444}][But] it was added a water soluble dye to water to better distinguish the two phases.

The experimental binodal curves were fitted as described elsewhere.[5] Tie-lines (TLs), which correspond to the composition of each phase for a given mixture composition, were determined by a gravimetric method originally proposed by Merchuk *et al.*[5] For the determination of each TL, a ternary mixture at the biphasic region was prepared by weight, vigorously stirred, and further submitted to centrifugation for 30 min at 25 (± 1) °C. Each phase was carefully separated and weighted, and each TL determined by the application of the lever-arm rule.

Aqueous solutions of each studied antioxidant were prepared (0.006 mol.dm^3 for gallic acid, and 0.030 mol.dm^3 for vanillic and syringic acids) and used as the aqueous solution required to form the biphasic systems in the separation studies. Two different mixture compositions were used: 35 wt% of carbohydrate + 40 wt% of [P_{4444}]Br, and 50 wt% of D-(-)-fructose + 25 wt% IL (IL = [P_{4444}]Br, [P_{4441}][$MeSO_4$], [P_{444}(OC_2)]Br, [N_{4444})]Br, and [N_{444}(OC_2)]Br]). For comparison purposes, the systems formed by 50 wt% of D-(-)-sorbitol or sucrose + 25 wt% [C_4mim][CF_3SO_3], and 25 wt% of [P_{4444}]Br + 38 wt% of $C_6H_5K_3O_7$, were also investigated. Each mixture was vigorously stirred and centrifuged for 30 min at 15, 25 and 45 °C. After a careful separation of both phases, the quantification of the antioxidants in each phase was carried by UV-spectroscopy, using a UV-spectrophotometry (SYNERGY|HT microplate reader, BioTek), at a wavelength of 272 nm for gallic acid, 280 nm for vanillic acid and 272 nm for syringic acid. At least three individual experiments were performed in order to determine the average in the partition coefficients and extraction efficiencies, as well as the respective standard deviations. Blank control samples without adding antioxidants were always used. The extraction studies at different pH values were attained using aqueous solutions of NaOH at different concentrations to prepare the IL solutions used in the partitioning studies. The pH of each aqueous phase was determined at 25 (± 1) °C using an HI 9321 Microprocessor pH meter (HANNA instruments).

The recovery of the studied phenolic acids from the IL-rich phase was performed by solid-phase extraction, with Oasis HLB cartridges previously washed with methanol (1 mL). Each IL-rich phase containing phenolic acids was passed through the column (SPE1), in which phenolic acids are adsorbed, followed by 1 mL of acidic water (pH ca. 2) (SPE2) and 1 mL of methanol (SPE3). All these fractions were collected since they contain the IL present in the original IL-rich phase. The phenolic fraction was finally desorbed by the addition of 1 mL of methanol (SPE4). All fractions were collected and the phenolic acids quantified by UV-Vis spectroscopy using calibration curves previously established. The IL recovery and absence in the phenolic acids fraction was confirmed through ^{1}H NMR spectroscopy (Bruker AMX 300) operating at 300 MHz, and the respective losses determined gravimetrically ($\pm 10^{-4}$ g).

After the phenolic acids separation through SPE, the fractions containing IL were submitted to evaporation under vacuum at room temperature, up to constant weight since only the IL and carbohydrate are the non-volatile species. The recovered IL + carbohydrate mixture was then reused in the creation of novel ternary systems, and their extraction performance for gallic acid accessed by HPLC-DAD (Shimadzu, model PROMINENCE). HPLC analyses were performed with an analytical C18 reversed-phase column (250 × 4.60 mm), kinetex 5 µm C18 100 A, from Phenomenex. The mobile phase used was a gradient system of 0.1% TFA-ultra-pure water with of TFA (phase A) and 0.1% TFA-acetonitrile (phase B), previously degassed by ultrasonication. The separation was conducted using the following gradient mode, 0 min 25% of B, 42 min 42% of B, 45 min of B, and then returned to initial conditions during 20 min to ensure the column stabilization. The flow rate used was 0.8 $\mathrm{mL{\cdot}min^{1}}$ and using an injection volume of 30 µL. DAD was set at 272 nm. Each sample was analysed at least in duplicate. The column oven and the autosampler operated at a controlled temperature of 25 °C. Under these conditions, gallic acid displayed a retention time of 3.4 min.

