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PAPER

Improved recovery of ionic liquids from contaminated aqueous streams using aluminium-based salts†

Catarina M. S. S. Neves, Mara G. Freire and João A. P. Coutinho*

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The number of applications involving ionic liquids has dramatically increased in the past few years, and their production and use in a large scale will inevitably lead to their dispersion into water streams (either by wastewater disposal or accidental leakage). Studies on the removal and recovery of ionic liquids from wastewater streams are therefore of crucial importance, yet particularly scarce. In this work, the use of aluminium salts is proposed to concentrate and remove ionic liquids from aqueous solutions. Two aluminium-based salts ($\text{Al}_2(\text{SO}_4)_3$ and $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) were used to treat various aqueous solutions of ionic liquids containing imidazolium-, pyridinium- and phosphonium-based fluids. The gathered results show the enhanced ability of these salts to remove and recover ionic liquids from aqueous media. The minimum recovery efficiency achieved was 96%, whereas for a large array of systems recoveries of *circa* 100% of ionic liquid were attained. The residual concentrations of ionic liquids in water range from 0.01 to 6 wt%. The results reported disclose a novel promising technique for the recovery and treatment of aqueous effluents contaminated with ionic liquids by using salts commonly employed in water treatment processes, allowing thus its easy scale-up and adaptation to new processes involving ionic liquids.

Introduction

The beneficial use of ionic liquids in a diverse range of applications has become increasingly evident.^{1–3} Since ionic liquids are constituted by ionic species, they present outstanding properties not common in molecular solvents, such as a negligible vapour pressure, non-flammability, high thermal and chemical stabilities, among others. Moreover, the possibility of directing their properties, by the adequate manipulation of the cation and/or the anion, allows the design of these solvents aiming at presenting a selected set of properties for a particular application.^{4,5} This tailoring ability makes ionic liquids excellent alternative solvents, that coupled with their negligible vapour pressures, contributed to their classification as potential “green solvents” of industrial interest.⁶ The intrinsic non-volatile nature of ionic liquids provides the enhanced opportunity to reduce, or even completely eliminate, hazardous and toxic emissions to the atmosphere. However, although ionic liquids cannot contribute to air pollution, most fluids (even those considered hydrophobic) present a non-negligible solubility in water.^{7–12} Therefore, this

water miscibility, even if limited, will unavoidably lead to aquatic environmental impacts. It is well known that ionic liquids that have aromatic rings (like imidazolium or pyridinium-based fluids) are more toxic to aquatic environments than ionic liquids composed of saturated rings.^{13–18} On the other hand, ionic liquids constituted by cations that have functionalized groups in their alkyl chain are less toxic.^{13–18} Thus, despite the variable toxicity level imposed by the chemical structures of ionic liquids, their use in a large scale, either at the academic or industrial level, should also involve a treatment approach aiming at “cleaning” the discarded aqueous effluents, as well as to recover and recycle the ionic liquid used. In this context, the research and development of novel methods to remove and recover ionic liquids from wastewater streams with the final goal of creating “greener” and more sustainable processes is of vital significance.

An approach already described in literature for the treatment of aqueous solutions contaminated with ionic liquids relies on their physicochemical degradation. This type of treatment addresses the oxidative,^{19–21} thermal²² and photocatalytic^{23–28} degradations. These processes are only applicable at diluted solutions and do not allow the recovery of the ionic liquid. Nevertheless, it should be stressed that the products of the reactions—hydrocarbons, water and CO_2 —are usually less toxic than the ionic liquids.^{22,24} Another approach that has been studied for the removal of ionic liquids consists of their adsorption in activated carbon, commercially available or modified.^{29–31} Anthony *et al.*²⁹ were the first to propose the use of activated carbon for the adsorption of 1-butyl-3-methylimidazolium hexafluorophosphate. More recently,

Departamento de Química, CICECO (www.ciceco.ua.pt), Universidade de Aveiro, 3810-193 Aveiro, Portugal. E-mail: jcoutinho@ua.pt; Fax: +351 234 370 084; Tel: +351 234 370 200

† Electronic supplementary information (ESI) available: Weight fraction percentage binodal data for the ternary systems composed of ionic liquid (1), salt (2) and water (3) at 298 K; Othmer–Tobias and Bancroft correlations; density and viscosity values of the coexisting phases in the temperature range between 298.15 K and 328.15 K. See DOI: 10.1039/c2ra21535g

Palomar and co-workers^{30,31} reported a detailed study on the adsorption of different ionic liquids into activated carbon. Besides the adsorption step, the recovery of the ionic liquid was further attempted by the addition of acetone.³¹ Again, this approach is only possible in diluted solutions and degradation reactions between acetone and some ionic liquids are prone to occur.

Taking into consideration previous works^{32–39} which reported aqueous biphasic systems composed of ionic liquids and salting-out species, we explored herein such a possibility as an alternative pathway for recovering ionic liquids from aqueous effluents. Ionic-liquid-based aqueous biphasic systems (ABS) are formed when two mutually incompatible, though both miscible with water, ionic liquid/salt aqueous solutions are mixed. Above a critical concentration of those components, spontaneous phase separation takes place. The pioneering work of Rogers and co-workers³⁵ demonstrated that the addition of a “kosmotropic” salt (like K_3PO_4) to an aqueous solution of a given ionic liquid can induce the phase separation: a top ionic-liquid-rich phase and a bottom salt-rich phase. After this proof of principle, several ionic-liquid-based ABS were further tested^{32,36,38,39} with the aim of recovering ionic liquids from aqueous effluents. Deng *et al.*³² presented the recovery of 1-allyl-3-methylimidazolium chloride with three inorganic salts: K_3PO_4 , K_2HPO_4 and K_2CO_3 . They found that, for the same concentration of salt, the recovery efficiency of the ionic liquid follows the order: $K_3PO_4 > K_2HPO_4 > K_2CO_3$,³² which is in good agreement with the Hofmeister series.⁴⁰ The authors³² also concluded that the increase of the concentration of the salt increases the recovery efficiency of the ionic liquid. They reached a maximum recovery efficiency of 96.80% using 46.48 wt% of K_2HPO_4 .³² In the same line of research, Li *et al.*³⁶ studied the effect of some sodium-based salts to recover the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate from aqueous media. The salts used were Na_3PO_4 , Na_2CO_3 , Na_2SO_4 , NaH_2PO_4 and $NaCl$, and the highest extraction efficiency (98.77%) was achieved with 16.94 wt% of Na_2CO_3 .³⁶ In a different perspective, and with the goal of reducing the use of charged species to recuperate ionic liquids from aqueous solutions, Wu *et al.*^{38,39} reported the recovery of different ionic liquids from aqueous solutions making use of carbohydrates. A recovery efficiency of 65% of 1-allyl-3-methylimidazolium bromide and 63% of 1-allyl-3-methylimidazolium chloride was achieved by the addition of sucrose.³⁹ On the other hand, with a distinct ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, and changing the sugar, the recovery efficiencies observed were higher, but still not satisfactory: 74% with sucrose, 72% with xylose, 64% with fructose and 61% with glucose.³⁸ Despite the possibility of employing carbohydrates to remove ionic liquids from aqueous media, one must be aware that it increases the amount of organic matter in the aqueous streams if large scale applications are envisaged. In addition, the tests with tetrafluoroborate-based ionic liquids must be carried out with special care since these fluids suffer hydrolysis in contact with water.⁴¹

