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Extraction of Quercetin from Red Onion (Allium cepa L.) with Ionic Liquids

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ABSTRACT

The application of soluble in water Ionic Liquids (ILs) as alternatives to conventional organic solvents in liquid-liquid extraction of Quercetin (Q) from frozen red onion (Allium cepa L.) was investigated. The parameters affecting the extraction ability of ILs such as chemical structures of the IL cation and anion and the phase volume ratio of extracting solvent water-IL, as well as type of organic solvent such as 1-propanol, 2-propanol, ethyl acetate and butyl acetate were evaluated. Ten soluble in water imidazolium-, pyridinium-, pyrrolidynium-, or piperidinium-based ILs with different anions were investigated as co-solvents in extraction from ternary system {IL + butyl acetate + water}. Extract of Q was found in organic phase (butyl acetate) whereas other contaminations of red onion were found in water-IL phase. Experimental results indicated that ILs posse's strong interaction with water and improve the organic solvent such as butyl acetate extraction selectivity. The extraction efficiency is highly dependent on the structure of the ILs and their solubility in water. Different forces of the extraction processes include hydrogen-bonding interaction; hydrophobic interaction and steric hindrance effect were discussed in these systems. Specific quercetin composition was performed through HPLC measurements. The final separation effect from IL-butyl acetate-water/frozen quercetin samples was dependent mainly on anion of the IL. Using the most effective ILs in extraction, the 3.96 g·kg^{-1}, 3.35 g·kg^{-1} of pure quercetin from frozen red onion was obtained with 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIM][OTf], and 1-butyl-3-methylpyridinium trifluoromethanesulfonate, [1B3MPY][OTf], respectively

INTRODUCTION

Red onion is one of the flavenoids used from ages in our diet. It could be dried and preserved for several months. Red onion is known from anti-bacterial and anti-fungal activities and contamination of powerful antioxidants, sulfur and other numerous phenolic compounds which arouse great interests. The widespread distribution of onion and different flavonoids mean that they are used for centuries in herbal and traditional medicine. From many years people are interested in extraction of flavonoids from red onion and many different plants of low toxicity. Quercetin (Q), a flavonoids with significant antioxidant and chelating properties, containing five phenol functional groups, is a kind of amphoteric compound (Figure 1) found in fruits, vegetables, wines, teas, plants and in the lignin fraction of lignocellulosic raw materials [1-6]. Q is used in food technology to preserve food, in pharmacy industry and in chemical industry to prevent deterioration of rubbers and plastics. Few hydroxyl groups confirm the substantional antioxidant, chelating and prooxidant activity of the Q molecule. A double bond and carbonyl function increases activity by affording a more stable quercetin radical through conjugation and electron delocalization. Q has a wide range of biological actions including anti-carcinogenic, anti-inflammatory and antiviral activities; as well as attenuating lipid peroxidation, platelet aggregation and capillary permeability [7]. Q has demonstrated unique cardioprotective effects [1].

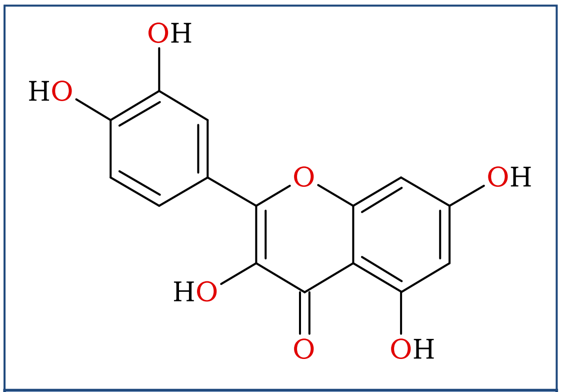


Figure 1: Chemical structure of quercetin.