Results

Table S1. Non-forming ABS composed of carbohydrates (CHs) and ionic liquids (ILs).

CHs	IL
D-(+)-maltose	$[P_{4444}]Br$
D-(+)-glucose	
D-(+)-xylose	
Sucrose	$[P_{4444}]Cl$
	$[P_{(4441)1}][MeSO_4]$
D-(+)-glucose	$[P_{444}(OC_2)]Br$
D-(+)-mannose	
D-(+)-maltose	

Table S2. Octanol-water partition coefficients (logK_{ow}) of the studied carbohydrates (CHs).[6]

CHs	logK_{ow}[6]
D-(-)-fructose	-3.27
D-(+)-glucose	-2.93
D-(+)-maltose	-4.70
sucrose	-4.53
maltitol	-5.50
xylitol	-3.10
D-sorbitol	-3.73

Table S3. Dissociation constants of the studied phenolic acids.[6]

Phenolic acid	pKa_1 (-COOH)	pKa_2 ($-NH_2$)	pKa_3 (-R)
VA	4.20	10.20	-
GA	4.40	9.40	11.00
SA	4.00	9.60	-

Table S4. Experimental weight fraction data for the ABS formed by [P_{4444}]Br (w_1) + D-(-)-CH (w_2) + H_2O at 25 °C and atmospheric pressure.[a]

D-(-)-fructose						Sucrose		Maltitol		Xylitol		D-sorbitol	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
75.65	11.18	36.52	29.29	24.44	36.63	57.90	16.94	44.66	26.96	57.06	21.39	48.19	13.28
73.62	12.09	35.82	29.66	24.10	36.74	56.29	18.09	49.94	23.90	54.36	22.61	44.69	17.35
70.90	13.39	35.15	30.01	23.79	36.84	51.04	18.99	42.38	28.22	42.95	26.65	43.09	17.97
67.42	14.66	34.25	30.74	23.26	36.78	47.78	20.73	37.72	29.69	42.63	27.18	37.71	24.76
64.34	15.63	32.77	31.41	22.96	37.00	45.01	21.37	37.59	29.80	36.45	30.92	34.74	27.40
62.54	16.88	32.03	31.93	22.86	36.99	42.29	23.22	32.69	35.17	33.30	34.49	30.74	33.26
59.88	17.67	30.80	32.59	22.55	37.13	40.19	24.52	28.96	38.78	25.12	40.48	27.95	37.48
57.78	18.06	30.28	32.73	21.87	38.12	38.99	25.0			24.85	40.71	22.15	47.87
55.52	19.02	29.39	33.60	21.63	38.24	38.39	25.04					20.50	52.82
53.88	20.00	28.70	33.85	21.240	38.63	37.83	25.54						
52.09	20.84	28.19	34.12	20.99	38.75	37.72	26.22						
47.42	22.71	27.39	34.74	20.73	38.99	29.89	30.88						
46.17	23.49	26.97	35.02	20.30	39.30								
44.87	24.32	26.41	35.16	20.08	39.42								
43.56	25.21	25.96	35.47										
42.51	25.87	25.61	35.75										
41.41	26.53	25.08	36.26										
40.60	27.04	24.72	36.46										
39.47	27.26	24.44	36.63										
38.54	27.83	24.101	36.74										
37.81	28.19	23.79	36.84										

[a] The uncertainty in the weight fraction percentage (w) is 0.01, the uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

Table S5. Experimental weight fraction data for the ABS formed by IL (w_1) + D-(-)-fructose (w_2) + H_2O at 25 °C and atmospheric pressure.[a]