Taking into account these previous results,^{32,36,38,39} and our previous experience on the effect of salts upon the solubility of ionic liquids in aqueous media⁸ as well as on the preparation of ABS for extraction purposes,^{33,34,37} we tested here the ability of two strong salting-out inducing species— $Al_2(SO_4)_3$ and $AlK(SO_4)_2$ —to create ABS and recover ionic liquids from

aqueous solutions. Besides the strong salting-out aptitude of these salts (according to the Hofmeister series⁴⁰) that may easily induce the phase separation of ionic liquids from aqueous media, they are actually used in water treatment processes.⁴² According to the USEPA (United States Environmental Protection Agency), alum, chlorine, lime and coagulant aids can be added directly to the public water storage and distribution systems to treat water, and make it suitable for public consumption.⁴² Therefore, here, ABS based on aluminium-based salts with imidazolium-, pyridinium- and phosphonium-based ionic liquids were studied, and are here reported, with the goal of developing improved systems for the removal and recovery of ionic liquids from aqueous streams. All the ternary systems studied were additionally characterized by measuring some of their tie-lines and tie-line lengths. The physical properties of the coexisting phases, namely density, viscosity, conductivity and pH values were also determined to fully characterize and gather a broader picture on the applicability of these systems. The adequacy of this approach to a series of removal/recovery cycles is also reported.

Results and discussion

The ternary phase diagrams of the two salts ($Al_2(SO_4)_3$ and $AlK(SO_4)_2$) and a large array of ionic liquids were firstly determined to obtain a wide characterization of these novel ABS. Contrarily to previous works,^{32,36,38,39} a large array of ionic liquids were studied here. The ionic liquids investigated, and that could be recovered from aqueous solutions by the addition of the $Al_2(SO_4)_3$, were $[C_2mim][CF_3SO_3]$, $[C_4mim][CF_3SO_3]$, $[C_4mim][Tos]$, $[C_4mim][N(CN)_2]$, $[C_8py][N(CN)_2]$, $[C_7H_7mim][C_2H_5SO_4]$, $[P_{1(444)}][Tos]$, $[P_{4444}Br]$, $[P_{4444}Cl]$ and $[P_{1444}][CH_3SO_4]$. On the other hand, with $AlK(SO_4)_2 \cdot 12H_2O$, from the series of ionic liquids investigated, only $[C_4mim][CF_3SO_3]$ and $[C_8py][N(CN)_2]$ could be recovered. Moreover, the ionic liquids $[C_4mim]Br$, $[C_4mim][C_2H_5SO_4]$ and $[C_8mim]Cl$ were also tested and found to be not sufficiently “hydrophobic” to undergo liquid–liquid demixing in the presence of the acidic aqueous solution of $Al_2(SO_4)_3$. Since we are dealing with acidic aqueous solutions, only a limited range of ionic liquids are capable of creating ABS, as shown in a previous work where we provided a critical assessment regarding the formation of ionic-liquid-based ABS under acidic media.⁴³ Besides the salting-out ability of the inorganic salt, the pH of the aqueous solution seems to play an important role on the formation of ionic-liquid-based ABS.

The structures of the ionic liquids that were successfully removed are depicted in Fig. 1.

The experimental solubility phase diagrams obtained, at 298 K and at atmospheric pressure, for the ternary systems composed of ionic liquid + salt + water are presented in Fig. 2.

The phase diagrams are separated by salts, and reported in weight fraction percentage units (the phase diagrams in molality units are provided in ESI†). Aiming at providing a general trend and to allow the reader to know the mass fraction content at a given point, Table 1 presents the parameters obtained by regression of the experimental binodal curves (in weight fraction percentage units) by the application of eqn (1)⁴⁴ described according to,

$$[IL] = A \exp[(B \times [Salt]^{0.5}) - (C \times [Salt]^3)] \quad (1)$$

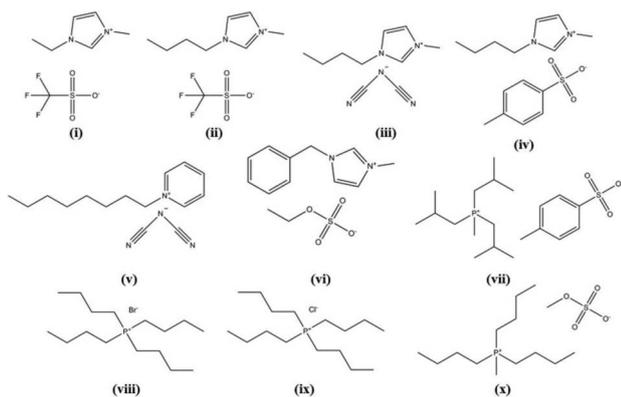


Fig. 1 Chemical structures of the ionic liquids used to form ABS: (i) [C₂mim][CF₃SO₃]; (ii) [C₄mim][CF₃SO₃]; (iii) [C₄mim][N(CN)₂]; (iv) [C₄mim][Tos]; (v) [C₈py][N(CN)₂]; (vi) [C₇H₇mim][C₂H₅SO₄]; (vii) [P₁₍₄₄₄₎₁][Tos]; (viii) [P₄₄₄₄]Br; (ix) [P₄₄₄₄]Cl; (x) [P₄₄₄₁][CH₃SO₄].

where [IL] and [Salt] are the ionic liquid and salt weight fraction percentage, respectively, and *A*, *B* and *C* are fitted constants obtained by the regression. In general, good correlation coefficients were obtained which indicate the reliability of eqn (1) in describing the experimental data.

