Supporting Information

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

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Table S1.1: Parameters obtained through the Merchuk equation with the respective standard deviations (std) along with the weight fraction data (w) for the quaternary systems composed of NaPA 8000 (1) + PEG 8000 (2) + H_2O + cationic surfactants.

0.01 wt% CTAB				**0.1 wt% CTAB**		**0.01 wt% TTAB**				**0.1 wt% TTAB**	
A ± std = 16.81 ± 3.02				A ± std = 13.69 ± 3.37		A ± std = 16.83 ± 4.77				A ± std = 13.24 ± 0.73	
B ± std = -0.254 ± 0.080				B ± std = -0.214 ± 0.130		B ± std = -0.301± 0.110				B ± std = -0.231 ± 0.028	
C ± std = $1.48\times10^{-4} \pm 6.46\times10^{-5}$				C ± std = $1.46\times10^{-4} \pm 2.09\times10^{-5}$		C ± std = $8.11\times10^{-5} \pm 5.14\times10^{-5}$				C ± std = $5.28\times10^{-4} \pm 2.21\times10^{-5}$	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
4.10	14.58	9.70	4.04	5.86	9.85	3.85	15.14	6.48	9.22	4.00	16.31
4.18	14.84	10.34	4.31	6.05	10.17	3.90	15.35	6.60	8.44	4.11	16.77
4.35	13.39	10.69	2.77	6.18	9.28	4.01	14.38	6.83	8.73	4.25	15.59
4.63	14.25			6.47	9.71	4.15	14.90	7.08	7.28	4.37	16.00
4.84	12.61			6.83	7.50	4.31	13.59	7.49	7.70	4.65	13.78
5.75	10.54			7.15	7.85	4.48	14.14	7.83	5.78	4.86	14.40
5.98	10.95			7.43	6.23	4.59	13.29	8.12	5.99	5.10	12.61
6.07	10.32			7.89	6.62	4.69	13.57			5.27	13.03
6.21	10.56			8.31	4.36	4.76	12.98			5.47	11.65
6.35	9.70			8.71	4.58	4.86	13.24			5.61	11.95
6.58	10.05			8.89	3.67	4.98	12.32			5.88	10.14
6.80	8.72			9.55	3.94	5.08	12.56			6.14	10.59
7.16	9.18			9.94	2.08	5.23	11.43			6.41	8.83
7.39	7.88					5.36	11.72			8.83	3.00
7.87	8.39					5.55	10.41			10.55	0.99
8.16	6.84					5.76	10.81				
8.57	7.19					5.96	9.45				
8.89	5.61					6.19	9.81				
9.31	5.88					6.31	8.98				

Table S1.2: Parameters obtained through the Merchuk equation with the respective standard deviations (std) along with the weight fraction data (*w*) for the quaternary systems composed of NaPA 8000 (1) + PEG 8000 (2) + H_2O + cationic surfactants.

0.01 wt% CPC		**0.1 wt% CPC**	
A **± std = 52.712± 4.21**		***A*** **± std = 44.75 ± 13.53**	
B **± std = -0.597 ± 0.040**		***B*** **± std = -0.485 ± 0.130**	
C **± std = $6.70\times10^{-4} \pm 6.96\times10^{-5}$**		***C*** **± std = $8.47\times10^{-4} \pm 1.13\times10^{-4}$**	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**
3.6	16.5	5.99	11.22
3.8	15.6	6.40	10.62
4.0	15.0	6.96	9.51
4.3	14.7	7.45	8.39
4.6	14.3	7.86	7.52
5.0	13.0	9.47	5.01
5.3	11.9	9.89	4.06
5.7	11.1	10.73	3.20
6.1	10.1	12.18	1.93
6.6	9.5	5.99	11.22
7.1	8.4	6.40	10.62
7.7	7.4	6.96	9.51
8.7	5.5	7.45	8.39
10.6	3.4	7.86	7.52
12.3	2.0	9.47	5.01
		9.89	4.06
		10.73	3.20
		12.18	1.93

Table S2.1: Parameters obtained through the Merchuk equation with the respective standard deviations (std) along with the weight fraction data (w) for the quaternary systems composed of NaPA 8000 (1) + PEG 8000 (2) + H_2O + anionic surfactants.

0.01 wt% SDS $A \pm$ std = 15.46 ± 1.92 $B \pm$ std = -0.285 ± 0.052 $C \pm$ std = $1.03\times10^{-4} \pm 2.84\times10^{-5}$				**0.1 wt% SDS** $A \pm$ std = 18.02 ± 4.04 $B \pm$ std = -0.360 ± 0.086 $C \pm$ std = $8.17\times10^{-4} \pm 3.48\times10^{-5}$				**1.0 wt% SDS** $A \pm$ std = 14.70 ± 3.73 $B \pm$ std = -0.352 ± 0.091 $C \pm$ std = $7.52\times10^{-5} \pm 3.29\times10^{-5}$					
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
2.83	17.09	4.92	11.35	2.67	16.57	5.29	10.11	2.49	16.17	4.21	10.47	5.21	7.59
2.91	17.58	5.16	11.89	2.80	17.37	5.86	8.85	2.56	16.65	4.30	10.71	5.32	7.74
2.98	16.75	5.40	10.11	2.96	15.54	5.93	8.32	2.68	15.11	4.34	10.33		
3.05	17.14	5.69	10.66	3.10	16.25	6.07	8.51	2.82	15.87	4.40	10.47		
3.17	15.93	6.04	8.23	3.18	15.34	6.14	8.00	2.92	14.58	4.45	10.07		
3.26	16.38	6.56	8.95	3.25	15.67	6.25	8.14	3.03	15.14	4.49	10.17		
3.41	14.81	6.85	7.14	3.32	14.90	6.33	7.60	3.13	14.04	4.53	9.78		
3.57	15.50	7.23	7.54	3.39	15.21	6.46	7.76	3.22	14.45	4.58	9.88		
3.72	14.06	7.46	6.19	3.46	14.48	6.54	7.23	3.36	12.83	4.61	9.62		
3.85	14.56	7.90	6.55	3.54	14.80	6.70	7.41	3.45	13.17	4.65	9.71		
3.97	13.43	8.26	4.59	3.67	13.54	6.79	6.84	3.50	12.66	4.69	9.39		
4.07	13.74	9.59	2.65	3.87	14.26	6.91	6.96	3.57	12.91	4.74	9.50		
4.11	13.34			3.98	13.20	7.03	6.23	3.64	12.18	4.78	9.17		
4.22	13.68			4.05	13.44	7.26	6.44	3.72	12.45	4.81	9.23		
4.31	12.90			4.13	12.75			3.85	11.14	4.85	8.93		
4.42	13.24			4.25	13.11			3.99	11.55	4.90	9.02		
4.55	12.19			4.37	12.07			4.03	11.17	4.94	8.64		
4.66	12.49			4.49	12.40			4.07	11.28	4.98	8.71		
4.74	11.88			5.04	11.20			4.11	10.95	5.03	8.28		
4.83	12.10			5.21	9.94			4.14	11.04	5.11	8.41		

Table S2.2: Parameters obtained through the Merchuk equation with the respective standard deviations (std) along with the weight fraction data (w) for the quaternary systems composed of NaPA 8000 (1) + PEG 8000 (2) + H_2O + anionic surfactants.