$[P_{444}(OC_2)]Br$				$[P_{4441}][MeSO_4]$	
w_1	w_2	w_1	w_2	w_1	w_2
67.25	23.59	19.40	44.14	83.97	4.16
66.48	24.13	18.70	45.08	74.93	11.00
59.63	25.86	18.10	45.21	74.59	11.86
53.40	26.98	17.73	45.59	61.66	20.58
53.33	27.81	17.39	45.86	61.59	20.79
46.79	29.74	16.36	46.53	56.19	23.99
46.23	31.81	16.30	46.81	51.99	26.95
41.33	32.92	14.99	47.92	45.85	31.27
35.57	35.91	14.32	48.40	40.77	35.34
35.49	36.45	13.69	49.40	37.19	37.83
32.50	37.45	13.31	49.47	28.92	41.74
32.13	37.72	12.80	49.69		
29.75	39.14	11.91	50.75		
29.10	39.19	10.35	52.81		
28.34	39.32	10.32	53.41		
26.78	40.34	9.47	54.66		
26.01	40.62	8.95	54.98		
24.99	40.78				
24.49	41.48				
23.42	41.54				
22.59	42.40				
21.53	42.62				
20.90	43.25				
20.46	43.27				

[a] The uncertainty in the weight fraction percentage (w) is 0.01, the uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

Table S6. Experimental weight fraction data for the ABS formed by IL (w_1) + D-(-)-fructose (w_2) + H_2O at 25 °C and atmospheric pressure.[a]

[N$_{4444}$]Br		[N$_{444}$(OC$_2$)]Br	
w_1	w_2	w_1	w_2
58.02	22.92	56.62	28.58
44.13	31.37	52.81	30.78
39.43	34.63	31.22	43.26
34.05	38.69	27.85	45.56
30.08	41.57	24.17	49.27
27.07	43.79	19.30	54.61
23.95	46.26		

[a] The uncertainty in the weight fraction percentage (w) is 0.01, the uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

Table S7. Experimental weight fraction data for the ABS formed by IL (w_1) + D-(-)-fructose (w_2) + H_2O at 25 °C and atmospheric pressure.[a]

[P$_{4444}$][Oct]		[P$_{4444}$][Hex]		[P$_{4444}$][But]	
w_1	w_2	w_1	w_1	w_1	w_1
43.10	38.21	52.91	31.67	46.52	38.19
28.77	42.83	41.07	38.17	28.89	46.80
16.812	50.77	35.15	40.24	25.88	47.66
19.93	49.59	28.06	42.73	21.73	49.92
18.47	50.02	26.82	43.42		
16.81	50.77	20.72	46.86		
		18.71	48.02		

[a] The uncertainty in the weight fraction percentage (w) is 0.01, the uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

Table S8. Experimental weight fraction data for the ABS formed by IL (w_1) + D-(-)-fructose (w_2) + H_2O at different temperatures (15, 35, 45 °C), and atmospheric pressure.[a]

15 °C		35 °C		45 °C	
w_1	w_2	w_1	w_2	w_1	w_2
47.67	22.19	39.20	29.03	47.60	23.41
44.95	23.68	46.80	23.02	43.90	25.24
39.57	26.66	43.57	25.05	41.64	26.57
37.08	28.09	41.31	26.36	36.47	30.76
34.50	29.62	36.04	30.39		

[a] The uncertainty in the weight fraction percentage (w) is 0.01, the uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

Table S9. *A*, *B* and *C* parameters of the equation proposed by Merchuk et *al.*[6] and respective correlation coefficients, R^2, for the ABS formed by IL + CH + H_2O at 25 °C and atmospheric pressure.[a]