The larger the biphasic region, the higher the ability of the salt to recover and remove the ionic liquid from solution. From the gathered data, the tendency of the ionic liquids to be recovered

Table 1 Parameters used for the regression of the experimental data by eqn (1) and the respective standard deviation, σ , and correlation coefficient, R^2 , for each ionic liquid + salt + H₂O system at 298 K

Ionic liquid	<i>A</i> ± σ	<i>B</i> ± σ	$10^5 (C \pm \sigma)$	R^2
Al ₂ (SO ₄) ₃				
[C ₂ mim][CF ₃ SO ₃]	84 ± 1	-0.267 ± 0.004	2.4 ± 0.1	0.9994
[C ₄ mim][CF ₃ SO ₃]	102 ± 3	-0.469 ± 0.013	6.6 ± 0.1	0.9888
[C ₄ mim][Tos]	118 ± 2	-0.355 ± 0.007	4.0 ± 0.2	0.9994
[C ₄ mim][N(CN) ₂]	73 ± 1	-0.259 ± 0.003	4.2 ± 0.1	0.9992
[C ₈ py][N(CN) ₂]	111 ± 1	-0.598 ± 0.004	3.8 ± 0.4	0.9983
[C ₇ H ₇ mim][C ₂ H ₅ SO ₄]	91 ± 1	-0.265 ± 0.002	2.3 ± 0.1	0.9998
[P ₁₍₄₄₄₎₁][Tos]	154 ± 4	-0.534 ± 0.010	8.6 ± 0.4	0.9977
[P ₄₄₄₄]Br	151 ± 6	-0.666 ± 0.016	4.2 ± 0.8	0.9912
[P ₄₄₄₄]Cl	145 ± 6	-0.564 ± 0.014	2.3 ± 0.3	0.9958
[P ₄₄₄₁][CH ₃ SO ₄]	132 ± 7	-0.551 ± 0.023	1.5 ± 1.1	0.9874
AlK(SO ₄) ₂				
[C ₄ mim][CF ₃ SO ₃]	89 ± 1	-0.473 ± 0.002	1.9 ± 0.1	0.9998
[C ₈ py][N(CN) ₂]	92 ± 1	-0.579 ± 0.009	1.6 ± 0.2	0.9972

by the addition of Al₂(SO₄)₃ follows the order: [C₈py][N(CN)₂] > [P₄₄₄₄]Br > [C₄mim][CF₃SO₃] > [P₁₍₄₄₄₎₁][Tos] ≈ [P₄₄₄₁][CH₃SO₄] ≈ [P₄₄₄₄]Cl > [C₄mim][N(CN)₂] > [C₄mim][Tos] > [C₂mim][CF₃SO₃] > [C₇H₇mim][C₂H₅SO₄]. Concerning the AlK(SO₄)₂ salt, [C₈py][N(CN)₂] is more easily removed from solution than [C₄mim][CF₃SO₃]. Although this latter salt could only salt-out two of the studied ionic liquids it has the advantage that the concentration necessary to promote ABS, and consequently to remove ionic liquids from water streams, is lower than that required by using Al₂(SO₄)₃. In general, the trends found for the ionic liquids ability in creating ABS are in good agreement with our previous works using distinct inorganic salts.^{37,43,45,46} For these different salts, concentrations of ≈ 22 wt% of Na₂SO₄⁴³ or ≈ 40 wt% of K₃PO₄^{37,45,46} were needed to salt-out the different ionic liquids.

The tie-lines (TLs) and tie-line lengths (TLLs) for each system were also determined at 298 K. The consistency of the TLs was further checked using the Othmer–Tobias⁴⁷ and Bancroft⁴⁸ correlations—the correlation of each system is provided in ESI†. The total mixture compositions, the weight fraction percentage compositions of the coexisting phases (TLs), and the respective TLLs, are reported in Table 2.

In addition, the critical point of each system (the mixture composition for which the composition of the two aqueous phases are equal) is presented in Table 3. Due to the low solubility of the salt AlK(SO₄)₂ in water it was only possible to have one TL for each system. Therefore the calculation of the critical points was not carried out with this type-based systems. As an example, Fig. 3 depicts the results obtained for the TLs and critical point for the system composed of [P₄₄₄₄]Br + Al₂(SO₄)₃ + H₂O.

Aiming at exploring the viability of the proposed systems for wastewater treatment and to recover ionic liquids from aqueous effluents, Table 2 presents the values of the recovery efficiencies of the various ionic liquids determined according to,

$$\%R = \frac{[\text{IL}]_{\text{IL}} \times m_{\text{IL}}}{[\text{IL}]_{\text{IL}} \times m_{\text{IL}} + [\text{IL}]_{\text{Salt}} \times m_{\text{Salt}}} \times 100 \quad (2)$$

where “IL” and “Salt” symbolize, respectively, the ionic-liquid- and salt-rich phases, [Salt] and [IL] are the weight fraction percentage of inorganic salt and ionic liquid, and *m* is the mass of each phase.

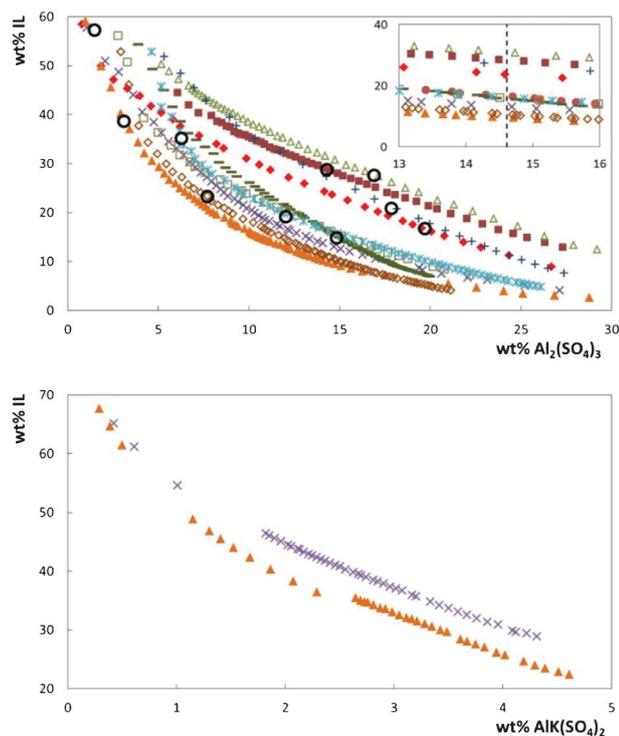


Fig. 2 Ternary phase diagrams for systems composed of ionic liquid + aluminium-based salt + water at 298 K and atmospheric pressure (weight fraction units): ■, [C₂mim][CF₃SO₃]; ×, [C₄mim][CF₃SO₃]; +, [C₄mim][Tos]; ◆, [C₄mim][N(CN)₂]; ▲, [C₈py][N(CN)₂]; △, [C₇H₇mim][C₂H₅SO₄]; —, [P₁₍₄₄₄₎₁][Tos]; ◇, [P₄₄₄₄]Br; ✱, [P₄₄₄₄]Cl; □, [P₄₄₄₁][CH₃SO₄]; ○, critical point.

