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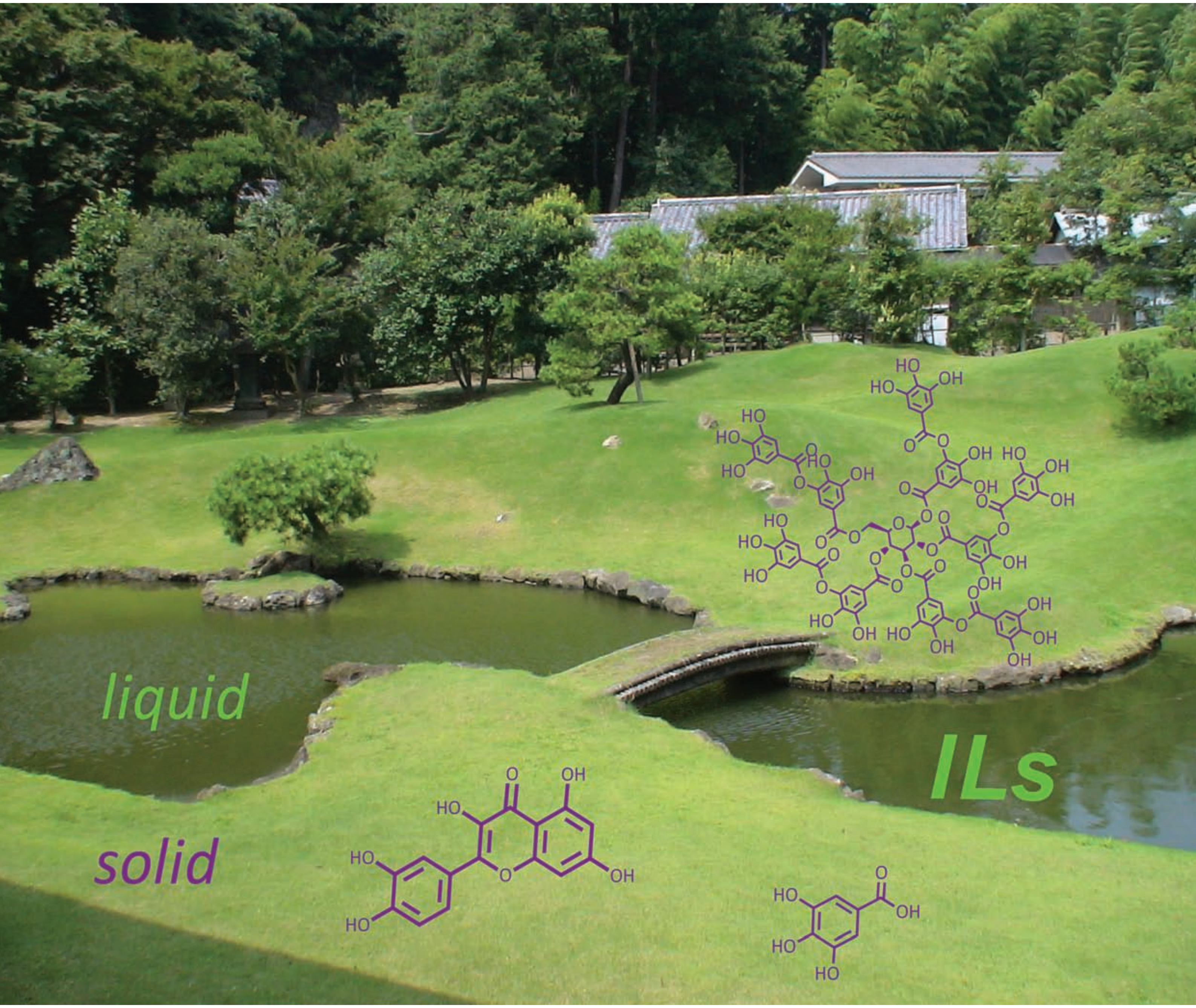

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Phase equilibrium phenomena in solutions involving tannins, flavonoids and ionic liquids

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This work presents a foremost systematic study on the solubility of phenolic compounds (tannic acid, quercetin and gallic acid) in ionic liquids. A series of 1-butyl-3-methylimiazolium salts of hexafluorophosphate, tetrafluoroborate, trifluoromethanesulfonate and bis(trifluoromethylsulfonyl)amide derivatives were used in this research. The solid–liquid equilibrium measurements in binary systems were carried out by using a dynamic method from 273 K to 413 K. Among all tested ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate was found to be the best solvent for tannic acid. The solubility of tannic acid was lower for [bmim][PF_6] and decreased for [bmim][OTf] and [bmim][NTf_2]. The solubility of tannic acid in ionic liquids follows the E^N_T polarity scale of the studied ionic liquids. Furthermore, tetrafluoroborate and hexafluorophosphate ionic liquids confirmed their ability to form hydrofluoric acid at elevated temperatures and in the presence of water traces. Differential scanning calorimetry was used to determine the melting point, the enthalpy of melting and the temperature and enthalpies of the solid–solid phase transitions, for the first time for the investigated valuable phenolic compounds. The obtained results accompanied by the solubility of carbohydrates in ionic liquids can serve for a design of the future extraction of value added compounds from raw biomass.