ABS					
IL	CHs	$A \pm \sigma$	$B \pm \sigma$	$10^5\,(C \pm \sigma)$	R^2
$[P_{4444}]Br$	sucrose	392 ± 53	-0.47 ± 0.06	0.19 ± 0.27	0.950
	D-sorbitol	266 ± 35	-0.35 ± 0.02	0.47 ± 0.01	0.999
	maltitol	121 ± 29	-0.04 ± 0.00	0.00 ± 0.00	0.970
	xylitol	141 ± 18	-0.04 ± 0.01	0.00 ± 0.00	0.990
	D-(-)-fructose	124 ± 6	-0.16 ± 0.01	1.41 ± 0.09	0.999
$[P_{4441}][MeSO_4]$		107 ± 34	-0.11 ± 0.08	0.93 ± 0.41	0.999
$[P_{444}(OC_2)]Br$		230 ± 40	-0.25 ± 0.04	0.95 ± 0.75	0.999
$[P_{4444}][Oct]$		629 ± 278	-0.07 ± 0.01	0.00 ± 0.00	0.989
$[P_{4444}][Hex]$		359 ± 174	-0.06 ± 0.01	0.00 ± 0.00	0.966
$[P_{4444}][But]$		673 ± 411	-0.07 +0.01	0.00 ± 0.00	0.995
$[N_{4444}]Br$		$137 \pm 8E^{-6}$	-0.17 ± 0.01	0.57 ± 0.05	0.950
$[N_{444}(OC_2)]Br$		$490 \pm 2E^{-6}$	-0.39 ± 0.01	0.21 ± 0.05	0.950

[a] The uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

Table S10. Weight fraction compositions for the IL + CH + H_2O systems at 25 °C, and respective values of tie-line length (TLL). Initial mixture compositions are represented as $[CH]_M$ and $[IL]_M$, whereas $[CH]_{CH}$ and $[IL]_{CH}$ are the composition of IL and carbohydrate at the IL-rich phase, respectively, and vice-versa.[a]

IL	CHs	Weight fraction composition/ wt %								
		$[IL]_{IL}$	$[CH]_{IL}$	pH	$[IL]_M$	$[CH]_M$	$[IL]_{CH}$	$[CH]_{CH}$	pH	TLL
$[P_{4444}]Br$	Sucrose	58.47	16.57	1.52	39.83	35.13	20.02	54.88	1.57	54.27
	D-sorbitol	66.60	15.24	1.42	39.92	34.54	7.22	58.21	1.35	73.32
	maltitol	57.73	20.54	1.46	36.88	34.87	24.2	43.60	1.34	40.71
	Xylitol	58.03	20.60	1.29	40.10	34.85	17.47	52.06	1.25	51.96
	D-(-)-fructose	89.09	3.93	2.20	24.88	49.6	0.51	66.72	1.95	109.28
$[P_{4441}][MeSO_4]$		84.65	4.83	1.70	25.02	49.82	2.92	66.49	1.62	102.38
$[P_{444}(OC_2)]Br$		79.09	17.01	4.01	25.12	50.03	2.69	63.75	3.92	89.56
$[N_{4444}]Br$		77.12	10.67	2.15	24.95	49.99	8.99	62.02	2.30	85.30
$[N_{444}(OC_2)]Br$		42.47	35.76	4.67	25.03	50.11	17.92	55.98	3.95	31.81
$[C_4mim][CF_3SO_3]$	sucrose	84.28	2.14	6.61	25.13	49.87	0.05	70.10	6.65	108.22
	D-sorbitol	96.08	0.16	6.68	24.95	49.80	0.00	66.51	6.67	115.64

[a] The uncertainty in the weight fraction percentage composition (w) is 0.01, the uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

Table S11. Extraction efficiencies (*EE/%*) and partition coefficients (*K*) of phenolic acids to the IL-rich phase at 25 °C. [a]