Table 2 Weight fraction percentage of ionic liquid and salt (wt%) in the total mixture and in the ionic-liquid-rich and salt-rich phases, at 298 K, and respective values of TLL. The percentage recovery efficiency of each ionic liquid at a given TL is given as %R

Ionic liquid	weight fraction percentage/wt (%)						TLL	%R
	[IL] _{IL}	[Salt] _{IL}	[IL] _M	[Salt] _M	[IL] _{Salt}	[Salt] _{Salt}		
	Al ₂ (SO ₄) ₃							
[C ₂ mim][CF ₃ SO ₃]	56.84	2.21	44.96	9.96	6.10	35.34	60.60	97.1
	63.19	1.19	45.00	13.01	3.44	40.02	71.27	97.9
	68.32	0.64	45.08	15.85	1.89	44.14	79.41	98.7
	60.20	1.62	39.82	15.04	4.20	38.48	67.04	96.4
[C ₄ mim][CF ₃ SO ₃]	73.51	0.47	44.97	9.96	4.49	23.43	72.74	96.1
	76.21	0.37	44.96	13.02	1.10	30.77	81.02	99.0
	82.14	0.20	44.92	15.90	0.41	34.67	88.70	99.7
[C ₄ mim][Tos]	57.09	4.10	45.06	13.00	0.20	46.16	70.75	99.9
	61.49	3.31	44.98	15.88	0.06	50.08	77.21	100.0
	54.02	4.74	40.10	15.00	0.33	44.31	66.69	99.8
[C ₄ mim][N(CN) ₂]	58.66	0.68	45.09	9.94	0.95	40.04	69.85	99.6
	63.53	0.27	44.90	13.03	0.41	43.51	76.51	99.8
	69.30	0.03	44.98	15.88	0.28	45.01	82.38	99.8
	61.45	0.42	40.12	14.96	0.62	41.87	73.61	99.5
[C ₈ py][N(CN) ₂]	59.03	1.12	24.99	14.98	3.69	23.66	59.75	91.1
	66.54	0.73	45.04	9.95	1.94	28.41	70.29	98.8
	70.82	0.57	45.08	12.99	0.72	34.41	77.84	99.6
	75.38	0.42	44.98	15.88	0.31	38.60	84.22	99.8
[C ₇ H ₇ mim][C ₂ H ₅ SO ₄]	53.66	4.01	45.02	9.98	5.46	37.35	58.61	98.1
	59.88	2.54	44.70	13.10	2.92	42.15	69.38	98.4
	65.37	1.59	44.95	15.99	1.44	46.67	78.22	99.0
	56.77	3.21	39.86	15.03	3.82	40.20	64.58	97.1
[P _{i(444)1}][Tos]	56.15	3.53	45.16	9.93	0.10	36.17	64.86	100.0
	61.88	2.89	44.87	13.04	0.02	39.81	72.04	100.0
	67.99	2.32	44.80	15.93	0.01	42.22	78.82	100.0
[P ₄₄₄₄ Br]	63.40	1.69	44.94	9.97	1.37	29.51	67.98	99.2
	70.60	1.30	45.05	13.00	0.68	33.32	76.91	99.5
	76.70	1.03	44.82	15.93	0.33	36.72	84.30	99.7
[P ₄₄₄₄ Cl]	55.46	2.90	37.49	14.03	1.59	36.28	63.37	98.6
	55.44	2.90	44.85	10.00	1.01	39.42	65.55	99.6
	60.13	2.43	44.90	12.98	0.50	43.71	72.53	99.8
[P ₄₄₄₁][CH ₃ SO ₄]	58.34	2.21	44.95	9.97	2.81	34.38	64.18	98.7
	63.89	1.75	44.76	13.07	1.81	38.49	72.13	98.9
	70.16	1.33	45.03	15.87	1.33	41.14	79.52	99.1
	61.75	1.91	40.11	14.97	1.91	38.00	69.88	98.4
	AlK(SO ₄) ₂							
[C ₄ mim][CF ₃ SO ₃]	61.21	0.61	51.00	2.18	4.77	9.27	57.11	97.4
[C ₈ py][N(CN) ₂]	68.62	0.26	50.99	2.18	6.00	15.86	53.07	95.8

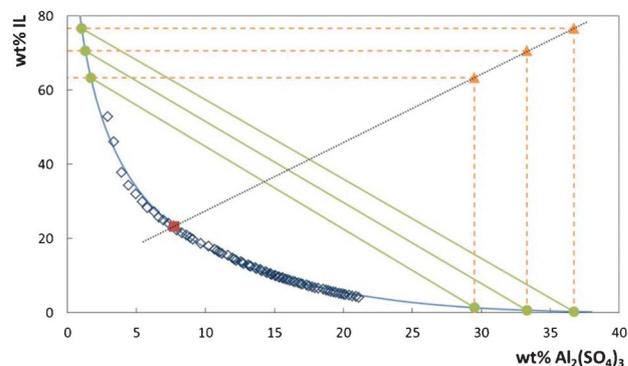
For an easier analysis of the recovery efficiencies of all ionic liquids, all the gathered results are depicted in Fig. 4 and 5.

Fig. 4 shows the results for phosphonium- and pyridinium-based ionic liquids, whereas Fig. 5 illustrates the effect of the ionic liquid anion and cation composing imidazolium-based fluids.