Introduction

Recently, ionic liquids (ILs) have become the subject of significant attention due to their unique properties that distinguish them from conventional solvents. Particularly, the physicochemical properties, such as polarity,[1] solvent power,[2] viscosity and the affinity of numerous ILs towards water and other compounds can direct their processing in multiphase systems.[3]

Ionic liquids are intrinsically excellent candidates for industrial applications in comparison to volatile organic solvents (VOCs). The fact of having negligible vapour pressure[4] permits their use instead of hazardous VOCs. An example of such an application is the extraction of products from *i.e.* post-esterification reaction mixture[5] that can be carried out by supercritical CO_2 in the presence of IL.[6] Among "green" solvents, ILs are attractive catalysts, battery electrolytes and lubricants.[7]

The literature about the cytotoxicity of ILs has been growing extensively in the past few years.[8,9] However, studies on the toxicity of ILs are not yet very conclusive, since little is still known about their biodegradability and biotoxicity.[10] That is why it is difficult to employ ILs in a large scale applications. Furthermore, ILs containing anions, such as [BF_4^-] and [PF_6^-] cause additional problems because in the presence of water at elevated temperatures HF acid is formed.

An immeasurable combination of cations and anions forming ionic liquids opens the space for potentially endless employment in various fields of science. However, a proper design of reaction or process requires the knowledge of thermophysical properties of ILs, such as melting temperature (T_m), temperature of phase transitions (T_{tr}) and so on. This data set proved to be important both to perform data processing and to determine the reaction temperature range.[11]

Among the various investigated ionic liquids the most studied ILs are composed of organic cations, such as: imidazolium, ammonium, phosphonium, pyrazolium and pyridinium, and contain counterions, such as: [BF_4^-], [PF_6^-], [$CF_3SO_3^-$] ([OTf^-]) and [$(CF_3SO_2)_2N^-$] ([NTf_2^-]). The ionic liquids studied in this work are illustrated in Fig. 1.

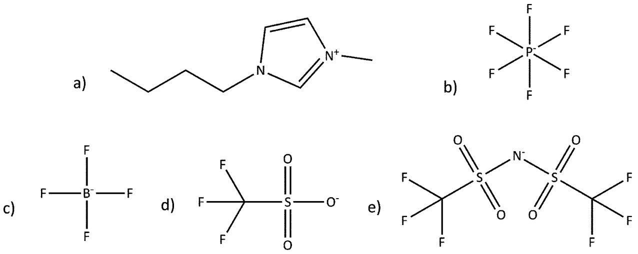

Fig. 1 The ions of the ionic liquids studied in this work: a) cation: 1-butyl-3-methylimidazolium; anions: b) hexafluorophosphate, c) tetrafluoroborate, d) trifluoromethanesulfonate, e) bis(trifluoromethylsulfonyl)amide.

A second group of compounds being the subject of this work are phenolics. Tannins (tannic acid) and flavonoids (quercetin) similarly to gallic acid belong to phenols. These groups of

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compounds are bioactive substances exhibiting a variety of beneficial effects, including being antioxidant, anti-microbial, anti-inflammatory and anti-tumour agents. Antioxidants are substances that reduce the effects of oxidation reactions by removing free radicals of oxygen. In industry they are used to preserve food and prevent deterioration of rubbers and plastics. At biological level antioxidants limit damage to cells and tissues caused by external agents, such as toxins and pollutants.[12] In nature, tannins and flavonoids are found in many families of plants mostly in the skin of fruit, leaves, roots and seeds and in the lignin fraction of lignocellulosic raw material. It is thought that the biological function of tannins is to protect plants against infections and insects.

The groups of compounds represented by the studied chemicals are class of water soluble phenolic compounds with molecular weight between 300 and 3000 Da. Based on structural characteristics it is possible to divide the tannins in four groups: gallotaninns, ellagitannins, complex tannins and condensed tannins.[13] Tannic acid (Fig. 2a) is a commercial form of gallotannins (molecules of gallic acid + glucose). Its chemical formula is $C_{76}H_{52}O_{46}$, but in fact it is a mixture of various forms of this compound. Gallic acid (Fig. 2b) ($C_6H_2(OH)_3COOH$), is a simple phenolic, abundant in tea. It has anticancer properties, showing cytotoxicity against tumour cells.[14] Flavonoids are another class of compounds studied intensively due to their chemo-preventative properties. Structurally they consist of two phenolic rings connected to a heterocyclic pyrone group.[15] Quercetin (Fig. 2c) is one of the antioxidant flavonoids widely distributed in the plant kingdom. The *para*-hydroxyl group of catechol ring B is responsible for the active elimination of free radicals.[16]