Q has been found to inhibit xanthine oxidase activity, resulting in a decrease in oxidative injury [8]. Q reveals strong antimicrobial activity and detoxification activity against mercury, cadmium and lead in rats [9-11]. The extraction of Q from natural resources usually involves the use of liquid-liquid extraction which adopts conventional organic solvents such as mixture (methanol/water, 75:15) or with n-hexane from Guava Leaves (Psidium guajava) [12], or with ethanol-water from red onion [13], or with toluene, dichloromethane, ethanol from red onion (partitioned with diethyl ether, ethyl acetate, or 1-butanol) [14], or with ethyl acetate from red onion [10], or with imidazolium–based ionic liquids (ILS) and one pyridinium-based IL from Guava Leaves (Psidium guajava), or Smilax china tubers [5]. Optimized extraction of bioactive compounds including Q from Herba Artemisiae Scopariae with ILs and deep eutectic solvents as co-solvents with water-methanol binary solvent mixture was recently published with the best result using 1-butyl-3-methylimidazolium bromide, [BMIM][Br] (about 0.9 g/kg of Q) [2].

ILs are known from many years as attractive solvents for extraction processes from water phase [15-17]. The conventional solvents are volatile, irritant, and flammable. Therefore, it is a hot spot to find environmentally benign solvents to replace the conventional solvents in the extraction process of flavenoids, or in general bioactive compounds [5,18-21]. ILs have been studied as solvents, co-solvents, co-surfactants, electrolytes, and adjuvantes, as well as used in the creation of IL-pharmaceutical materials for better solubility.

The most popular for pharmaceutical applications and drug delivery systems are ammonium-based ILs, known as non-toxic and biodegradable since they are naturally occurring in several biological functions [22]. We tested already a few ammonium-based ILs soluble in water in our previous work using different techniques of extraction, longer time and co-solvents with average results [23].

In this work we used different method of extraction in short time and using only imidazolium-, pyridinium, pyrrolidynium- and piperidynium-based ILs soluble in water. Thus in this work the extraction of Q from frozen red onion using ten hydrophilic ILs as co-solvents with selected organic solvent and water was investigated. The relationship between the IL structure and the extraction ability was studied. Parameters affecting the extraction efficiency were optimized.

MATERIALS AND METHODS

Materials and sample preparation

Quercetin and solvents were delivered from Sigma-Aldrich and few other products. The structure of Q is presented in Figure 1. Solvents are listed in Table 1. The freshly activated molecular sieves of type 4Å (Union Carbide) were used for drying solvents. A list of the investigated in this work ILs, miscible with water, along with their suppliers, CAS numbers, purity and purification/analysis methods are summarized in Table 2 [24]. ILs were purified before use during 24 h under low pressure at T = 368 K.

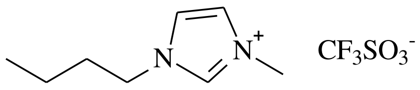
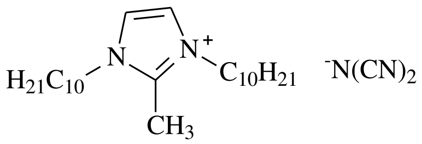
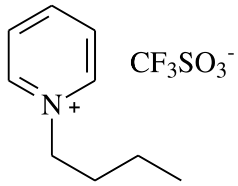
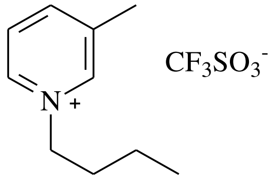
Water content

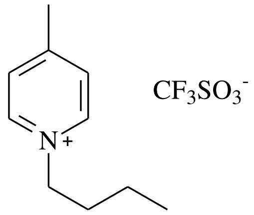
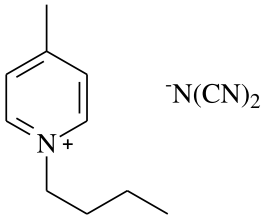
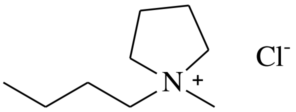
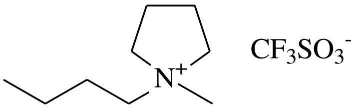
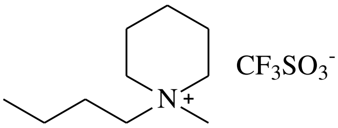
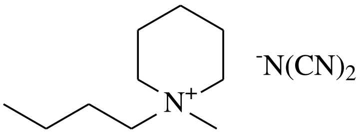
The water content was analyzed by the Karl-Fischer titration technique (method TitroLine KF). The water contamination in all compounds (Tables 2) was below 1000 ppm.

Table 1: Summary of chemical sample information for the investigated quercetin and solvents.