0.01 wt% SDBS A ± std = 13.96 ± 1.47 B ± std = -0.225 ± 0.050 C ± std = $1.26\times10^{-4} \pm 4.31\times10^{-5}$				**0.1 wt% SDBS** A ± std = 16.86 ± 11.19 B ± std = -0.327 ± 0.220 C ± std = $7.21\times10^{-5} \pm 5.27\times10^{-5}$				**1.0 wt% SDBS** A ± std = 57.22 ± 79.77 B ± std = -0.800 ± 0.481 C ± std = $7.90\times10^{-6} \pm 1.49\times10^{-3}$			
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
2.65	17.69	9.55	2.68	2.50	17.82	4.64	12.00	2.43	14.67	3.62	11.41
3.36	15.60	10.37	2.91	2.63	18.77	4.79	12.40	2.49	15.01	3.74	11.78
3.57	16.58	10.81	0.97	2.78	17.02	4.90	11.53	2.53	14.45	3.81	11.13
3.89	13.70			2.92	17.85	5.06	11.90	2.61	14.92	3.91	11.44
4.23	14.93			2.98	17.13	5.28	10.26	2.65	14.34	3.97	10.85
4.38	13.72			3.07	17.66	5.48	10.66	2.70	14.60	4.08	11.14
4.56	14.27			3.18	16.48	5.64	9.50	2.73	14.26	4.15	10.49
4.92	11.44			3.25	16.80	5.87	9.87	2.76	14.43	4.25	10.74
5.15	11.97			3.35	15.69			2.81	13.80	4.31	10.11
5.32	10.80			3.48	16.28			2.88	14.11	4.44	10.42
5.46	11.08			3.58	15.28			2.93	13.43	4.51	9.84
5.63	9.87			3.65	15.59			3.00	13.72	4.68	10.21
6.01	10.54			3.77	14.52			3.05	13.07		
6.28	8.83			3.86	14.90			3.13	13.40		
6.64	9.34			3.97	13.92			3.20	12.53		
6.85	8.06			4.08	14.30			3.29	12.87		
7.22	8.49			4.17	13.53			3.36	12.06		
7.59	6.38			4.23	13.72			3.42	12.27		
7.91	6.65			4.34	12.75			3.47	11.76		
8.22	4.96			4.49	13.20			3.56	12.08		

Table S3: Parameters obtained through the Merchuk equation with the respective standard deviations (std) along with the weight fraction data (w) for the quaternary systems composed of NaPA 8000 (1) + PEG 8000 (2) + H_2O + imidazolium-based ILs.

0.01 wt% [C_{12}mim]Cl ***A*** **± std = 16.03 ± 1.58** ***B*** **± std = -0.299 ± 0.047** ***C*** **± std = $1.16\times10^{-4} \pm 4.10\times10^{-5}$**				**0.1 wt% [C_{12}mim]Cl** ***A*** **± std = 15.69 ± 1.22** ***B*** **± std = -0.306 ± 0.037** ***C*** **± std = $7.90\times10^{-5} \pm 4.42\times10^{-5}$**				**0.01 wt% [C_{14}mim]Cl** ***A*** **± std = 50.90 ± 2.17** ***B*** **± std = -0.580 ± 0.020** ***C*** **± std = $4.0\times10^{-4} \pm 2.4\times10^{-5}$**				**0.1 wt% [C_{14}mim]Cl** ***A*** **± std = 14.94 ± 1.68** ***B*** **± std = -0.283 ± 0.056** ***C*** **± std = $1.23\times10^{-4} \pm 8.27\times10^{-5}$**			
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
3.64	13.90	6.43	7.83	4.66	12.17	6.97	6.38	3.99	14.30	6.37	8.95	5.21	10.93	8.25	4.26
3.75	14.32	6.79	8.26	4.80	12.54	7.12	6.51	4.08	14.62	6.54	9.19	5.07	10.65	8.58	4.44
3.80	13.87	7.11	6.29	5.03	10.75	7.20	6.03	4.18	13.80	6.64	8.56	5.51	10.01	8.80	3.26
3.90	14.24	7.35	6.50	5.20	11.13	7.38	6.18	4.27	14.08	6.82	8.79	5.37	9.75	9.77	2.15
3.98	13.53	7.44	5.96	5.32	10.28	7.50	5.47	4.33	13.58	6.97	7.85	5.81	9.31		
4.05	13.79	7.71	6.17	5.37	10.39	7.63	5.56	4.46	14.00	7.19	8.09	5.65	9.05		
4.19	12.58	8.00	4.57	5.45	9.82	7.70	5.15	4.62	12.71	7.29	7.48	6.04	8.49		
4.36	13.08	8.61	4.93	5.57	10.04	7.83	5.24	4.73	13.00	7.59	7.78	5.95	8.35		
4.45	12.28	8.85	3.73	5.66	9.40	7.94	4.64	4.87	11.92	7.78	6.73	6.32	8.33		
4.54	12.54	9.11	3.84	5.70	9.47	8.20	4.80	5.02	12.28	8.03	6.94	6.11	8.05		
4.65	11.65	9.29	2.93	5.77	8.97	8.35	3.96	5.10	11.64	8.20	6.00	6.69	7.29		
4.78	11.98	9.97	3.14	5.91	9.19	8.67	4.11	5.23	11.93	8.55	6.25	6.51	7.09		
4.95	10.62	10.17	2.21	6.02	8.42	8.82	3.31	5.34	11.11	8.73	5.33	6.99	6.80		
5.17	11.08			6.15	8.61	9.13	3.43	5.43	11.29	8.98	5.48	6.79	6.61		
5.39	9.40			6.25	7.95	9.33	2.43	5.56	10.40	9.14	4.69	7.25	6.28		
5.67	9.89			6.39	8.13			5.73	10.73	9.62	4.94	7.09	6.15		
5.77	9.23			6.50	7.42			5.83	10.09	9.84	3.93	7.79	5.60		
5.93	9.50			6.61	7.54			5.95	10.30	10.29	4.12	7.41	5.32		
6.09	8.45			6.68	7.10			6.02	9.80	10.56	2.94	7.95	4.71		
6.29	8.74			6.83	7.26			6.19	10.09			8.15	4.83		

Table S4: pH of bottom and top phases of the polymer-based ABS.

Electrolyte	pH ± 0.01	
	pH of top-phase	pH of bottom-phase
SDS	7.59	7.08
SDBS	7.66	7.08
TTAB	7.67	7.06
CTAB	7.65	7.08
CPC	7.66	7.08
[C_{12}mim]Cl	7.62	7.07
[C_{14}mim]Cl	7.64	7.07

Table S5: Partition coefficient values of the phenolic compounds (K_{PC}) by applying the polymer-based ABS with different ionic surfactants acting as electrolytes.