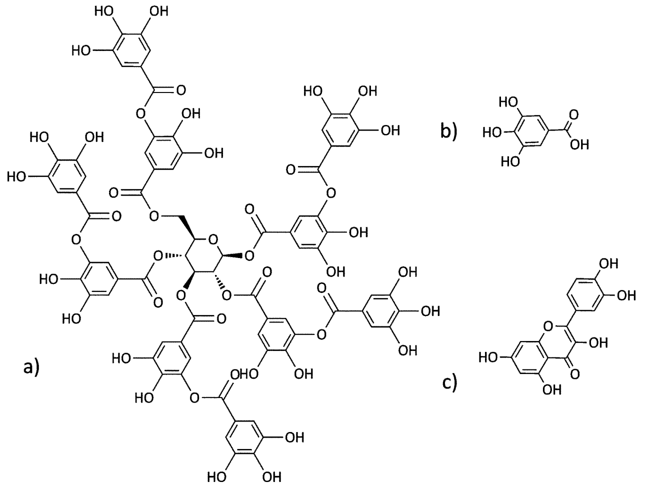

Fig. 2 Molecular structures of a) tannic acid, b) gallic acid, c) quercetin.

Ionic liquids are good solvents due to their ability to create various types of interactions with solutes. The most common interactions formed between ionic liquids and solutes are hydrogen bonds, van der Waals interactions, dipole–dipole, dispersive, π–π, n–π and ionic/charge–charge.[3,17,18,19,20,21,22]

This work demonstrates the interactions between ILs and phenols. The interactions between ionic liquids and the studied compounds are investigated based on the solubility of phenols in ILs. Due to the dual nature, ionic liquids exhibit significant differences of polarities that can be adjusted by changing either cation or anion. As already mentioned above, ILs are good solvents for a large variety of compounds including organic molecules containing hydroxyl groups, such as polyphenolic compounds studied in this work. However, the literature search revealed that there are no studies about the solubility of this class of compounds in ionic liquids. There is a limited number of papers related to the extraction of natural phenolic compounds using ILs from medicinal plants (*e.g. Nelumbo nucifera* Geartn,[23] *Psidium guajava* Linn.,[24] *Smilax china*[24]) or *Picea abies*[25] wood samples, however, these data are scarce. Generally, imidazolium based ionic liquids were tested and these ILs were able to extract phenolic compounds with equal or higher efficiency than classical solvents. It was also found that hydrophobicity, ability to form hydrogen bonds, coordinating characters of the anion and other properties of ionic liquids strongly differentiate the extraction yield of phenolics from the medicinal plants.[23,24]

Usually, the aromatic, polar protic compounds exhibit high solubility in ionic liquids[26] which favours possible selective extraction of phenolic compounds from the raw biomass.[23,24,25] According to the literature it is caused by the clouds of delocalized π electrons in aromatic systems that produce an electrostatic field interacting with the cation of the IL.[27] Additionally, the protic polyols have a great tendency to form the hydrogen bonds with electronegatively charged anions of ILs.

The investigation of solubility is one of the important experimental techniques because allows to determine conditions for the selective extraction of high value products from cheap raw resource *e.g.* biomass. A number of papers that focus on the lignocellulosic biomass conversion is continuously increasing as biomass is used to produce 2nd generation of biofuels and platform chemicals, such as xylitol, levulinic acid, lactic acid and others. Furthermore tannins, flavonoids and other types of phenolic compounds obtained from lignin fractions of biomass are high value products that can be recovered from the waste material by selective extraction.

Experimental

Chemicals

For the purpose of this investigation, the following ionic liquids were selected: [bmim][PF$_6$], [bmim][BF$_4$], [bmim][NTf$_2$] and [bmim][OTf]. All of them were purchased from Iolitec with a stated purity of >99 mol%. They were pre-treated before the experiments by being degassed, dried and freed from any traces of volatile compounds by applying a vacuum (0.1 Pa) at moderate temperature (60 °C). Tannic acid ($C_{76}H_{52}O_{46}$; FW = 1701.23 g mol^{-1}), gallic acid ($C_7H_6O_5$; FW = 170.12 g mol^{-1}) and quercetin ($C_{15}H_{10}O_7$; FW = 302.24 g mol^{-1}) were obtained from Sigma-Aldrich. The studied compounds underwent drying procedures that were carried out for 48 h and fresh samples of each chemical were used to prepare the solutions, always immediately prior to the phase diagram determination. The Karl–Fischer titrations revealed the water contents as follows: [bmim][PF$_6$] –530 ppm; [bmim][BF$_6$] –4190 ppm, [bmim][OTf] –3910 ppm, [bmim][NTf$_2$] –340 ppm, tannic acid –310 ppm, gallic acid –190 ppm, quercetin –220 ppm.