Compound	**Supplier**	**Mass fraction purity/ water content (mass fraction)**	**Purification method**	**Analysis Method**	**CAS Number, *M*/ g mol^{-1}**
Quercetin	Sigma-Aldrich	0.95			117-39-5/ 302.24
Methanol	Sigma-Aldrich	for HPLC 0.999/30x10^{-6}	Molecular Sieves	GC	67-56-1/ 32.04
1-Propanol	POCH	0.99/90 x10^{-6}	Molecular Sieves	GC	71-23-8/ 60.10
Ethyl acetate	CHEMPUR	0.995/120x10^{-6}	Molecular Sieves	GC	141-78-6 88.11
Butyl acetate	Sigma-Aldrich	0.99/130x10^{-6}	Molecular Sieves	GC	123-86-4 116.16
Acetonitrile	Sigma-Aldrich	for HPLC 0.999/30x10^{-6}		GC	75-05-8 41.05
Trifluoroacetic acid	Sigma-Aldrich	0.99/60x10^{-6}		GC	76-05-1 114.02

Table 2: Properties of the investigated ionic liquids, miscible with water: structure, name, abbreviation of name, supplier, CAS No., molar mass (M), mass fraction purity and water content.

Structure	**Name, abbreviation, supplier, CAS number**	**M/ (g · mol^{-1})**	**Purity (weight percentage)/ water content**
	1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIM][OTf], Io-Li-Tec, 174899-66-2	288.29	≥0.97/ 630 · 10^{-6}
	1,3-didecyl-2-methylimidazolium dicyanamide, [$C_{10}C_{10}$MIM][DCA], Synthesized [24]	429.68	≥0.97/ 976 · 10^{-6}
	1-butylpyridinium trifluoromethanesulfonate, [BPY][OTf] Io-Li-Tec, 390423-43-5	285.29	≥0.97/ 720 · 10^{-6}
	1-butyl-3-methylpyridinium trifluoromethanesulfonate, [^{1}B^{3}MPY][OTf] Io-Li-Tec, IL-0179-HP	299.32	≥0.97/ 570 · 10^{-6}

Structure	Name, abbreviation, supplier, CAS number	M/ (g · mol^{-1})	Purity (weight percentage)/ water content
	1-butyl-4-methylpyridinium trifluoromethanesulfonate, [^{1}B^{4}MPY][OTf] Io-Li-Tec, 882172-79-4	299.32	≥0.97/ 640 · 10^{-6}
	1-butyl-4-methylpyridinium dicyanamide, [^{1}B^{4}MPY][DCA] Io-Li-Tec	216.32	≥0.97/ 990 · 10^{-6}
	1-butyl-1-methylpyrrolidinium chloride, [BMPYR][Cl] Sigma-Aldrich, 479500-35-1	177.71	≥0.98/ 420 · 10^{-6}
	1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate, [BMPYR][OTf] Io-Li-Tec, 367522-96-1	291.33	≥0.99/ 370 · 10^{-6}
	1-butyl-1-methylpiperidinium trifluoromethanesulfonate, [BMPIP][OTf], Sigma-Aldrich, 49384	305.36	≥0.97/ 740 · 10^{-6}
	1-butyl-1-methylpiperidinium dicyanamide, [BMPIP][DCA] Io-Li-Tec (custom synthesis)	222.38	≥0.97/ 420 · 10^{-6}

Measurements

The extraction of Q was provided at temperature T = 303.0±0.5 K. Mixture of 0.5 mg (probe 1), or 1 mg (probe 2), or 2 mg (probe 3) of the IL was added to 1.2 g of frozen red onion and 6 g of solvent. The proportion of mass of red onion/solvent was 1:5. The mixtures of three compounds with compositions inside the immiscible region of the ternary system were introduced into a jacketed glass cell with a volume of 10 cm^3. Temperature was controlled with a thermostatic water bath (LAUDA Alpha) to maintain a constant temperature of T = 303.0±0.5 K. Mixture was under vigorous stirring (1250 rpm) for 3 h, which was assumed as a time achieving extraction equilibrium. The temperature and time of extraction were optimized according to our preliminary experiments and to minimize the costs as well as after the analysis of published data [2]. Next, after filtration two phases were separating after 6 h. After getting the phase separation, the organic phase was purified under reduced pressure for about 1 tor and analyzed with HPLC. The LaChrom (Merck Hitachi) HPLC system equipped with a L-7420 UV-VIS visible dual wavelength detector, four-solvents low pressure gradient pomp type L-7100 was used for analysis of Q. System was controlled by the HPLC System Manager Model D-7000 program: the 0.1 g of organic or water phase was concentrated and next dissolved in 0.5 ml mixture of methanol-water (4:1 in mass). The separation column was Atlantis ® T3 (4.6 mm × 250 mm, 5 μm). The liquid mobile phase was a mixture of 0.05w% aqueous solution of trifluoroacetic acid (A) and acetonitrile (B) of changing in time concentration. The “Q in final extract/w %” was a results from HPLC.