		Phenolic acids		
ABS		VA	GA	SA
$[P_{4444}]Br$ + sucrose	*EE/%*	94.2 ± 0.2	99.3 ± 0.0	96.5 ± 0.1
	K	14.0 ± 0.6	95.3 ± 1.2	34.6 ± 0.5
$[P_{4444}]Br$ + D-sorbitol	*EE/%*	95.9 ± 0.4	99.1 ± 0.0	96.8 ± 0.7
	K	16.4 ±1.0	92.7 ± 2.8	24.5 ± 2.9
$[P_{4444}]Br$ + xylitol	*EE/%*	94.2 ± 0.1	96.6 ± 0.3	91.6 ± 2.4
	K	14.2 ± 0.1	15.1 ± 1.4	9.1 ± 1.8
$[P_{4444}]Br$ + maltitol	*EE/%*	96.1 ± 0.6	98.3 ± 0.0	96.5 ± 0.4
	K	13.8 ± 0.2	29.3 ± 0.0	13.4 ± 2.0
$[P_{4444}]Br$ + D-(-)-fructose	*EE/%*	95.6 ± 0.4	98.1 ± 0.6	93.7 ± 0.1
	K	58.9 ± 0.1	144.7 ± 42.2	40.6 ± 0.4
$[P_{4441}][MeSO_4]$ + D-(-)-fructose	*EE/%*	95.9 ± 0.0	94.5 ± 1.6	93.8 ± 1.5
	K	45.1 ± 0.2	41.5 ± 8.9	37.4 ± 4.1
$[P_{444}(OC_2)]Br$ + D-(-)-fructose	*EE/%*	72.0 ± 0.4	72.8 ± 2.2	65.1 ± 3.0
	K	6.4 ± 0.1	5.4 ± 0.4	3.6 ± 0.5
$[N_{4444}]Br$ + D-(-)-fructose	*EE/%*	90.4 ± 0.5	86.7 ± 1.0	87.7 ± 1.0
	K	30.7 ± 1.8	21.4 ± 1.9	23.4 ± 1.0
$[N_{444}(OC_2)]Br$ + D-(-)-frutose	*EE/%*	81.5 ± 3.3	70.8 ± 3.9	82.7 ± 1.7
	K	11.5 ± 2.4	6.1 ± 1.1	11.9 ± 1.4
$[C_4mim][CF_3SO_3]$ + Sucrose	*EE/%*	6.7 ± 1.1	6.7 ± 0.7	12.2 ± 0.2
	K	0.2 ± 0.0	0.2 ± 0.0	0.4 ± 0.0
$[C_4mim][CF_3SO_3]$ + D-sorbitol	*EE/%*	29.6 ± 4.1	8.5 ± 0.7	33.4 ± 1.6
	K	1.1 ± 0.2	0.2 ± 0.0	1.3 ± 0.0
$[P_{4444}]Br + C\ H\ K_3O$	*EE/%*	99.0 ± 0.1	86.6 ± 0.3	98.5 ± 0.1
	K	267.6 ± 8.8	17.3 ± 0.4	175.7 ± 8.9

[a] The uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

Table S12. Extraction efficiencies (*EE/*%) and partition coefficient (*K*) of phenolic acids to the IL-rich phase in [P_{4444}]Br-based ABS at 25 °C at different pH values. [a]

		Phenolic acids		
		VA	GA	SA
D-(-)-fructose pH 5	*EE/%*	86.6 ± 0.5	85.9 ± 2.2	78.9 ± 3.7
	K	16.1 ± 0.8	18.8 ± 4.1	15.5 ± 0.3
D-(-)-fructose pH 6	*EE/%*	45.8 ± 6.0	79.3 ± 0.3	74.5 ± 0.7
	K	2.7 ± 1.0	9.5 ± 0.2	7.3 ± 0.3
D-sorbitol pH 5	*EE/%*	97.7 ± 0.2	94.5 ± 0.2	86.0 ± 2.0
	K	31.1 ± 3.2	13.0 ± 0.4	7.9 ± 0.5
D-sorbitol pH 6	*EE/%*	85.0 ± 3.1	76.6 ± 3.6	54.3 ± 1.3
	K	7.8 ± 0.1	4.5 ± 0.9	1.5 ± 0.1

[a] The uncertainty in the pH is 0.02, the uncertainty in the temperature is 1 °C, and the uncertainty in pressure is 0.1 atm.