Table 1 Thermophysical constants of pure tannic acid, gallic acid and quercetin determined by the DSC measurements

Compound	T_m/K	ΔH_m/kJ mol^{-1}	T_{tr}/K	ΔH_{tr}/kJ mol^{-1}
Tannic acid	490.77	13.63	377.91; 336.58	29.89; 13.10
Gallic acid	524.19	62.39	351.31	19.28
Quercetin	587.84	51.08	381.58	4.88

Differential scanning calorimetry

The melting point, the enthalpy of fusion, glass transition temperature and the related heat capacity of the investigated phenols were obtained using a differential scanning calorimetry (DSC), according to the following procedure: a sample up to 6 mg was encapsulated in an aluminium 40 μL crucible. The sample was scanned in the temperature range from 273 to 673 K (0 to 400 °C). In all the scans the heating rate was 5 K min^{-1}. The results are the average of at least three of the scans. The DSC instrument (Mettler Toledo DSC 822e) was each time calibrated with the sample of indium and zinc, both with the 99.9999 mol% purity. The indium and zinc samples were selected because zinc allows for the calibration in the range of temperatures corresponding to the expected range for high melting point compounds. The calorimetric accuracy was ±1% and the precision was ±0.5%. In respect to glass transition temperatures and melting points, the uncertainty was estimated at the level of ±0.5 K. The obtained thermodynamic data are compiled in Table 1.

Experimental procedure

Solid–liquid equilibrium (SLE) phase envelopes of studied systems were obtained at ambient pressure of 0.1 MPa and a temperature range starting from 273 to 413 K using the dynamic (synthetic) method described previously.[21] The solutions were prepared in Pyrex conical 5 mL flasks (Supelco) by weighing the pure components with accuracy 10^{-4}g. The mixture of solute and solvent was heated very slowly (at less than 2Kh^{-1} near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell, placed in a thermostat. Water (273–333 K) or silicon (333–413 K) were used as the thermostatic fluid. The last crystal disappearance temperatures, detected visually, were measured with a calibrated DOSTMANN electronic P600 thermometer equipped in a Pt 100 probe totally immersed in the thermostating liquid. The uncertainty of the temperature measurements was ±0.02 K and that of the mole fraction did not exceed ±0.0005.

pH measurements

The samples of pure compounds (phenols and ionic liquids) or one phase solutions of phenolic compounds in the investigated ionic liquids with a constant mole fraction of phenols in ILs were prepared and diluted in water to obtain the concentration of phenol in the final aqueous solution close to 0.035 mol L^{-1}. The pH combined electrode was immersed in the prepared solutions and the pH was measured using pH meter (CRISON pH 25) calibrated before each experiment using pH buffer solutions (pH = 4.01, pH = 7.00, pH = 9.21). The experiments were done at ambient temperature.

Results and discussion

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements allows obtaining the melting point, enthalpy of fusion, temperature of solid–solid phase transitions and enthalpy of solid–solid phase transitions. The thermographs of the investigated compounds are presented in Fig. 3. The thermograph of pure tannic acid shows two solid–solid phase transitions at 377.91 K and 336.58 K. The visual observation of the phase changes of pure tannic acid reveals that the transition at 336.58 K with an enthalpy of solid–solid phase transition equals to 29.89 kJ mol^{-1} is a transition between a γ_1 crystalline form and a β_1 plastic form of tannic acid. At 377.91 K the transition between two β_1 and α_1 non-crystalline forms occurs with a heat effect of 13.10 kJ mol^{-1}. A graphical illustration of α_1, β_1, γ_1, α_2 stable solid forms of tannic acid and [bmim][OTf] is presented in Fig. 4.

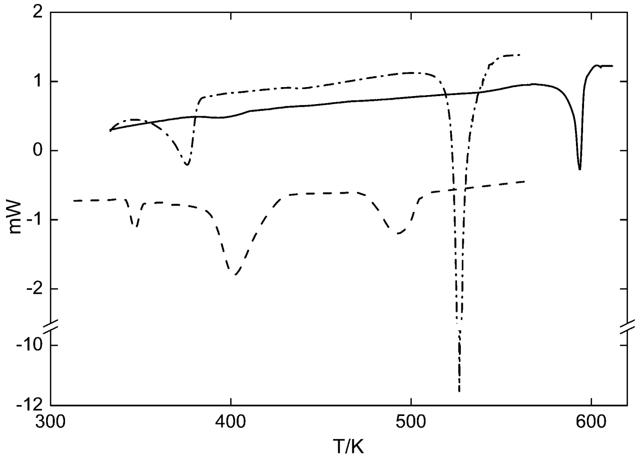

Fig. 3 The thermographs of tannic acid (dashed line), quercetin (solid line) and gallic acid (dashed-dotted line) obtained from differential scanning calorimetry. The lines representing the mathematical manipulation (integration, T_{onset} lines) were removed to enhance the clarity of the figure.

Either gallic acid or quercetin exhibit only one solid–solid phase transition and for gallic acid a β_1 crystalline form undergoes transition to an α_1 plastic form at 351.31 K with an enthalpy equal to 19.28 kJ mol^{-1}. A similar behaviour was observed for quercetin at 381.58 K with an enthalpy equal to 4.88 kJ mol^{-1}. All of the studied compounds demonstrate a high melting point. The obtained thermodynamic data are compiled in Table 1. The solubility measurements confirmed the observed solid–solid phase transition for either quercetin or gallic acid. For tannic acid only the phase transition at 336.58 K was observed in the solid–liquid phase equilibrium measurements because the next one was above the experimental range for the solubility experiment.