Extraction with different solvents

In the first examinations 1-propanol and 2-propanol were used for the extraction with the addition of 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIM][OTf] IL. Our earlier results of solubility of Q in 1-propanol have shown large solubility, however lower than that in ILs [23]. Product of extraction (alcohol phase) was dried during 6 h in vacuum and analyzed by HPLC. The results are shown in Table 3.

Table 3: Extraction of quercetin (Q) from frozen sample with 1-propanol and 2-propanol at T = 303.0 ± 0.5 K after 3h with different amount of the IL ([BMIM][OTf]).

IL/probe	Mass of the IL/ (g)	Mass of frozen red onion/ (g)	Solvent/(6g)	Mass of extract/ (g)	*Q* in final extract/w %
[BMIM][OTf]/(1)	0.0038	1.2076	1-propanol	0.1015	4.11
[BMIM][OTf]/(2)	0.0075	1.2043	1-propanol	0.1049	4.95
[BMIM][OTf]/(3)	0.0153	1.2079	1-propanol	0.0891	8.48
[BMIM][OTf]/(1)	0.0038	1.2056	2-propanol	0.0954	3.54
[BMIM][OTf]/(2)	0.0076	1.2009	2-propanol	0.0805	3.96
[BMIM][OTf]/(3)	0.0155	1.2047	2-propanol	0.0827	3.53

In the second examination the ethyl acetate and butyl acetate was tested as an extractant agent with imidazolium-based ILs. The results are shown in Table 4.

Table 4: Extraction of quercetin (Q) from frozen sample with ethyl acetate and butyl acetate at T = 303.0 ± 0.5 K after 3h with different amount of the imidazolium-based ILs.

IL/probe	Mass of the IL/ (g)	Mass of frozen red onion/ (g)	Solvent/(6g)	Mass of extract/ (g)	*Q* in final extract/w %
[BMIM][OTf]/(1)	0.0034	1.1999	Ethyl acetate	0.0042	35.08
[BMIM][OTf]/(2)	0.0068	1.2015	Ethyl acetate	0.0054	25.36
[BMIM][OTf]/(3)	0.0134	1.1997	Ethyl acetate	0.0070	21.34
[BMIM][OTf]/(1)	0.0034	1.2016	Butyl acetate	0.0074	49.73
[BMIM][OTf]/(2)	0.0067	1.2092	Butyl acetate	0.0051	70.71
[BMIM][OTf]/(3)	0.0134	1.2095	Butyl acetate	0.0064	74.84
[$C_{10}C_{10}$ MIM][DCA]/ (1)	0.0033	1.2019	Ethyl acetate	0.0063	20.46

[$C_{10}C_{10}$ MIM][DCA] /(2)	0.0066	1.2030	Ethyl acetate	0.0105	21.00
[$C_{10}C_{10}$ MIM][DCA] / (3)	0.0133	1.2027	Ethyl acetate	0.0148	13.72
[$C_{10}C_{10}$ MIM][DCA]/ (1)	0.0035	1.2090	Butyl acetate	0.0073	44.91
[$C_{10}C_{10}$ MIM][DCA] /(2)	0.0068	1.2092	Butyl acetate	0.0086	43.88
[$C_{10}C_{10}$ MIM][DCA] /(3)	0.0136	1.2008	Butyl acetate	0.0138	20.57

Extraction with Butyl Acetate and ILs soluble in water

The extraction of Q was continued with the same method with pyridinium-based, pyrrolidinium-based and piperidinium-based ILs and butyl acetate as a solvent to increase the extraction. After filtration and getting the phase separation after for about 6 h, two phases were separated and solvent organic phase was after evaporation analyzed with HPLC. The results for pyridinium-based ILs, pyrrolidinium-based and piperidinium-based ILs are listed in (Table 5-7) respectively.