Table 3 Critical point of each system composed of ionic liquid + Al₂(SO₄)₃ + H₂O at 298 K

Ionic liquid	Critical Point/wt (%)	
	[IL]	[Salt]
[C ₂ mim][CF ₃ SO ₃]	14.32	28.72
[C ₄ mim][CF ₃ SO ₃]	1.49	57.15
[C ₄ mim][Tos]	17.88	20.79
[C ₄ mim][N(CN) ₂]	19.72	16.68
[C ₈ py][N(CN) ₂]	3.13	38.55
[C ₇ H ₇ mim][C ₂ H ₅ SO ₄]	16.91	27.50
[P _{i(444)1}][Tos]	14.86	14.78
[P ₄₄₄₄ Br]	7.72	23.25
[P ₄₄₄₄ Cl]	35.03	6.29
[P ₄₄₄₁][CH ₃ SO ₄]	12.05	19.04

Fig. 4 and 5, and Table 2, show that remarkable results on the recovery of ionic liquids from aqueous media can be obtained. The recovery efficiencies of the diverse ionic liquids are always above 96% and for a large number of systems *circa* 100% of

**Fig. 3** Binodal curve, TLLs and critical point for the system composed of [P₄₄₄₄Br] + Al₂(SO₄)₃ + H₂O at 298 K: ◇, experimental binodal data; ●, TLL data; ▲, TLLs relation; ■, critical point.

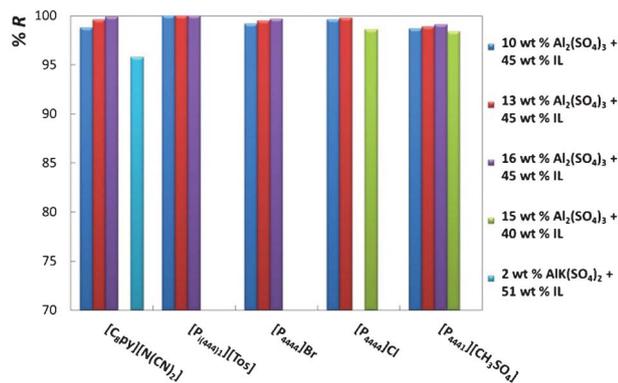


Fig. 4 Percentage recovery efficiencies (%R) of phosphonium- and pyridinium-based ionic liquids at diverse mixture compositions.

recuperation was achieved. In particular, the fluids $[C_4mim][Tos]$, $[P_{i(444)1}][Tos]$ and $[C_4mim][N(CN)_2]$ show recovery efficiencies above 99.5%, and for $[C_4mim][N(CN)_2]$ the amount of inorganic salt at the IL-rich phase is inferior to 0.7 wt%. In addition, the ionic liquid concentration in the salt-rich phase is low, and ranges from 0.01 wt% with $[P_{i(444)1}][Tos]$ to 6.10 wt% with $[C_2mim][CF_3SO_3]$, both with the salt $Al_2(SO_4)_3$. For a fixed concentration of ionic liquid, and increasing the concentration of inorganic salt, there is an increase on the recovery efficiency of the ionic liquid, as depicted in Fig. 4 and 5. These results agree with the observations reported before by other authors.^{32,36} Regarding the $AlK(SO_4)_2$, the recoveries of the ionic liquids are also high (97.4% for $[C_4mim][CF_3SO_3]$ and 95.8% for $[C_8py][N(CN)_2]$), and remarkably they were achieved using only 2 wt% of salt in the total mixture composition. The main handicap of this salt is its inability to promote ABS with a larger matrix of ionic liquids.

The results gathered show that it is possible, by a proper selection of the salting-out species used, to achieve an enhanced recovery of ionic liquids from aqueous solutions. Previous works reported recovery efficiencies of ionic liquids substantially lower: 61–74% with carbohydrates^{38,39} and 96.80% with the addition of 46.48 wt% of K_2HPO_4 ³³ or 98.77% with the addition of 16.94 wt% of Na_2CO_3 .³⁶ With aluminium-based salts, commonly used in water treatment processes, the recovery efficiencies of

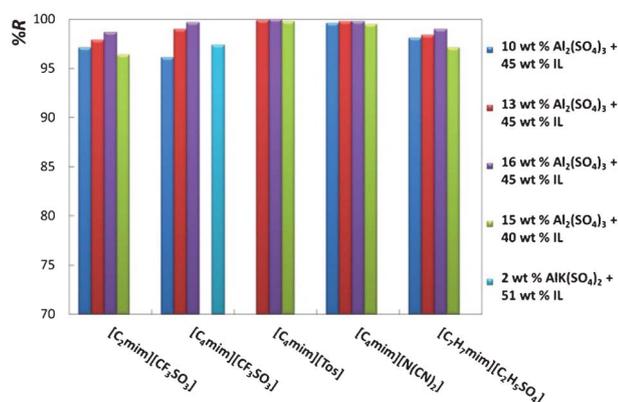


Fig. 5 Percentage recovery efficiencies (%R) of imidazolium-based ionic liquids at diverse mixture compositions.

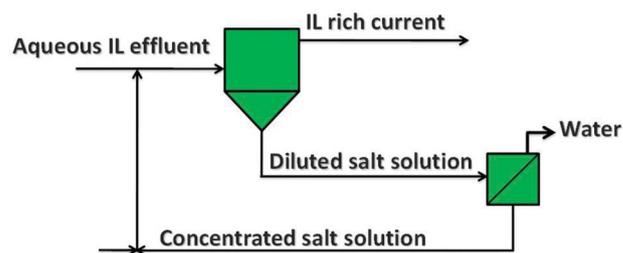


Fig. 6 Configuration of the global process for the recovery of ionic liquids from aqueous effluents.

ionic liquids are greatly improved. Moreover, the amount of inorganic salt used in this work is substantially lower than those previously reported with other salts.^{32,36}

Based on the enhanced recovery efficiencies obtained, the use of aluminium-based two-phase systems, and their scale-up and adaptation to new processes involving ionic liquids, is straightforwardly envisaged. A graphical representation of the process configuration is depicted Fig. 6. This process was tested with the ionic liquid $[P_{i(444)1}][Tos]$ in several recovery cycles, and the results obtained are depicted in Fig. 7. For each cycle, the recovery is always *circa* to 100% and proves the recyclability of the inorganic salt.

Since we are dealing with two charged species, one of the main concerns is the possibility of ion exchange. Therefore, aiming at evaluating if any ion exchange is occurring during the formation of ABS and further phase separation—to check if the ionic liquid recovered is a non-contaminated fluid—several analytical and spectroscopic techniques were applied to the characterization of the recovered coexisting phases of the systems composed of $[P_{i(444)1}][Tos]$ and $[C_4mim][N(CN)_2]$. The detection of the sulfate anion was carried out with Fourier Transform Infrared spectroscopy. The Al^{3+} and $[P_{i(444)1}]^+$ cations, at both aqueous phases, were quantified by Inductively Coupled Plasma Optical Emission Spectrometry. The imidazolium cation and tosylate anion contents were quantified by UV-Vis spectroscopy. From the results obtained we can guarantee that there is no ion exchange in these systems, and that the amount of each ion at each phase is in good agreement with those estimated from the tie-lines.