Solid-liquid equilibria

The (solid + liquid) phase diagrams for tannic acid, gallic acid or quercetin in ILs ([bmim][PF$_6$], [bmim][BF$_4$], [bmim][OTf], [bmim][NTf$_2$]) have been measured by a dynamic method in the range of temperature 273 K to 413 K.

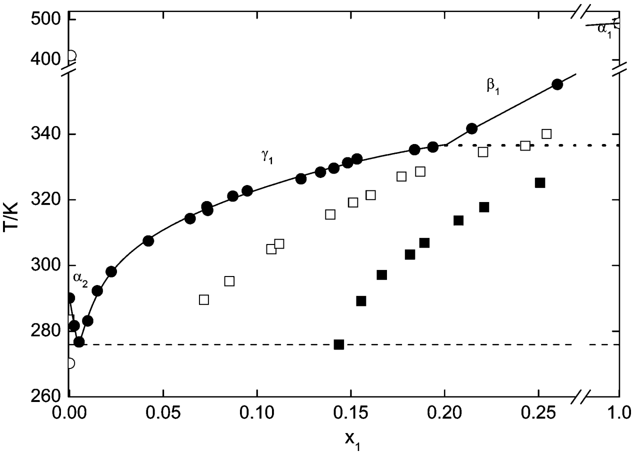

Fig. 4 The solid–liquid phase diagram for the system consisting of {tannic acid (1) + ([bmim][BF_4] - ■, or [bmim][PF_6] - □, or [bmim][OTf] - ●, or [bmim][NTf_2] - ○)(2)}. The dotted line represents the solid–solid phase transition between the $\gamma_1$crystalline form and the β_1 plastic - non crystalline form of tannic acid. The dashed line symbolises the (eutectic) temperature below which the solid solution (crystals of [bmim][OTf] + crystals of tannic acid) exists. The solid line illustrates the liquidus curve with the marked α_1, β_1, γ_1, α_2 stable solid forms of tannic acid and [bmim][OTf].

Table 2 Experimental solid–liquid equilibrium temperatures (T, phases α_1, α_2, β_1 and γ_1) for {tannic acid, or gallic acid or quercetin (1) + ionic liquids (2)} systems

x_1	T/K	x_1	T/K
Tannic acid + [bmim][BF_4]			
1.000	490.77 (α_1)	0.1816	303.30 (γ_1)
0.2509	325.15 (γ_1)	0.1665	297.09 (γ_1)
0.2211	317.75 (γ_1)	0.1556	289.15 (γ_1)
0.2074	313.69 (γ_1)	0.1437	275.91 (γ_1)
0.1893	306.86 (γ_1)	0.0000	185.77 (α_2)[34] (T_g)
Tannic acid + [bmim][PF_6]			
1.0000	490.77 (α_1)	0.1512	319.17 (γ_1)
0.2544	340.04 (β_1)	0.1391	315.49 (γ_1)
0.2431	336.41 (γ_1)	0.1119	306.57 (γ_1)
0.2205	334.54 (γ_1)	0.1077	304.96 (γ_1)
0.1870	328.57 (γ_1)	0.0853	295.19 (γ_1)
0.1770	327.06 (γ_1)	0.0717	289.54 (γ_1)
0.1607	321.41 (γ_1)	0.0000	283.51 (α_2)[36]
Tannic acid + [bmim][OTf]			
1.0000	490.77 (α_1)	0.0871	321.11 (γ_1)
0.2601	351.13 (β_1)	0.0737	316.79 (γ_1)
0.2145	341.67 (β_1)	0.0732	317.90 (γ_1)
0.1937	336.06 (γ_1)	0.0643	314.27 (γ_1)
0.1840	335.24 (γ_1)	0.0421	307.47 (γ_1)
0.1533	332.45 (γ_1)	0.0223	298.11 (γ_1)
0.1483	331.27 (γ_1)	0.0149	292.29 (γ_1)
0.1410	329.63 (γ_1)	0.0098	283.15 (γ_1)
0.1338	328.41 (γ_1)	0.0052	276.71 (γ_1)
0.1235	326.37 (γ_1)	0.0026	281.68 (α_2)
0.0948	322.74 (γ_1)	0.0000	290.10 (α_2)
Tannic acid + [bmim][NTf_2]			
1.0000	490.77 (α_1)	0.0000	270.22 (α_2)[34]
0.0008	410.59 (α_1)		
Gallic acid + [bmim][OTf]			
1.0000	524.19 (α_1)	0.0998	296.07 (β_1)
0.3596	398.42 (α_1)	0.0922	293.54 (β_1)
0.3382	391.28 (α_1)	0.0710	279.14 (β_1)
0.2926	375.45 (α_1)	0.0580	273.78 (β_1)
0.2437	356.51 (α_1)	0.0304	277.84 (α_2)
0.2157	344.74 (β_1)	0.0223	281.68 (α_2)
0.1917	338.17 (β_1)	0.0122	285.80 (α_2)
0.1665	328.17 (β_1)	0.0055	289.02 (α_2)
0.1429	316.10 (β_1)	0.0000	290.10 (α_2)
0.1182	306.80 (β_1)		
Gallic acid + [bmim][NTf_2]			
1.0000	524.19 (α_1)	0.0000	270.22 (α_2)[35]
0.0052	400.15 (α_1)		
Quercetin + [bmim][OTf]			
1.0000	587.84 (α_1)	0.1046	332.17 (β_1)
0.3954	363.97 (β_1)	0.0535	323.53 (β_1)
0.3390	358.15 (β_1)	0.0400	320.43 (β_1)
0.2848	350.10 (β_1)	0.0238	315.06 (β_1)
0.2498	347.96 (β_1)	0.0187	311.94 (β_1)
0.2047	343.50 (β_1)	0.0109	294.40 (β_1)
0.1843	341.17 (β_1)	0.0026	286.82 (α_2)
0.1443	337.14 (β_1)	0.0000	290.10 (α_2)
Quercetin + [bmim][NTf_2]			
1.0000	587.84 (α_1)	0.0000	270.22 (α_2)[34]
0.0022	411.21 (α_1)		