Table 5: Extraction of quercetin (Q) from frozen sample with butyl acetate (6.0 g) at T = 303.0 ± 0.5 K after 3h with different amount of the pyridinium-based ILs.

IL/probe	Mass of the IL/ (g)	Mass of frozen red onion/ (g)	Mass of extract/ (g)	*Q* in final extract/w %
[BPY][OTf]/(1)	0.0038	1.2046	0.0047	57.98
[BPY][OTf]/(2)	0.0064	1.2018	0.0010	56.60
[BPY][OTf]/(3)	0.0136	1.2016	0.0031	60.37
[$^1B^3$MPY][OTf]/(1)	0.0034	1.2099	0.0047	86.22
[$^1B^3$MPY][OTf]/(2)	0.0069	1.2006	0.0031	81.36
[$^1B^3$MPY][OTf]/(3)	0.0136	1.2062	0.0044	81.17
[$^1B^4$MPY][OTf]/(1)	0.0034	1.2082	0.0041	52.95
[$^1B^4$MPY][OTf]/(2)	0.0068	1.2091	0.0034	42.64
[$^1B^4$MPY][OTf]/(3)	0.0136	1.2041	0.0046	43.57
[$^1B^4$MPY][DCA]/(1)	0.0034	1.2081	0.0046	54.93
[$^1B^4$MPY][DCA]/(2)	0.0069	1.2046	0.0055	53.10
[$^1B^4$MPY][DCA]/(3)	0.0139	1.2075	0.0061	54.23

Table 6: Extraction of quercetin (Q) from frozen sample with butyl acetate (6.0 g) at T = 303.0 ± 0.5 K after 3h with different amount of the pyrrolidinium-based ILs.

IL/probe	Mass of the IL/ (g)	Mass of frozen red onion/ (g)	Mass of extract/ (g)	Q in final extract/w %
[BMPYR][Cl]/(1)	0.0033	1.2052	0.0040	62.99
[BMPYR][Cl]/(2)	0.0068	1.2038	0.0037	62.54
[BMPYR][Cl]/(3)	0.0138	1.2031	0.0043	70.89
[BMPYR][OTf]/(1)	0.0036	1.2083	0.0034	Bd.
[BMPYR][OTf]/(2)	0.0069	1.2064	0.0033	26.53
[BMPYR][OTf]/(3)	0.0134	1.2056	0.0038	21.23

Table 7: Extraction of quercetin (Q) from frozen sample with butyl acetate (6.0 g) at T = 303.0 ± 0.5 K after 3h with different amount of the piperidinium-based ILs.

IL/probe	Mass of the IL/ (g)	Mass of frozen red onion/ (g)	Mass of extract/ (g)	Q in final extract/w %
[BMPIP][OTf]/(1)	0.00348	1.2033	0.0042	16.60
[BMPIP] [OTf]/(2)	0.00685	1.2021	0.0088	23.10
[BMPIP] [OTf]/(3)	0.01378	1.2032	0.0099	22.14
[BMPIP][DCA]/(1)	0.00349	1.2064	0.0054	32.37
[BMPIP][DCA]/(2)	0.00688	1.2085	0.0030	23.92
[BMPIP][DCA]/(3)[a]	0.01381	1.2003	0.0033	29.67

[a] For 6.8 g of solvent.