Surfactant electrolyte	K_{CA}	K_{GA}	K_{VA}	K_{VN}	K_{SA}
SDS	0.90 ± 0.28	1.33 ± 0.21	2.53 ± 0.22	0.11 ± 0.01	0.12 ± 0.01
SDBS	1.49 ± 0.29	1.020 ± 0.005	3.35 ± 1.25	0.11 ± 0.01	0.23 ± 0.01
TTAB	0.45 ± 0.01	0.44 ± 0.05	1.04 ± 0.03	0.073 ± 0.003	0.18 ± 0.02
CTAB	0.68 ± 0.02	0.31 ± 0.01	0.86 ± 0.08	0.06 ± 0.01	0.18 ± 0.01
CPC	0.65 ± 0.04	0.32 ± 0.03	0.71 ± 0.03	0.08 ± 0.01	0.055 ± 0.005
[C_{12}mim]Cl	0.99 ± 0.22	0.58 ± 0.03	0.42 ± 0.03	0.28 ± 0.02	0.15 ± 0.03
[C_{14}mim]Cl	0.18 ± 0.02	0.511 ± 0.003	0.53 ± 0.06	0.27 ± 0.03	0.16 ± 0.01

Table S6: Recovery of the phenolic compounds towards the PEG-rich phase (% R_{Top}) by applying the polymer-based ABS with different ionic surfactants acting as electrolytes.

Surfactant Electrolyte	Caffeic acid	Gallic acid	Vanillic acid	Vanillin	Syringaldehyde
	R_{Top} (%)	R_{Top} (%)	R_{Top} (%)	R_{Top} (%)	R_{Top} (%)
SDS	75.11 ± 6.79	83.33 ± 2.06	90.52 ± 0.76	28.06 ± 0.95	30.25 ± 3.11
SDBS	89.05 ± 6.11	79.43 ± 0.02	95.60 ± 2.49	27.56 ± 0.10	45.38 ± 1.42
TTAB	63.39 ± 0.21	61.84 ± 3.99	76.73 ± 1.85	24.07 ± 0.71	40.47 ± 4.53
CTAB	72.20 ± 0.50	51.08 ± 1.05	76.79 ± 1.31	22.49 ± 0.51	44.93 ± 1.96
CPC	72.70 ± 1.38	54.09 ± 2.11	74.99 ± 0.58	24.41 ± 0.74	18.56 ± 1.58
[C_{12}mim]Cl	82.52 ± 2.17	71.19 ± 1.63	64.10 ± 1.62	53.12 ± 1.49	40.73 ± 2.66
[C_{14}mim]Cl	47.04 ± 3.41	66.10 ± 2.01	67.97 ± 1.66	51.38 ± 3.06	42.08 ± 1.49

Table S7: Water content in both phases (top and bottom), through evaporation method using lyophilisation as water removal technique from the separated phases.

Electrolyte	Water content in both phases (g)	
	Top-phase	Bottom-phase
SDS	3.0553	0.6485
SDBS	2.8549	0.7446
TTAB	2.9750	0.7795
CTAB	2.9740	0.7414
CPC	3.0424	0.6533
$[C_{12}mim]Cl$	2.9683	0.6988
$[C_{14}mim]Cl$	2.9225	0.8443

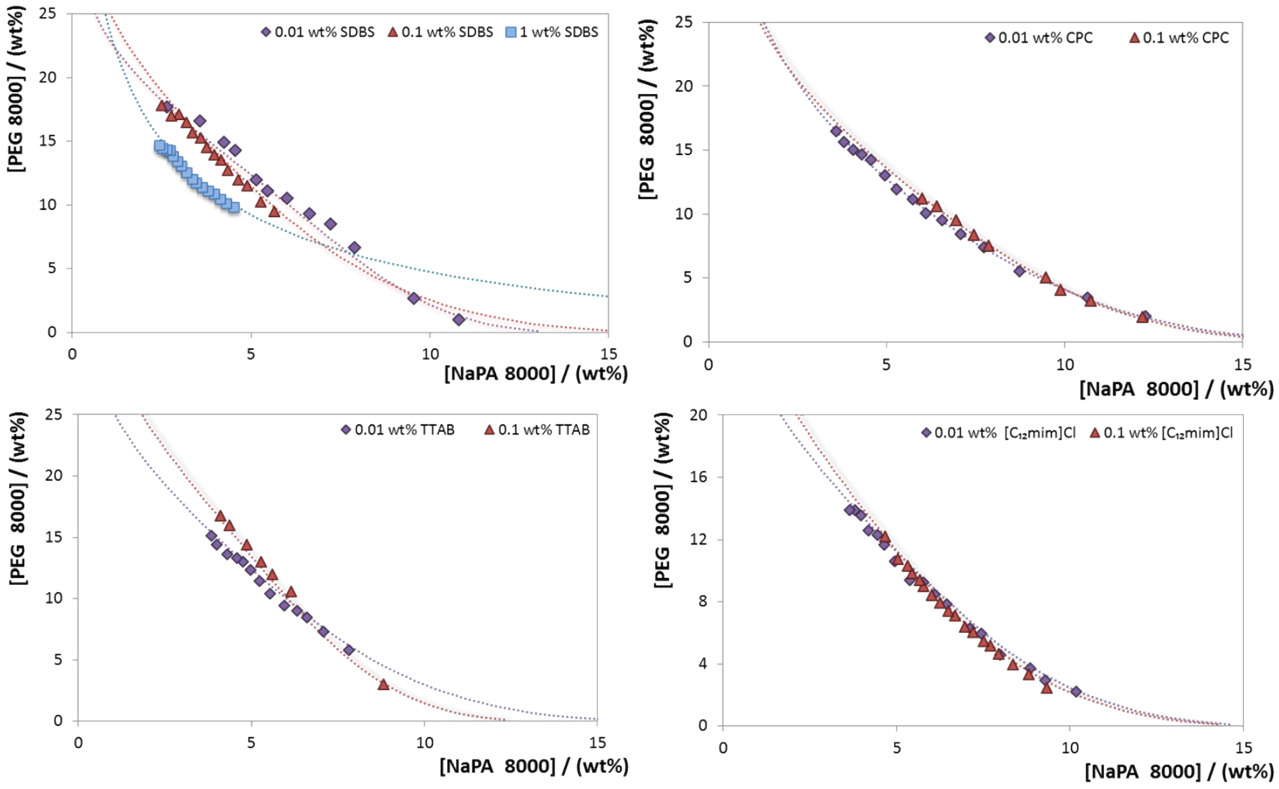


Fig. S1: Phase diagrams of the polymer-based ABS prepared at different concentrations for the three classes of electrolytes, using: SDBS, TTAB, CPC and $[C_{12}mim]Cl$. The binodal curves fitted through Eq. 1 are represented by the dashed lines.