The solubility data of phenolic compounds in the investigated ionic liquids are shown in Table 2. The table includes the direct experimental results of the SLE, temperatures, T_1 (α_1, β_1, γ_1, α_2 stable solid forms) *versus* x_1, the mole fraction of the solute, phenols in the saturated solution for the investigated systems. Additionally, the solubility of tannic acid in 1-butyl-3-methylimidazolium based ionic liquids is presented in Fig. 4.

The experimental phase diagrams of SLE investigated in this work are not easily interpreted, inherently because the solutes and solvents are very structurally complicated and are highly interacting molecules. Nevertheless, the obtained results demonstrate that solubility of phenols in ionic liquids strongly depends on both, the ability of phenols to form intra- and intermolecular bonds and the polarity of the ionic liquids. Due to unlimited possible combinations of cations and anions, the description of ionic liquids polarity is a complicated issue as it cannot be defined by one parameter. For molecular solvents polarity can be expressed by the dielectric constant. Another way of illustrating the polarity can be achieved by employing the Kamlet–Taft parameters.[28,29,30,31] There are three Kamlet–Taft parameters characterising the polarity of compounds: the hydrogen bond acidity (α), the hydrogen bond basicity (β) and the polarisability effect (π*). Compared to conventional solvents, ionic liquids have generally higher π* and the variation of their values depends on both the anion and cation.[32] The value of α is dictated largely by the nature of cation and in the case of imidazolium ILs is determined by the acidity of the C-2 proton in the imidazolium ring. Contrary to α, the hydrogen bond basicity of the solvent is described by β parameter. The values for the ionic liquids are rather moderate and dominated by the nature of the anion. The literature reports show that the β parameter approximates the Coulombic contribution to the hydrogen bonds formed between ILs and the solute.[32] One of the good general scales of polarity used for ILs is E^N_T scale. The values of E^N_T, determined *versus* Reichardt's dye, describe the solvating ability of a wide range of ILs. The ability of the solutes - phenolic compounds and solvents to form hydrogen bonds is an important feature and affects the solubility of phenols in ILs. For tannic acid the differences in solubilities between studied ILs are noticeable and the solubility increases in the following order: [bmim][NTf_2] < [bmim][OTf] < [bmim][PF_6] < [bmim][BF_4]. The literature search allows the conclusion that this trend is coherent with an increase of the E^N_T values for ionic liquids. The E^N_T values for the four ionic liquids studied here are as follows: 0.670 ([bmim][BF$_4$]), 0.669 ([bmim][PF$_6$]), 0.656 ([bmim][OTf]) and 0.644 ([bmim][NTf$_2$]).[32] As aforementioned, the E^N_T is a more general parameter describing polarity as it depicts the solvating ability and particularly the hydrogen bond donor acidity, although it is also sensitive to the local electric field effect.[32] These subtle although noticeable differences in solubilities of phenols in the investigated ionic liquids are difficult to describe. However, it is worth underlining that the observed differences in solubilities of tannic acid in ILs find the response in the differences of the E^N_T values for these ILs. The difference in solubility between [BF$_4^-$] and [PF$_6^-$] ionic liquids is not only reflected by the difference in E^N_T values for both ILs. Tetrafluoroborate ionic liquid, contrary to hexafluorophosphate ionic liquid, is hydrophilic and additionally favours the formation of hydrogen bonds with weak acids, such as tannic acid and therefore increases their solubility in [BF$_4^-$] IL. In summary, the observed trend in solubility of tannic acid in ILs is governed by the E^N_T polarity scale of ILs and is complemented by the hydrophilicity of the studied ionic liquids. A more efficient extraction of phenolic compounds from *Nelumbo nucifera* Gaertn using [BF$_4^-$] than [PF$_6^-$] ionic liquid[23] described by Lu is a good confirmation of our results.