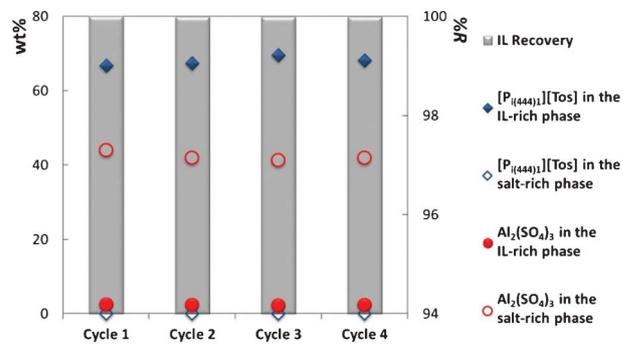


Fig. 7 Recovery of $[P_{i(444)1}][Tos]$ in several cycles using 16 wt% $Al_2(SO_4)_3$ + 45 wt% IL, and concentration of salt and ionic liquid in both aqueous phases at the end of each cycle.

The thermophysical properties of the coexisting phases are of crucial relevance to evaluate the applicability and potential scale up of the process here proposed. Therefore, the density, viscosity, conductivity and pH values of the coexisting phases were measured for ABS composed of 15 wt% of $\text{Al}_2(\text{SO}_4)_3$ + 45 wt% of water + 40 wt% of ionic liquid, and 2 wt% of $\text{AlK}(\text{SO}_4)_2$ + 45 wt% of water + 51 wt% of ionic liquid. The data obtained at 298 K are reported in Table 4. The compositions of each phase correspond to the TLs compositions reported in Table 2.

The results obtained indicate that for almost all systems the two phases present low pH values. Although these low pH values are a result of the acidic nature of the inorganic salt by itself (pH = 2.12 for an aqueous solution with 15 wt% of $\text{Al}_2(\text{SO}_4)_3$ and pH = 3.15 for an aqueous solution with 5 wt% of $\text{AlK}(\text{SO}_4)_2$), the influence of the ionic liquid is also noted. The greatest impact is shown in ABS containing ionic liquids with the alkaline anion $[\text{N}(\text{CN})_2]^-$ that increases the pH values of the phases (albeit remaining acidic). This trend was previously verified by us with a distinct inorganic salt and a broad number of ionic liquids.⁴³

The conductivity of the coexisting phases in ionic-liquid-based ABS is here reported for the first time. This property is also crucial since it reflects the charge density of the phase and the mobility of the ions in aqueous solutions. The values obtained range between (10.5 and 46.4) mS cm^{-1} for $[\text{P}_{i(444)1}][\text{Tos}]$ and $[\text{CF}_3\text{SO}_3]$ -based ionic liquids, respectively, in the ionic-liquid-rich phase and with the salt $\text{Al}_2(\text{SO}_4)_3$. Regarding the salt-rich phase the values range between 6.20 mS cm^{-1} for $[\text{C}_4\text{mim}][\text{Tos}]$ and 32.0 mS cm^{-1} for the system composed of $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ and $\text{AlK}(\text{SO}_4)_2$.

The density and viscosity are relevant properties when envisaging the application of these systems in a large scale at

an industrial level. Concerning the $\text{Al}_2(\text{SO}_4)_3$, the viscosity of the ionic-liquid-rich phase ranges from 3.74 mPa s^{-1} for the system containing $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ to 19.4 mPa s^{-1} for the system composed of $[\text{P}_{4444}]\text{Br}$. On the other hand, in the salt-rich phase, the values range between (8.18 and 17.2) mPa s^{-1} for the ionic liquids $[\text{P}_{4444}]\text{Br}$ and $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$, respectively. Albeit it was expected that the ionic-liquid-rich phase would be more viscous, this is not observed for most of the systems evaluated. Indeed, this trend is only verified in the systems composed of $[\text{C}_8\text{py}][\text{N}(\text{CN})_2]$, $[\text{P}_{4444}]\text{Br}$ and $[\text{P}_{i(444)1}][\text{Tos}]$. These ionic liquids present a larger biphasic region and, consequently, their concentration at the salt-rich phase is smaller when compared with other ionic liquids. This can also be explained by the amount of water at the coexisting phases, since these systems present lower water contents at the ionic-liquid-rich phase. Comparing the viscosity of $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ -based ABS formed with other salts⁴⁹ and sugars,³³ the data here reported indicate slightly higher viscosities, albeit well below to those displayed by common polymer-based ABS.^{50–52} With the salt $\text{AlK}(\text{SO}_4)_2$, the viscosity is higher for the ionic-liquid-rich phase (3.95 mPa s^{-1} for the system containing $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ and 6.92 mPa s^{-1} for the system with $[\text{C}_8\text{py}][\text{N}(\text{CN})_2]$) when compared with the salt-rich phase, and is generally lower when compared with those displayed by the salt $\text{Al}_2(\text{SO}_4)_3$.

The density data shows that, for almost all systems, the salt-rich phase is denser than the ionic-liquid-rich phase. The exception to that rule is the system with $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ and $\text{AlK}(\text{SO}_4)_2$, and where an inversion of the phases was observed. These results are in close agreement with other systems previously reported.^{34,46,50} This is a direct consequence of the low concentration of salt at the ionic-liquid-rich phase and of the high density of the fluorinated ionic liquid.³³ The values for the ionic-liquid-rich phase range from 1.00 g cm^{-3} for the system containing the $[\text{P}_{4444}]\text{Cl}$ and 1.24 g cm^{-3} for the system employing the $[\text{C}_2\text{mim}][\text{CF}_3\text{SO}_3]$. For the salt-rich phase the values range between 1.04 g cm^{-3} for the system with $[\text{C}_8\text{py}][\text{N}(\text{CN})_2]$ + $\text{AlK}(\text{SO}_4)_2$ and 1.31 g cm^{-3} for the aqueous system composed of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ + $\text{Al}_2(\text{SO}_4)_3$. In general, the systems here reported present lower densities than the ones already reported in literature with ionic liquids and other salts,^{45,49} as well as those involving polymers.^{50–52}

Conclusions

This work discloses a novel and efficient method to remove and recover ionic liquids from contaminated water streams. It makes use of the strong salting-out inducing ability of aluminium-based salts to create ABS that allow the removal of hydrophilic ionic liquids from diluted aqueous solutions by concentrating them into a second liquid phase. Aiming at gathering a broader picture on the amount of salts necessary to treat the contaminated effluents, the ternary phase diagrams, critical points, TLs and TLLs were determined at 298 K. The addition of $\text{Al}_2(\text{SO}_4)_3$ and $\text{AlK}(\text{SO}_4)_2$ to aqueous solutions containing ionic liquids leads, for most of the systems, to a recovery efficiency of *circa* 100%, while reducing the ionic liquid concentration in the aqueous solution from 45 wt% to values around 1 wt%. By applying several cycles in the process here proposed, it was possible to guarantee that the salt can be recycled and the ionic liquid is completely recovered.