RESULTS AND DISCUSSION

Extraction of Q from frozen sample of ([BMIM][OTf] + 1-propanol, or 2-propanol) with different amounts of the IL shows that the best result is on the level of 8.48 w% of Q in extract (Table 3) with 1-propanol (probe 3). This is very unsatisfied result in comparison with butyl acetate, 27.92 w% obtained with the same method and 81.48 w% obtained in our previous work, however with different method of extraction [23]. Thus in the next examinations, the ethyl acetate and butyl acetate were used as extraction solvents with imidazolium-based ILs. The final yield of the extraction was the best with [BMIM][OTf], which is 74.84 w% with butyl acetate (probe 3) in comparison with ethyl acetate (probe 3) (21.34 w%) (Table 4). In general, the addition of the imidazolium-based IL increases the extraction ability in both solvents. Increasing the alkane chain and changing the anion of the IL for dicyanamide did not improve the extraction. Three oxygen atoms in the [OTf]- anion reveal stronger interaction with water than two CN groups and parallel larger extraction of Q into the solvent phase. In our previous work the 1-ethyl-3-methylimidazolium trifluoroacetate, [EMIM][TFA] and 1-allyl-3-methylimidazolium dicyanamide, [AMIM][DCA] were used with final extraction of 12.66 w% and 7.80 w%, respectively [23].

To find out the optimal ILs and evaluate its performance in solvent extraction, the ILs with different cations and anions were tested in this work. The structure of the IL has significant influence on the extraction results owing greatly to their dissolving ability. To facilitate the discussion of the relationship between the chemical structures of ILs and their extraction ability, the additional experiments were performed using pyridinium-, pyrrolidynium- and piperidinium-based ILs.

As can be seen from (Table 5,6), some interesting results were obtained in terms of the influence of the IL cation structure. For the pyridinium-based ILs with different anions, the extraction ability is higher than those for imidazolium-, or pyrrolidinium-, or piperidinium-based ILs. The best results were obtained using [^{1}B^{3}MPY][OTf], for which the extraction of Q was larger than 85 w% in butyl acetate phase (86.22 w%, probe 1). Changing the position of methyl group from 3 to 4 ([^{1}B^{4}MPY][OTf]), the extraction was much lower (52.95 w%, probe 1). The explanation of this fact is possible on the level of steric hydrance- for the [^{1}B^{4}MPY][OTf] the possible association between cations of the IL may be stronger than that of [^{1}B^{3}MPY][OTf], and at the same time the interaction with water is lower and the influence on the extraction of Q is also lower.

Actually, all pyridinium-based ILs soluble in water revealed extraction > 40 w%, (Table 5). Changing the anion on [DCA]- we can observed slightly better extraction on the level of 54.93 w% (probe 1) for [^{1}B^{4}MPY][DCA]. The comparison with measured earlier N-(3-hydroxypropyl)pyridinium dicyanamide, [N-C$_3$OHPY][DCA] shows similar results [23].

The average concentration of Q in the solvent phase (butyl acetate) was observed for [BMPYR][Cl], 70.89 w% (probe 3) (Table 6). The probe (1) with [BMPYR][OTf] was unsuccessful because three phases were observed. Probe (2) has shown maximum extraction equal 26.53 w %. Thus in this examination the [Cl]- anion was better for the extraction than [OTf]- anion. Previously measured (with different method) [BMPYR][OTf] was on the level of 11.56 w% from ethanol/water/IL/butyl acetate extraction [23].

Unexpected result, with lower final yield, was obtained for piperidinium-based ILs. After purification the 23.10 w% (probe 2) of Q was obtained with [BMPIP][OTf] IL and 32.37 w% (probe 1) of Q using [BMPIP][DCA]. The glycoside shows the main concentration in butyl acetate extract with a retention time of 23.6 min. Its contamination was larger than 50 w%. Previously measured (with different method) [BMPIP][DCA] was on the level of 4.63 w% from ethanol/water/IL/butyl acetate extraction [23].

In general, the addition of IL to the extraction solution improves the extraction ability of Q, especially with [^{1}B^{3}MPY][OTf] (probe 1, 86.22 w%), [BMIM][OTf] (probe 3, 74.84 w%), and [BMPYR][CL] (probe 3, 70.89 w%) comparing to the extraction with pure butyl acetate (27.92 w%). These conclusions have been indicated by the similar results of Q extraction from aqueous phase of P. guajava leaves with microwave method at higher temperature [5]. In that work the addition of IL soluble in water has increased the yield of extraction 2-5 times. The best results were obtained with 1-butyl-3-methylimidazolium dihydrogen phosphate, [BMIM][H_2PO_4] and 1-butyl-3-methylimidazolium bromide, [BMIM][Br] on the level of 74.5 w% and 69.5 w% [5]. The [BMIM][Br] IL was chosen as the best extractant for quercetin from Herba Artemisiae Scopariae [12]. The [DCA]- based ILs were on the average level in both works. In our previous work the best results were noticed for [EMIM][TFA] (85.5 w%), or [N$_{2,2,1,2OCH3}$][BF_4] (83.8 w%) or [N$_{4,1,1,2OH}$][Br] (78.6 w%) [23].