The liquids curve describing the solid–liquid equilibria for tannic acid and [bmim][NTf$_2$] is noticeably different than the others. For the mentioned system only two points were detected experimentally because the liquidus curve is very sharp and exposes that the solubility of tannic acid in [bmim][NTf$_2$] is very low (below 0.001 mole fraction) even at high temperatures (above 413 K). This strong dissimilarity in solubilities of tannic acid in [bmim][OTf] and [bmim][NTf$_2$] can be explained by the weak acidity and poor hydrogen bond donor ability of tannic acid and other phenolic compounds. Considering the solvent, [bmim][NTf$_2$] is a much worse hydrogen bond acceptor as the deficit of electrons in the [NTf$_2^-$] anion is better compensated contrary to smaller [OTf$^-$] ionic liquid. The literature data of the hydrogen bond basicity (β) of [bmim][OTf] and [bmim][NTf$_2$] confirms our conclusions. The basicity of hydrogen bond of both, [bmim][OTf] and [bmim][NTf$_2$] are significantly different and equals 0.464 and 0.243 for both ILs respectively.

The solubility measurements confirmed the previously detected by DSC solid–solid phase transition for tannic acid. Additionally, the system consisting of tannic acid, or gallic acid, or quercetin and [bmim][OTf] behaves as a simple eutectic. The eutectic mixtures were determined graphically and the composition and eutectic temperatures are presented in Table 3.

Moreover, the solubility experiments demonstrate other property characteristics for tetrafluoroborate and hexafluorophosphate ionic liquids. The one phase solution of tannic acid in either [BF$_4^-$] or [PF$_6^-$] ionic liquids exhibit low pH (3.19 and 3.78 correspondingly) and the strong acid odour is detected. These specific features of mixtures were detected only for samples with the mole fraction of tannic acid higher than 0.2 and at temperatures above 323.15 K. To avoid the formation of undesired HF further experiments with other studied solutes were performed using [bmim][OTf] and [bmim][NTf$_2$] ionic liquids.

Table 3 Experimental eutectic temperatures, $T_{1,e}$, and compositions, $x_{1,e}$, detected graphically for [bmim][OTf] + (tannic acid, or quercetin, or gallic acid)

Mixtures	$T_{1,e}$/K	$x_{1,e}$
[bmim][OTf] + tannic acid	275.90	0.0045
[bmim][OTf] + quercetin	282.00	0.0064
[bmim][OTf] + gallic acid	267.29	0.0485

The solubility data for either gallic acid or quercetin in systems with [bmim][OTf] and [bmim][NTf$_2$] confirm the observations for tannic acid with these ionic liquids. Similarly to tannic acid, both gallic acid (Fig. 5) and quercetin (Fig. 6) are much more soluble in [bmim][OTf] than in [bmim][NTf$_2$].

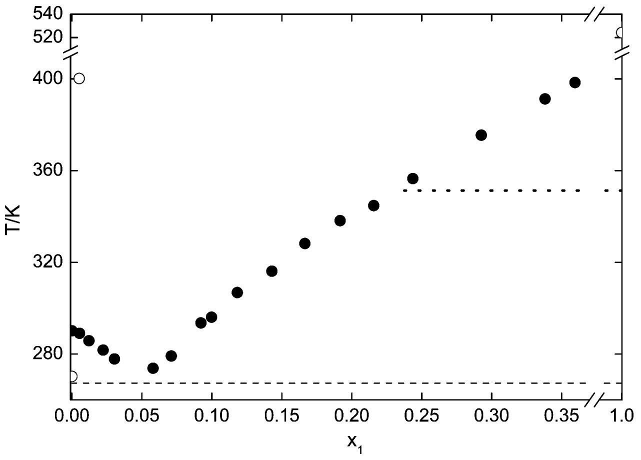

Fig. 5 The solid–liquid phase envelope for the system containing {gallic acid (1) + ([bmim][OTf] - ●, or [bmim][NTf$_2$] - ○) (2)}. The dotted line represents the solid–solid phase transition between the β_1 crystalline form and the α_1 plastic - non-crystalline form of gallic acid. The dashed line illustrates the eutectic temperature for the system with [bmim][OTf].