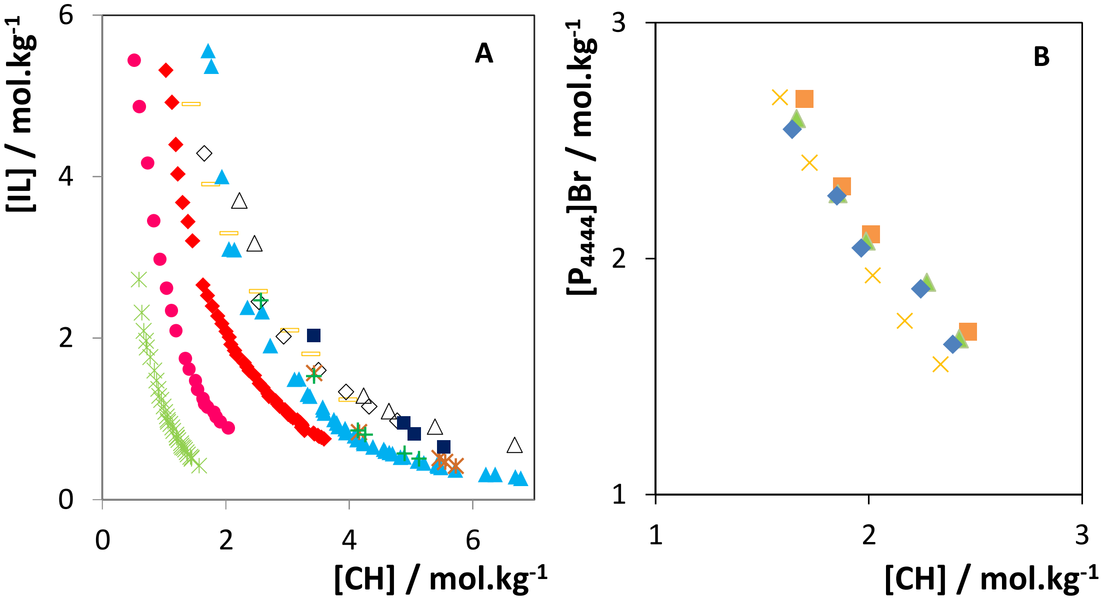

Figure S1. A) Ternary phase diagrams of ABS formed by ILs and D-(-)-fructose at 25 °C and atmospheric pressure (in molality units): $[C_2C_1py][C_4F_9SO_3]$ (×)[8]; $[C_4mim][CF_3SO_3]$ (●)[9]; $[P_{4444}]Br$ (♦); $[P_{444}(OC_2)]Br$ (▲); $[P_{4444}][Oct]$ (✶); $[P_{4444}][Hex]$ (+); $[P_{4444}][But]$ (■); $[P_{4441}][MeSO_4]$ (–); $[N_{4444}]Br$ (◇); $[N_{444}(OC_2)]Br$ (△). **B)** Ternary phase diagrams for ABS formed by $[P_{4444}]Br$ and D-(-)-fructose at different temperatures and atmospheric pressure (in molality units): 15°C (×), 25 °C (♦), 35 °C (▲) and 45 °C (■).