The strong interaction between the IL, water and quercetin, especially by hydrogen bonding, π-π, and n-π interaction contributing greatly to this extraction. Generally, hydrophobic interaction, hydrogen-bonding interaction and the steric hindrance are the key parameters affecting the extraction ability of ILs [25]. Usually, the increase of alkyl chain length of the IL cation increases the extraction from the aqueous phase [16]. This is the case for non-miscible with water IL. In this work the [C$_{10}$C$_{10}$MIM][DCA] probably is less soluble in water and reveals lower influence on extraction of Q as a co-solvent. The results are weaker than those for butyl-substituent of the other ILs. The hydrogen-bonding interaction should be considered simultaneously when explaining the affinity between IL/water and IL/Q in aqueous solutions. The results for different cations show stronger influence of the IL/water interaction than that of

IL/Q, which increases extraction of Q to the organic solvent phase.

The nature of acidity in ILs might be important in these interactions. Unfortunately, it is a particularly confused subject in the literature. The Hammett acidity measurements in several ILs were presented with two different colored indicators, in the same IL. The apparent acidity functions have been compared for several ILs such as [BMIM][NTf_2], [BMIM][BF_4], [BMIM][OTf], [BHIM][NTf_2], [BMIM][PF_6], [$HNEt_3$][NTf_2], to which an acid has been added [26]. The conclusions confirmed that the accessible acidity level is not influenced by the nature of the cation and that the nature of anion is very critical and the solvating power towards the proton follows the order: [OTf]- > [NTf_2]- > [BF_4]- > [PF_6]-. Thus, the more the proton is solvated, the less it is acidic [26]. For the imidazolium-based ILs, the NMR measurements show that the N–H proton is not labile, indicating that these ILs cannot really be considered as Brønsted acids [27]. A similar protocol was applied to characterize the acidity level of a series of ILs based on pyridine cations bearing sulfonic acid functions and to alkylammonium-based ILs [28]. The same conclusions were made for the pyrrolidinium-based ILs. The influence of the ILs cations was evaluated regarding the anion [NTf_2]- [29]. It was observed that for ILs, such as [BMIM][NTf_2], [BMPYR][NTf_2] and [$HNEt_3$][NTf_2], the effect of the cation was very limited [29]. Thus for imidazolum-based, or pyridinium-based, or pyrrolidinium-based ILs used in this work, the cation suppose to has no huge influence. Nevertheless, besides better results of the extraction with [OTf]- anion than those with [DCA]- anion the influence of cation is evident in this work.

The most effective ILs in the extraction of Q are [BMIM][OTf] (3.96 $g \cdot kg^{-1}$) and [1B3MPY][OTf] (3.35 $g \cdot kg^{-1}$) after 3h of mixing and 6h of separation of phases at temperature T = 303.0±0.5 K (Figure 2). The final extraction yield is taken from mass of extract and contamination of Q. For [$^1B^3MPY$][OTF] we have the contamination of Q on the level of 86.22 % but the mass of solid extract was only 0.0047g (in comparison with [BMIM][OTf]-0.0064g). However, the comparison of the results for pyridinium- and piperidinium-based ILs with the same cation and different anions have shown better results of the extraction for [DCA]- anion. In a case of pyrrolidinium-based ILs, the [OTf]- anion was much better than [Cl]- anion.

The final recovery of Q from the butyl acetate phase is realized by using the evaporation of solvent. The IL after the filtration from onion must be recycled from water phase by the evaporation of water, or crystallization of water.