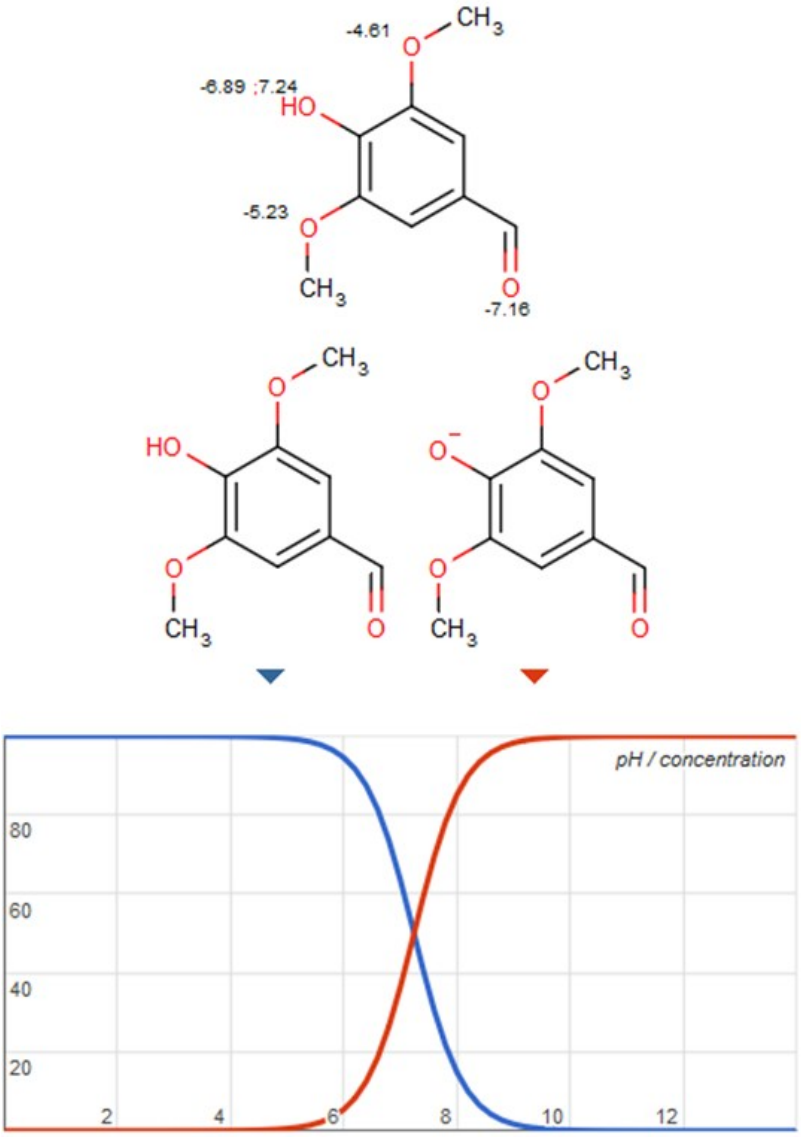


Fig. S2: Speciation of syringaldehyde (ChemSpider, accessed at 3rd May, 2016).

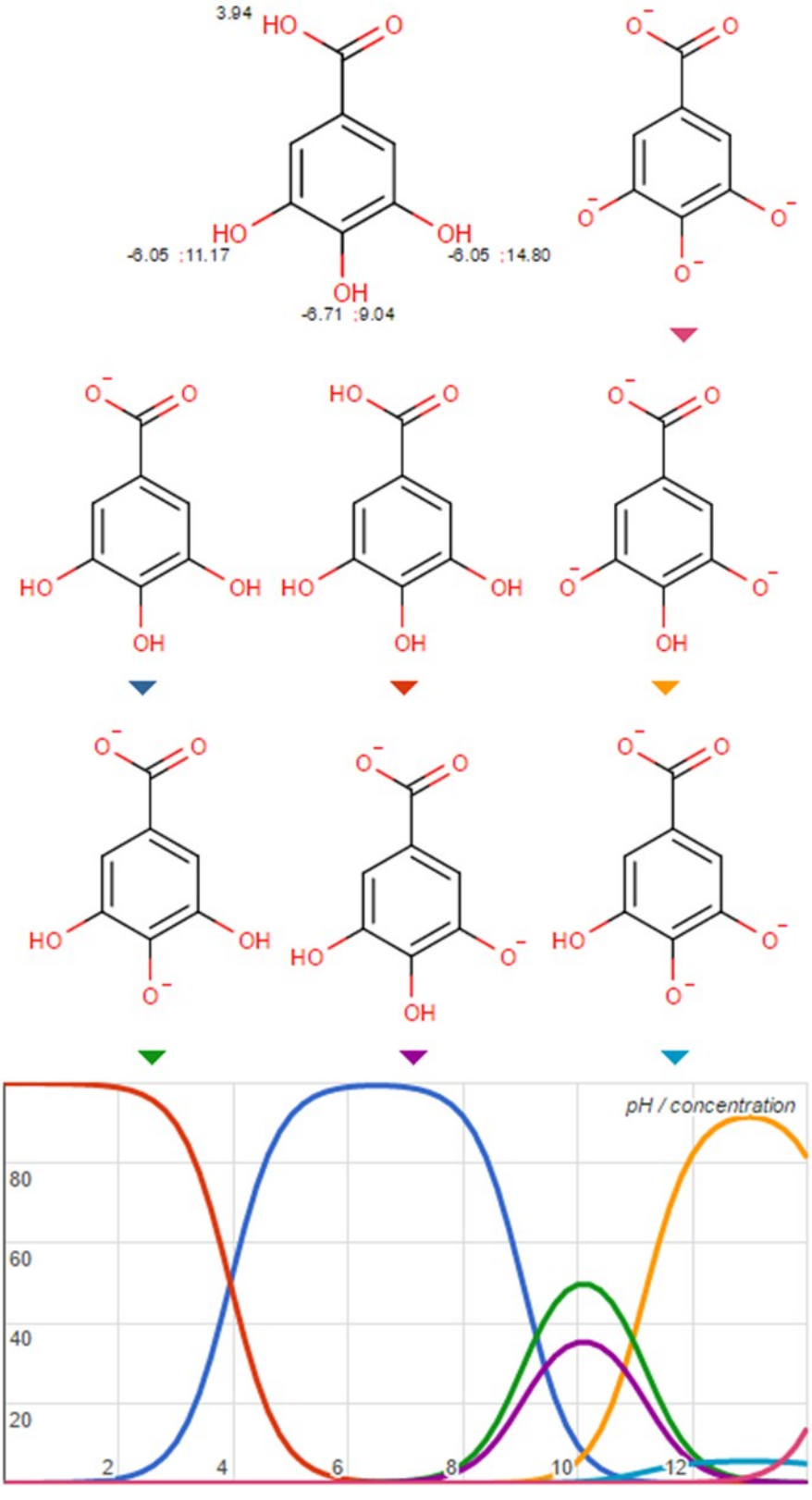


Fig. S3: Speciation of gallic acid (ChemSpider, accessed at 3rd May, 2016).