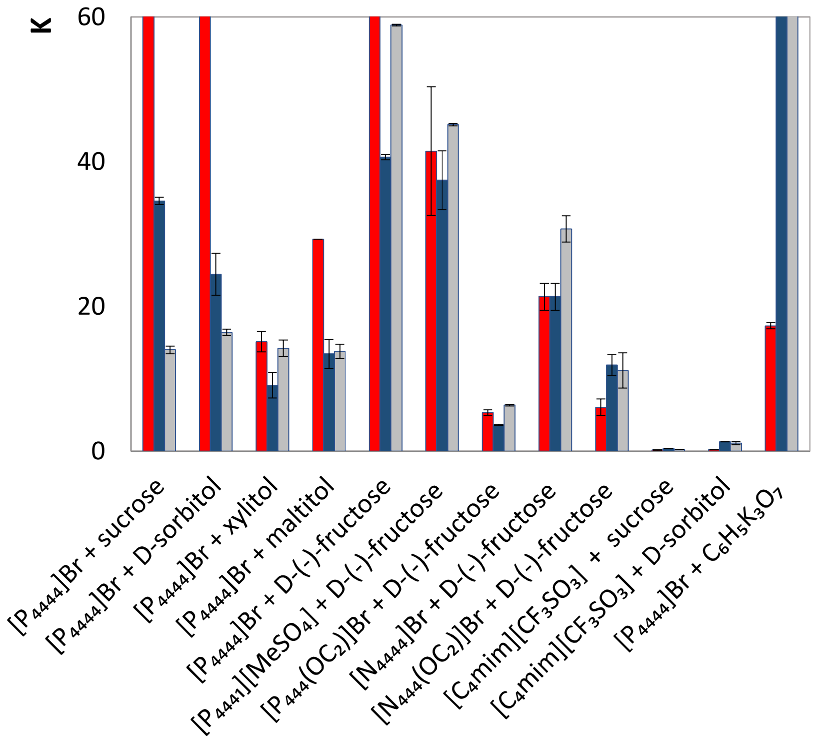

Figure S2. Partition coefficients of phenolic acids (*K*) in the studied systems at 25°C. ■■■ correspond to gallic acid (GA), syringic acid (SA) and vanillic acid (VA), respectively.

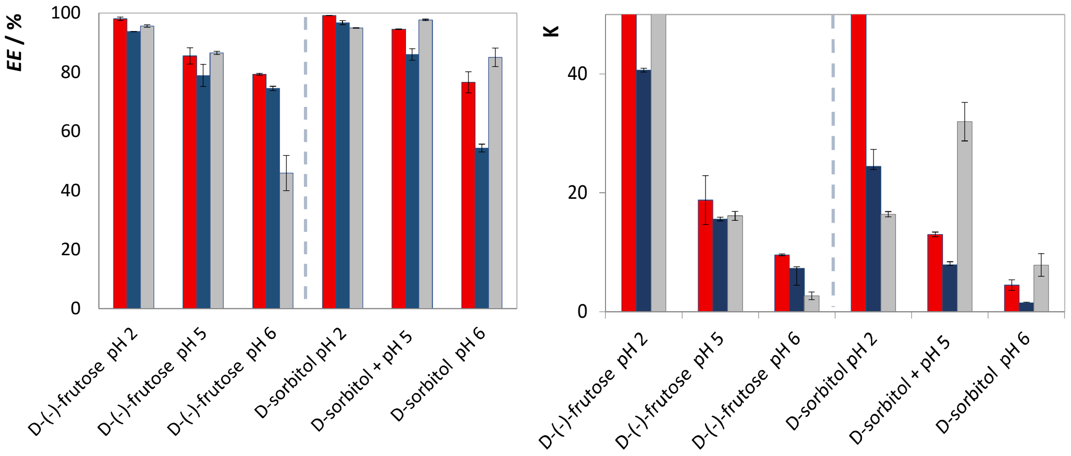

Figure S3. Extraction efficiencies (*EE/*%) of the studied systems for phenolic acids and partition coefficients (*K*) in the ABS formed by [P$_{4444}$]Br + CH + H$_2$O at 25°C, at different pH values. ■■■ correspond to gallic acid (GA), syringic acid (SA) and vanillic acid (VA), respectively.