Table 4 Experimental data of pH, conductivity (κ), density (ρ) and viscosity (η) of the coexisting phases in diverse ABS composed of 40 wt% of ionic liquid + 15 wt% of $\text{Al}_2(\text{SO}_4)_3$ + 45 wt% of H_2O or 51 wt% of ionic liquid + 2 wt% of $\text{AlK}(\text{SO}_4)_2$ + 47 wt% of H_2O at 298 K

Ionic liquid	Phase	pH	$\kappa/(\text{mS cm}^{-1})$	$\rho/(\text{g cm}^{-3})$	$\eta/(\text{mPa s})$
	$\text{Al}_2(\text{SO}_4)_3$				
[C ₂ mim][CF ₃ SO ₃]	IL	1.72	46.4	1.2394	3.7823
	Salt	1.63	13.7	1.2911	12.214
[C ₄ mim][CF ₃ SO ₃]	IL	1.84	46.4	1.2374	3.7387
	Salt	1.72	19.7	1.2899	12.128
[C ₄ mim][Tos]	IL	2.58	13.4	1.1355	9.3852
	Salt	1.58	6.20	1.2969	15.568
[C ₄ mim][N(CN) ₂]	IL	4.82	44.1	1.0415	4.5958
	Salt	2.53	13.5	1.3135	17.177
[C ₈ py][N(CN) ₂]	IL	5.07	24.6	1.0105	11.372
	Salt	2.61	17.9	1.2630	8.8931
[C ₇ H ₇ mim][C ₂ H ₅ SO ₄]	IL	1.81	20.3	1.1642	6.9866
	Salt	1.51	13.2	1.3061	15.242
[P _{i(444)1}][Tos]	IL	1.45	10.5	1.0709	14.363
	Salt	0.98	13.2	1.2802	10.527
[P ₄₄₄₄ Br]	IL	1.23	15.8	1.0591	19.382
	Salt	1.00	21.0	1.2696	8.1799
[P ₄₄₄₄ Cl]	IL	1.35	21.6	0.9999	12.795
	Salt	1.20	7.78	1.2928	13.020
[P ₄₄₄₁][CH ₃ SO ₄]	IL	1.87	12.8	1.0495	10.385
	Salt	1.52	7.94	1.3045	14.579
	$\text{AlK}(\text{SO}_4)_2$				
[C ₄ mim][CF ₃ SO ₃]	IL	3.83	29.2	1.1632	3.9547
	Salt	3.03	32.0	1.0596	1.3749
[C ₈ py][N(CN) ₂]	IL	5.77	25.4	1.0088	6.921
	Salt	3.74	18.8	1.0396	1.6005

The results here obtained constitute the first report on a complete recovery of ionic liquids from aqueous solutions making use of inorganic salts already used in water treatment processes, and could represent a major contribution for the development of industrial processes based on ionic liquids.

Experimental

Materials

Several ABS composed of the following ionic liquids: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (triflate), [C₂mim][CF₃SO₃], purity 99 wt%; 1-butyl-3-methylimidazolium trifluoromethanesulfonate (triflate), [C₄mim][CF₃SO₃], purity 99 wt%; 1-butyl-3-methylimidazolium tosylate, [C₄mim][Tos], purity 98 wt%; 1-butyl-3-methylimidazolium dicyanamide, [C₄mim][N(CN)₂], purity >98 wt%; 1-octylpyridinium dicyanamide, [C₈py][N(CN)₂], purity >98 wt%; 1-benzyl-3-methylimidazolium ethylsulfate, [C₇H₇mim][C₂H₅SO₄], purity 98 wt%; tri(isobutyl)methylphosphonium tosylate, [P_{i(444)}][Tos], purity 98 wt%; tetrabutylphosphonium bromide, [P₄₄₄₄][Br], purity 95 wt%; tetrabutylphosphonium chloride, [P₄₄₄₄][Cl], purity 97 wt%; tributylmethylphosphonium methylsulfate, [P₄₄₄₁][CH₃SO₄], purity 96–98 wt% were investigated in this work. All imidazolium- and pyridinium-based ionic liquids were purchased from Iolitec. The phosphonium-based ionic liquids were kindly supplied by Cytec Industries Inc. To reduce the volatile impurities contents to negligible values, individual samples of ionic liquids were further purified under constant agitation at vacuum and moderate temperature (343 K) for a minimum of 24 h. After this purification approach, the purity of each ionic liquid was checked by ¹H and ¹³C NMR spectra, and ¹⁹F and ³¹P NMR spectra whenever applicable, and found to be according to the purities given by the suppliers.

The inorganic salts Al₂(SO₄)₃ and AlK(SO₄)₂·12H₂O were acquired from Himedia (purity ≥ 98.0 wt%) and from Carlo Erba (purity ≥ 99.5 wt%), respectively. The water employed was double distilled, passed across a reverse osmosis system and further treated with Milli-Q plus 185 water purification equipment. The buffers used in the calibration of the pH meter equipment were solutions with pH values of 4.00 and 7.00, acquired from Panreac. In order to calibrate the conductivity meter, standard solutions of KCl with concentrations of 0.1 and 0.01 M were diluted from a standard solution of 1 M supplied by Mettler Toledo and used.

Methods

Phase diagrams and tie-lines. Aqueous solutions of Al₂(SO₄)₃ at ≈ 36 wt% and AlK(SO₄)₂ at ≈ 7 wt%, and aqueous solutions of the different hydrophilic ionic liquids at ≈ 90 wt%, were prepared and used for the determination of the ternary phase diagrams. Note that for the salt AlK(SO₄)₂ the concentrations reported on the phase diagrams were calculated without the contribution of the water complexed with the salt. The solubility curves were determined at 298 (±1) K and at atmospheric pressure through the cloud point titration method and as previously described by us.^{33,37,53} Drop-wise addition of each aqueous inorganic salt solution to each ionic liquid aqueous solution, or vice-versa, was carried out until the detection of a cloudy (liquid–liquid biphasic solution), followed by drop-wise addition of ultra-pure water until the observation of a clear and

limpid solution (fitting into the monophasic regime). Drop-wise additions were carried out under constant stirring. The ternary systems compositions were determined by weight quantification of all components within ± 10^{−4} g (using an analytical balance, Mettler Toledo Excellence XS205 DualRange). With the salt AlK(SO₄)₂·12H₂O only the ionic liquids [C₈py][N(CN)₂] and [C₄mim][CF₃SO₃] were found to undergo liquid–liquid demixing.