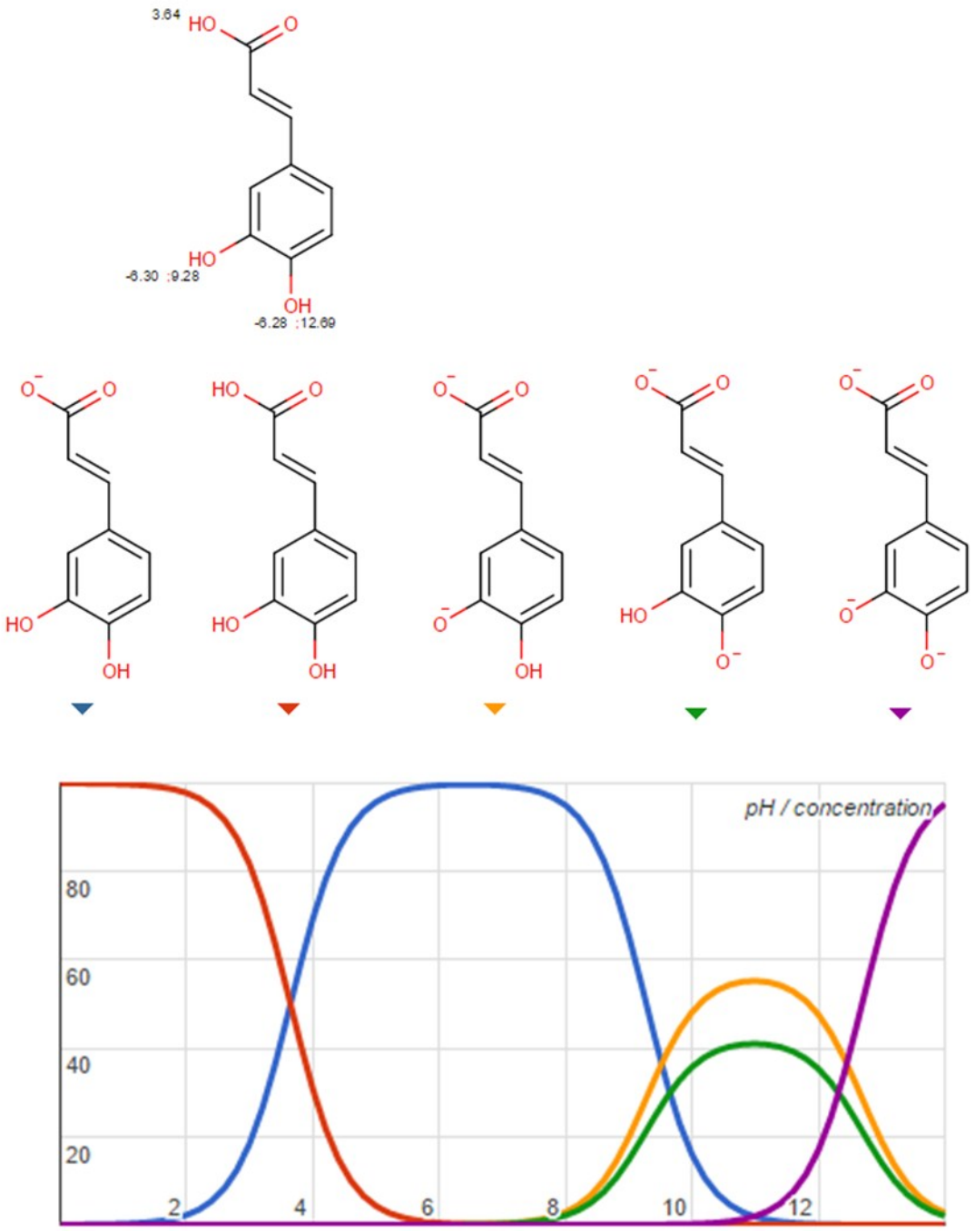


Fig. S4: Speciation of caffeic acid (ChemSpider, accessed at 3rd May, 2016).

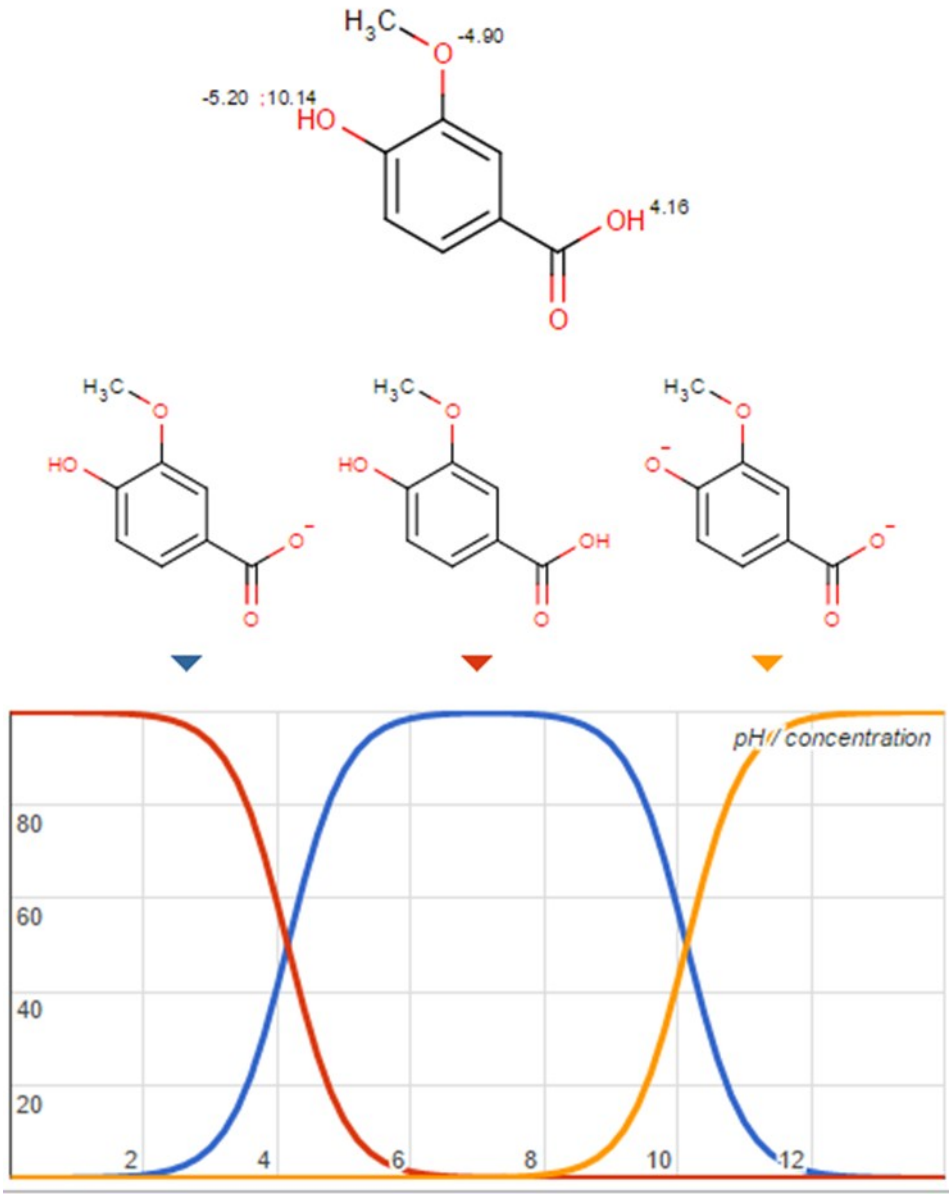


Fig. S5: Speciation of vanillic acid (ChemSpider, accessed at 3rd May, 2016).