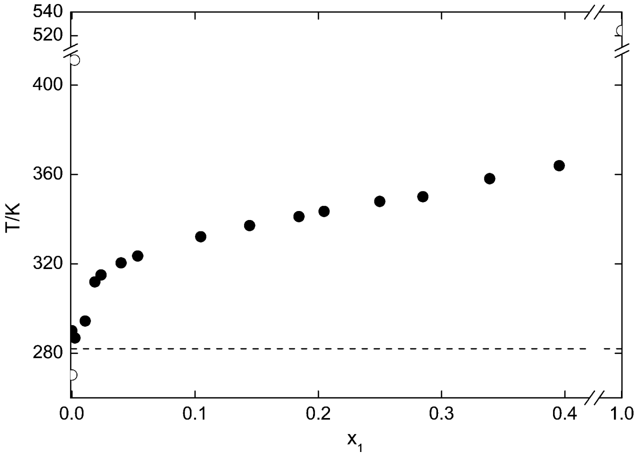

Fig. 6 The solubility of quercetin (1) in ([bmim][OTf] - ●, or [bmim][NTf$_2$] - ○) (2). The dashed line illustrates the eutectic temperature for the system with [bmim][OTf].

The solubility of gallic acid, quercetin and tannic acid in [bmim][OTf] is illustrated in Fig. 7. The differences in solubilities of the studied compounds in ILs are significant, especially for gallic acid; however, the trend is not very clear. As could be expected, gallic acid is the most soluble phenol among those examined for mole fraction below 0.2. Conversely, for high mole fraction (above 0.2) the solubility of gallic acid in ILs starts to be lower than the solubility of tannic acid or quercetin. The situation is even more complicated in the case of tannic acid and quercetin because the difference in solubility between tannic acid and quercetin in [bmim][OTf] is small and advantageous for tannic acid for mole fraction of tannin higher than 0.2. However, for the mole fraction lower than 0.2, the difference is even double and advantageous for tannic acid. The explanation of the observed liquidus curve trend is difficult, chiefly due to the complicated structure of phenols and the possible formation of the net of intra- and intermolecular bonds that may favour the solubility of tannic acid in ionic liquid. Nevertheless, the most important conclusion coming from this comparison is fact that at temperature around 380 K the solubility of phenols (especially gallic acid and quercetin) is close to or higher than 0.4 mole fraction of phenolic compounds. The obtained results reveal a potential application of ionic liquids in extraction of phenols. The extraction results presented in the literature confirm this observation.[23,24,25]

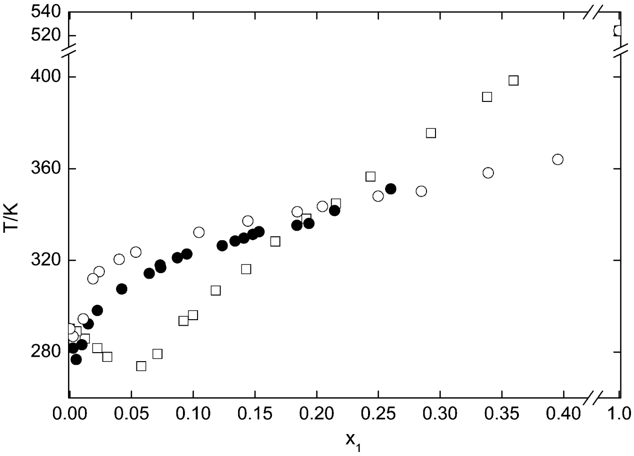

Fig. 7 Comparison of the solubility of tannic acid - ●, or gallic acid - □, or quercetin - ○ (1) in [bmim][OTf] (2).

The solubility of both quercetin and gallic acid in [bmim][NTf_2] is as low as tannic acid and does not exceed 0.002 and 0.005 at temperatures slightly above 400 K for quercetin and gallic acid correspondingly. The solubility of the studied compounds in the aforementioned [bmim][NTf_2] is negligible, however, increases with the decrease of the molar mass of phenol. It is most likely related to the large entropic effect that is caused by the difference in the size between IL and the investigated compounds. The large entropic effect guides to a negative deviation from the ideal solubility that might explain why gallic acid (smaller molecule) is more soluble in [bmim][NTf_2] than quercetin or tannic acid in the same IL. Unfortunately, the lack of basic data (*i.e.* association constant of the phenolic compounds, *etc.*) does not allow the confirmation of these suppositions by modelling of the solubility data using classical correlation equations.[19,20,33] Additionally, the solubility results for gallic acid and quercetin validate the DSC results and the solid–solid phase transition is observed for either gallic acid or quercetin.

Conclusions

The novel and unexplored field of solubilities of tannins, flavonoids and simple phenolics in ionic liquids is studied successfully and is presented in this work. The obtained results show that ionic liquids are good solvents for phenolic compounds. What is more, the solubility of either tannic acid, gallic acid or quercetin can be tuned by altering the anion of the ionic liquid as is presented in the case of [bmim][PF_6] and [bmim][NTf_2]. The high solubility of phenolic compounds, even up to 0.4 mole fraction, can be obtained at elevated, although industrially achievable, temperatures. The literature[23,24,25] provides sparse examples of extraction of valuable phenolic compounds from herbs or wood, however, for the first time systematic studies presented here confirm the potential extraction of phenolics. The obtained data accompanied by the solubility of carbohydrates in ionic liquids[2] are even more valuable because it allows the design and optimisation of conditions for the selective extraction of value added products from raw lignocellulosic biomass by ionic liquids.

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