Tie-lines (TLs) were determined by a gravimetric method originally proposed by Merchuk *et al.*⁴⁴ For that purpose, ternary mixtures of known total composition at the biphasic region and composed of ionic liquid + salt + water were gravimetrically prepared within ± 10^{−4} g, vigorously agitated, and left to equilibrate for at least 12 h at 298 (±1) K, aiming at a complete separation of both phases. After a careful separation step, both ionic liquid and salt phases were weighed within ± 10^{−4} g. Each TL was determined by a mass balance approach through the relationship between the ionic-liquid-rich mass phase composition and the overall system composition, and for which the following system of four equations (eqn (3)–(6)) and four unknown values ([IL]_{IL}, [IL]_{Salt}, [Salt]_{IL} and [Salt]_{Salt}) was solved:⁴⁴

$$[\text{IL}]_{\text{IL}} = A \exp[(B \times [\text{Salt}]_{\text{IL}}^{0.5}) - (C \times [\text{Salt}]_{\text{IL}}^3)] \quad (3)$$

$$[\text{IL}]_{\text{Salt}} = A \exp[(B \times [\text{Salt}]_{\text{Salt}}^{0.5}) - (C \times [\text{Salt}]_{\text{Salt}}^3)] \quad (4)$$

$$[\text{IL}]_{\text{IL}} = \frac{[\text{IL}]_{\text{M}}}{\alpha} - \frac{1-\alpha}{\alpha} \times [\text{IL}]_{\text{Salt}} \quad (5)$$

$$[\text{Salt}]_{\text{IL}} = \frac{[\text{Salt}]_{\text{M}}}{\alpha} - \frac{1-\alpha}{\alpha} \times [\text{Salt}]_{\text{Salt}} \quad (6)$$

where “IL”, “Salt” and “M” designate the ionic-liquid-rich phase, the salt-rich phase and the mixture, respectively; [Salt] and [IL] represent, respectively, the weight fraction percentage of salt and ionic liquid; and α is the ratio between the mass of the ionic-liquid-rich phase and the total mass of the mixture. The system solution results in the concentration (wt%) of the ionic liquid and inorganic salt in the ionic-liquid- and salt-rich phases, and thus, TLs can be simply represented.

For the calculation of individual tie-line lengths (TLLs), the following equation was employed:

$$\text{TLL} = \sqrt{([\text{Salt}]_{\text{IL}} - [\text{Salt}]_{\text{Salt}})^2 + ([\text{IL}]_{\text{IL}} - [\text{IL}]_{\text{Salt}})^2} \quad (7)$$

where “IL” and “Salt” symbolize, respectively, the ionic-liquid- and salt-rich phases, and [Salt] and [IL] are the weight fraction percentage of inorganic salt and ionic liquid, as described before.

The critical point (the mixture composition at which the composition of the two aqueous phases becomes identical) of each system was also estimated.^{54,55} This was accomplished by extrapolating the TL slopes of individual systems followed by a further fitting using eqn (8),

$$[\text{IL}] = f[\text{Salt}] + g \quad (8)$$

where [IL] and [Salt] are the concentration of ionic liquid and salt in weight fraction percentage, respectively, and *f* and *g* are the fitting parameters. The parameters values obtained and respective correlation coefficient (*R*²) are reported in ESI†.

The thermophysical properties of the coexisting phases, namely pH, conductivity, density and viscosity, were determined for total mixture compositions of 40 wt% of ionic liquid + 15 wt% of $\text{Al}_2(\text{SO}_4)_3$ + 45 wt% of water, and 51 wt% of ionic liquid + 2 wt% of $\text{AlK}(\text{SO}_4)_2$ + 45 wt% of water. For such mixture compositions, the respective TLs were determined in order to know the composition of each aqueous phase.

pH determination. The pH and conductivity measurements (± 0.02 and $\pm 0.5\%$, respectively) of the ionic-liquid-rich and inorganic-salt-rich aqueous phases were measured at 298 (± 1) K using a Mettler Toledo S47 SevenMulti™ dual meter pH/conductivity equipment. The calibration of the pH meter was carried out with two different buffers with pH values of 4.00 and 7.00, while the calibration of the conductivity meter was carried out with KCl aqueous solutions.

Density and viscosity determination. Density and viscosity measurements were performed at atmospheric pressure and in the temperature range between (298.15 and 328.15) K for both the ionic-liquid-rich and inorganic-salt-rich phases (the complete data with the dependence on temperature are available in ESI†), using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter uses Peltier elements for fast and efficient thermostatisation. Further details regarding the operation system can be found elsewhere.^{49,56} The uncertainty in temperature is within ± 0.02 K, the relative uncertainty for the dynamic viscosity is $\pm 0.35\%$ and the absolute uncertainty for the density is $\pm 5 \times 10^{-4}$ g cm⁻³.

Ultraviolet-visible spectroscopy/inductively coupled plasma-optical emission spectrometry/fourier transform infrared spectroscopy. The TL compositions for systems with the ionic liquids $[\text{P}_{i(444)}][\text{Tos}]$ and $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ were confirmed, aiming at checking that there is no ion exchange among the phases, by Ultraviolet-Visible (UV-Vis) spectroscopy, ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) and FTIR (Fourier Transform Infrared) spectroscopy. The amount of imidazolium- and tosylate-based ionic liquids in each aqueous phase was determined by UV-spectroscopy using a SHIMADZU UV-1700 Pharma-Spec Spectrophotometer at a wavelength of 211 and 222 nm (using calibration curves previously established), respectively. The aluminium and phosphonium content at the coexisting phases was quantified by ICP-OES using a Jobin Yvon 70 plus, power 880 W, under a plasma gas flow of 16 mL min⁻¹ and pressure of 2.6 bar. The FTIR spectra, with a resolution of 4 cm⁻¹, were obtained using a Perkin Elmer BX spectrometer operating in the attenuated total reflection (ATR) mode (equipped with a single horizontal Golden Gate ATR cell).

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