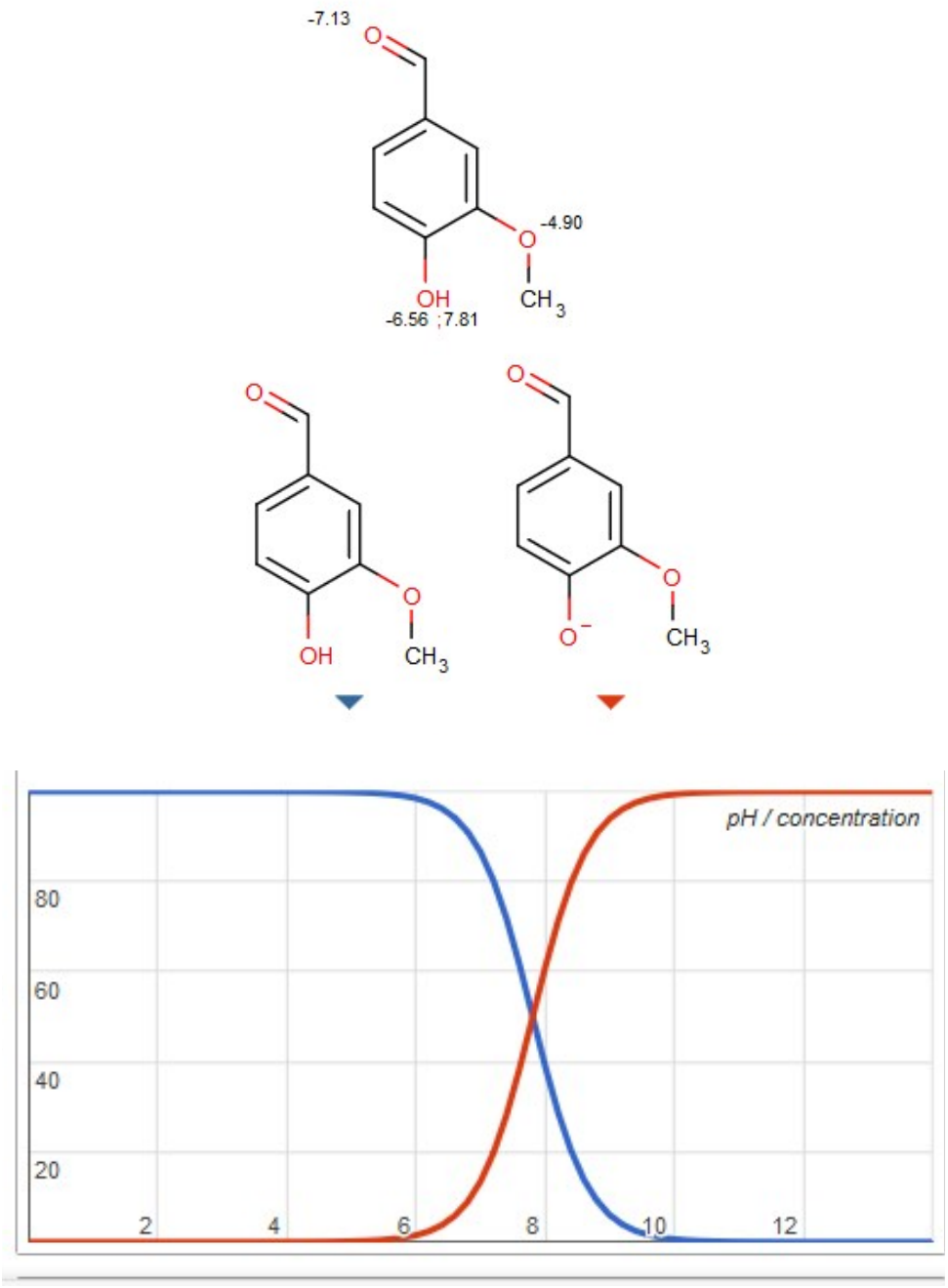


Fig. S6: Speciation of vanillin (ChemSpider, accessed at 3rd May, 2016).