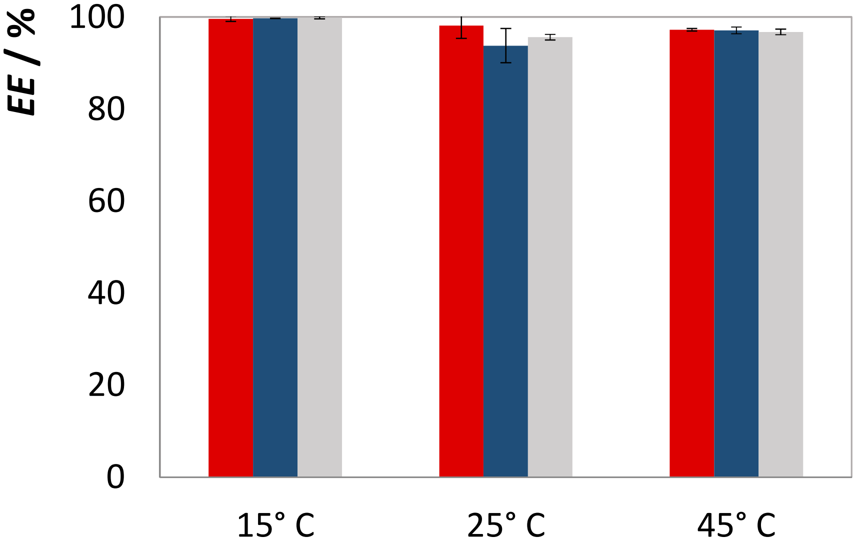

Figure S4. Extraction efficiencies (*EE/%*) of the ABS formed by $[P_{4444}]Br$ + D-(-)-fructose + H_2O at different temperatures for phenolic acids. 🟥🟦⬜ correspond to gallic acid (GA), syringic acid (SA) and vanillic acid (VA), respectively.

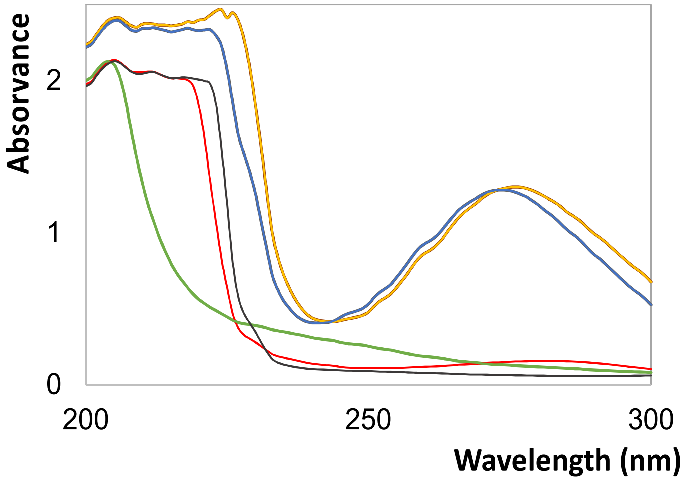

Figure S5. UV-Vis spectra of the different fractions obtained in the SPE experiment. SPE1 fraction ( ), SPE2 fraction ( ), SPE3 fraction ( ), SPE4 fraction ( ), and initial IL-rich phase containing gallic acid ( ).

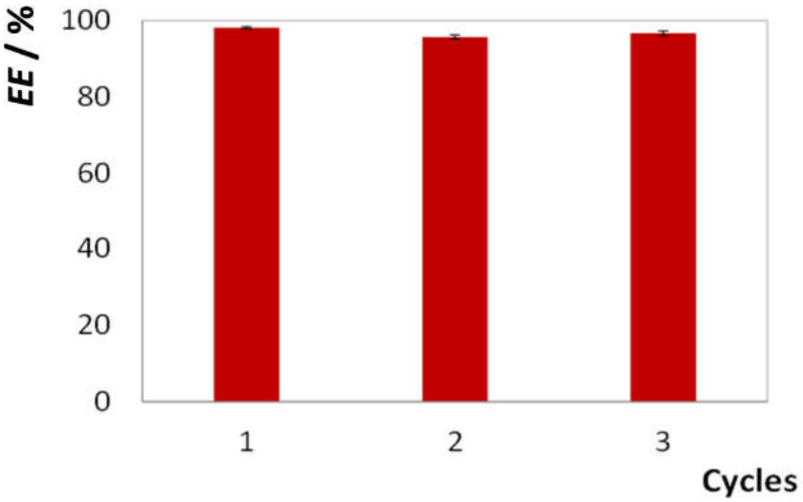

Figure S6. Extraction efficiencies (*EE/*%) of the ABS formed by [P_{4444}]Br + D-(-)-fructose for gallic acid in 3 cycles of extraction by reusing the employed IL.

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