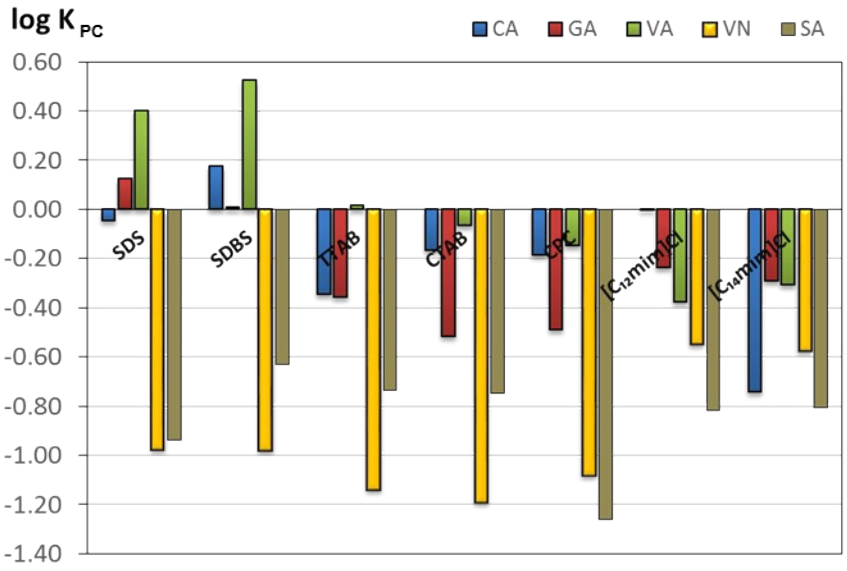
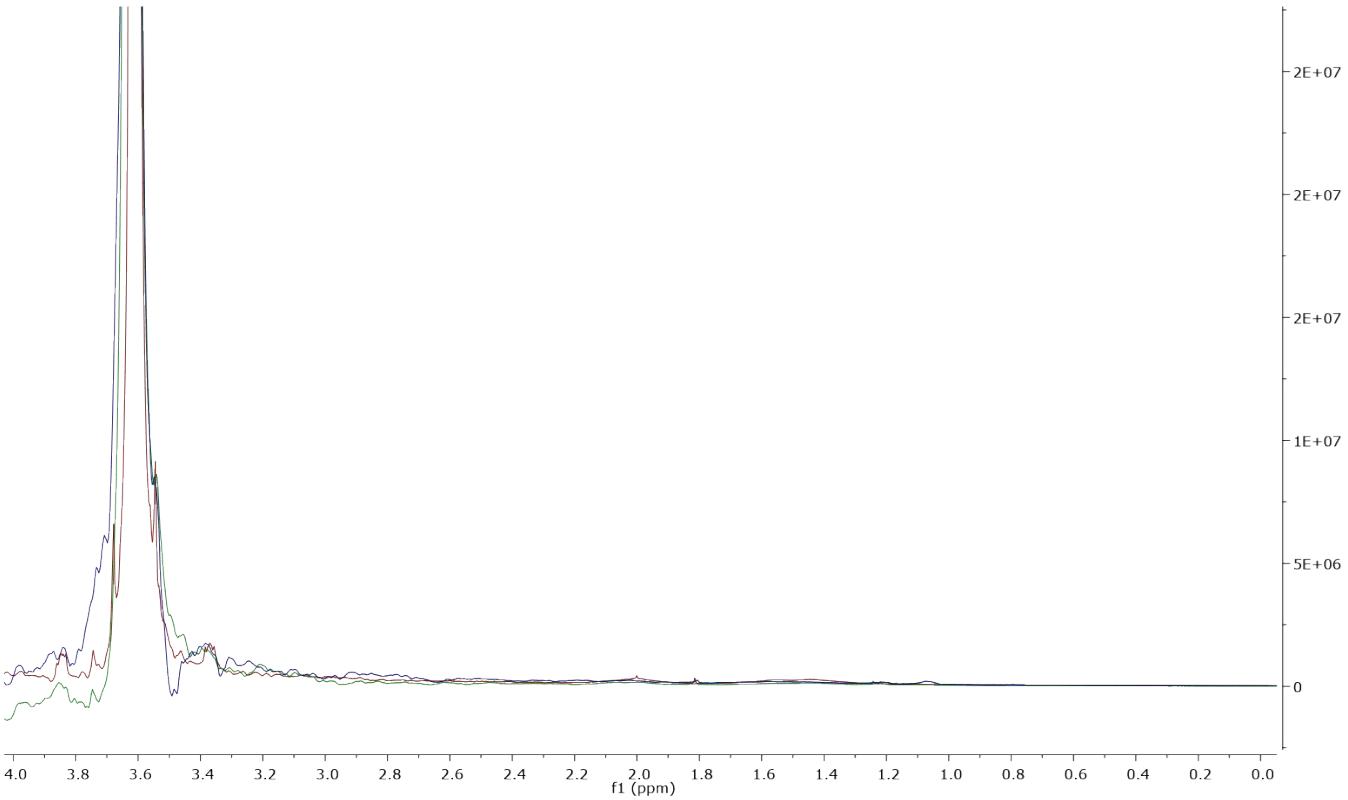
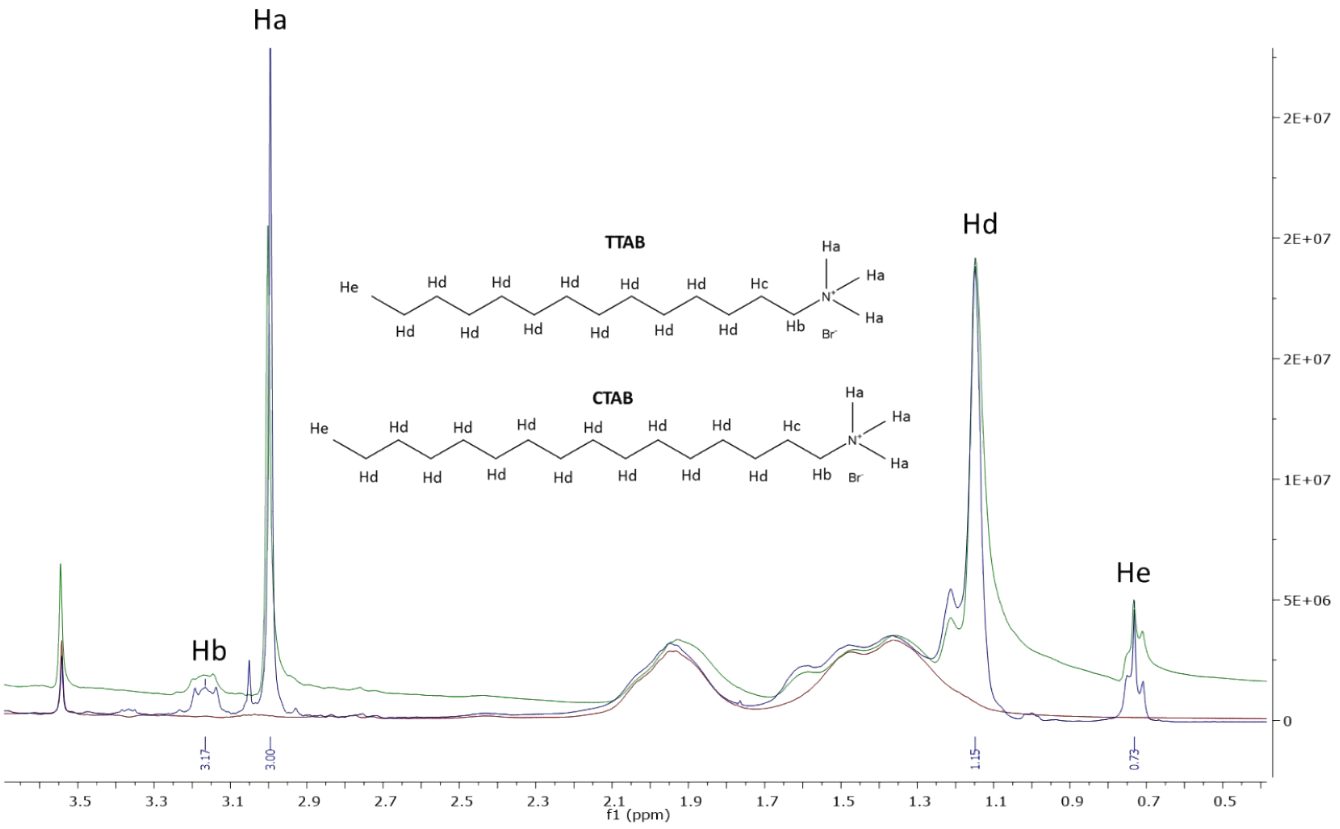


Fig. S7: Logarithmic function of the partition coefficient results found for the phenolic compounds (log K_{PC}) by the application of the various ABS studied in this work, employing common surfactants and tensioactive ionic liquids as electrolytes.



- Top phase of TTAB system - Top phase of CTAB system - Top phase of system without electrolyte



- Bottom phase of TTAB system - Bottom phase of CTAB system - Bottom phase of system without electrolyte

Fig. S8: ^{1}H NMR spectroscopy of top and bottom phase of the polymer-based ABS with TTAB, CTAB and control (without electrolyte).

Anionic surfactant

SDS

	K	Vanillic acid	Gallic acid	Caffeic acid	Syringaldehyde	Vanillin
		2.53	1.33	0.90	0.12	0.11
Vanillic acid	2.53					
Gallic acid	1.33	1.90				
Caffeic acid	0.90	2.80	1.48			
Syringaldehyde	0.18	14.05	7.41	5.01		
Vanillin	0.11	23.75	12.52	8.47	1.08	

SDBS

	K	Vanillic acid	Caffeic acid	Gallic acid	Syringaldehyde	Vanillin
		3.35	1.49	1.02	0.23	0.11
Vanillic acid	3.35					
Caffeic acid	1.49	2.24				
Gallic acid	1.02	3.29	1.46			
Syringaldehyde	0.23	14.30	6.37	4.35		
Vanillin	0.11	31.80	14.17	9.67	2.22	

Cationic surfactants

TTAB

	K	Vanillic acid	Caffeic acid	Gallic acid	Syringaldehyde	Vanillin
		1.04	0.45	0.44	0.18	0.07
Vanillic acid	1.04					
Caffeic acid	0.45	2.31				
Gallic acid	0.44	2.36	1.02			
Syringaldehyde	0.18	5.78	2.50	2.44		
Vanillin	0.07	14.86	6.43	6.29	2.57	

CTAB

	K	Vanillic acid	Caffeic acid	Gallic acid	Syringaldehyde	Vanillin
		0.86	0.68	0.31	0.18	0.06
Vanillic acid	0.86					
Caffeic acid	0.68	1.26				
Gallic acid	0.31	2.81	2.24			
Syringaldehyde	0.18	4.77	3.80	1.69		
Vanillin	0.06	13.24	10.54	4.70	2.77	

CPC

	K	Vanillic acid	Caffeic acid	Gallic acid	Vanillin	Syringaldehyde
		0.71	0.65	0.32	0.08	0.05
Vanillic acid	0.71					
Caffeic acid	0.65	1.09				
Gallic acid	0.32	2.20	2.01			
Vanillin	0.08	8.62	7.89	3.92		
Syringaldehyde	0.05	13.03	11.93	5.93	1.51	

Ionic Liquids (ILs)

[C_{12}mim]Cl

		Caffeic acid	Gallic acid	Vanillic acid	Vanillin	Syringaldehyde
	K	0.99	0.58	0.42	0.28	0.15
Caffeic acid	0.99					
Gallic acid	0.58	1.70				
Vanillic acid	0.42	2.35	1.38			
Vanillin	0.28	3.50	2.05	1.49		
Syringaldehyde	0.15	6.53	3.83	2.78	1.87	

[C_{14}mim]Cl

		Gallic acid	Vanillic acid	Vanillin	Caffeic acid	Syringaldehyde
	K	0.51	0.49	0.27	0.18	0.16
Gallic acid	0.51					
Vanillic acid	0.49	1.03				
Vanillin	0.27	1.91	1.85			
Caffeic acid	0.18	2.82	2.73	1.47		
Syringaldehyde	0.16	3.28	3.17	1.72	1.16	

Fig. S9: Selectivity values (S) of the phenolic compounds fractionated by polymer-based ABS varying the electrolyte nature.

0.01 wt% SDS

		Vanillic acid	Gallic acid	Caffeic acid	Vanillin	Syringaldehyde
	K	2.52	1.16	0.70	0.10	0.09
Vanillic acid	2.52					
Gallic acid	1.16	2.18				
Caffeic acid	0.70	3.58	1.64			
Vanillin	0.10	25.21	11.56	7.04		
Syringaldehyde	0.09	27.59	12.65	7.70	1.09	

1 wt% SDS

		Vanillic acid	Gallic acid	Caffeic acid	Syringaldehyde	Vanillin
	K	2.47	1.41	0.95	0.13	0.11
Vanillic acid	2.47					
Gallic acid	1.41	1.75				
Caffeic acid	0.95	2.61	1.49			
Syringaldehyde	0.13	19.44	11.12	7.45		
Vanillin	0.11	23.34	13.36	8.95	1.20	

0.1 wt% SDS

		Vanillic acid	Gallic acid	Caffeic acid	Syringaldehyde	Vanillin
	K	2.53	1.33	0.90	0.12	0.11
Vanillic acid	2.53					
Gallic acid	1.33	1.90				
Caffeic acid	0.90	2.80	1.48			
Syringaldehyde	0.18	14.05	7.41	5.01		
Vanillin	0.11	23.75	12.52	8.47	1.08	

Fig. S10: Selectivity values (S) of the phenolic compounds fractionated by polymer-based ABS varying the electrolyte concentration.

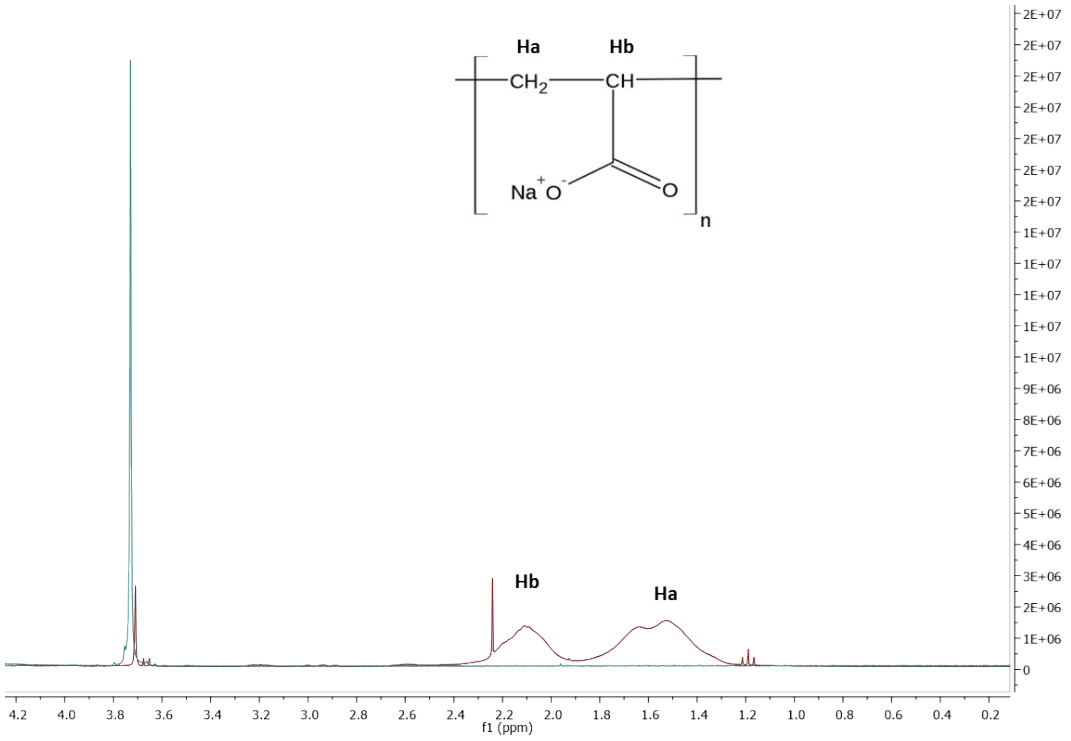


Fig. S11: ^{1}H NMR spectroscopy of bottom phase of the polymer-based ABS with SDS as electrolyte before and after NaPA precipitation with $CaCl_2$.