CONCLUSION

In this work, the extraction of quercetin from frozen red onion by 1-propanol, 2-propanol, ethyl acetate and butyl acetate was examined from water phase including water soluble ionic liquid at temperature T = 303.0±0.5 K. Ten ILs with different hydrogen bonding properties were conducted. It was found that the ability of extraction is dependent on the chemical structures of the cation and anion of the IL and on the volume ratio of IL/water in the sample of frozen red onion. The more efficient extraction from water phase was obtained using the ILs with [OTf]- anion in comparison with [DCA]- anion. The extraction efficiency increases with an increase on the phase volume ratio IL: water only for the imidazolium-based ILs. The driving forces governing the phase preference of quercetin involve the steric hindrance effect and hydrogen-bonding interaction.

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REFERENCES

1. Edewor-Kuponiyi, Ibibia T. (2013). A Review on Antimicrobial and Other Beneficial Effects of Flavenoids. Int J Pharm Sci Rev Res. 21: 20-33.
2. Ma W, Row KH. (2017). Optimized Extraction of Bioactive Compounds from Herba Artemisiae Scopariae with Ionic Liquids and Deep Eutectic Solvents. J Liq Chrom Rel Technol. 40: 459-466.
3. Heim KE, Tagliaferro AR, Bobilya DJ. (2002). Flavonoids Antioxidants: Chemistry, Metabolism and Structure-Activity Relationships. J Nutrit Biochem. 13: 572-584.
4. Askari G, Ghiasvand R, Feizi A, Ghanadian SM, Karimian J. (2012). The Effect of Quercetin Supplementation on Selected Markers of Inflammation and Oxidative Stress. J Res Med Sci. 17: 637-641.
5. Du F-Y, Xiao X-H, Luo X-J, Li G-F. (2009). Application of Ionic Liquids in the Microwave-assisted Extraction of

Polyphenolic Compounds from Medicinal Plant. Talanta. 78: 1177-1184

6. Wojdyło A, Oszmiański J, Czemerys R. (2007). Antioxidant Activity and Phenolic Compounds in 32 Selected Herbs. Food Chem. 105: 940-949.
7. Li Y, Yao J, Han Ch, Yang J, Chaudhry MT, et al. (2016). Quercetin, Inflammation and Immunity. Nutrients. 8: 167-169.
8. El-Abyad MS, Morsi NM, Zaki DA, Shaaban MT. (1990). Preliminary Screening of Some Egyptian Weeds for Antimicrobial Activity. Microbiosyn. 62: 47-57.
9. Woźnicka E, Kuźmiar A, Nowak D, Nykiel E, Kopacz M, et al. (2013). Comparative Study on the Antibacterial Activity of Some Flavonoids and their Sulfonic Derivatives. Acta Polon Pharm. 70: 567-571.
10. Olayerijua OS, Olaleye MT, Crown OO, Komolafe K, Boligon AA, et al. (2015). Ethylacetate Extract of Red Onion (Allium cepa L.) Tunic Affects Hemodynamic Parameters in Rats. Food Sci Human Well. 4: 115-122.
11. Jaiswal N, Kumar D, Rizvi SI. (2013). Red Onion Extract (Allium cepa L.) Supplementation Improves Redox Balance in Oxidatively Stressed Rats. Food Sci Human Well. 2: 99-104.
12. Batubara I, Suparto IH, Wulandari NS. (2017). The Best Extraction Technique for Kaempferol and Quercetin Isolation from Guava Leaves (Psidium guajava). IOP Conf. Series: Earth Environ Sci. 58: 012060.
13. Adamczewski B, Lutomski J, Marciniak K, Schmidt K. (1966). Pat. 56118, Poland, P116 568, 22.09.1966.
14. Singh BN, Singh BR, Singh RL, Prakash D, Singh DP, et al. (2009). Polyphenolic from Various Extractants of Red Onion (Allium cepa) Peel with Potent Antioxidant and Antimutagenic Activities. Food Chem Toxycol. 47: 1161-1167.
15. Domańska U. (2008). Ionic Liquids in Chemical Analysis. Chapter 1, General Review of Ionic Liquids and Their Properties. CRC Press. Taylor & Francis Group. https://www.crcpress.com/Ionic-Liquids-in-Chemical-Analysis/Koel/p/book/9781420046465.
16. Domańska U, Okuniewska P, Królikowski M. (2016). Separation of 2-Phenylethanol (PEA) from Water using Ionic Liquids. Fluid Phase Equilib. 423: 109-119.
17. Domańska U, Wlazło M, Karpińska M, Zawadzki M. (2017). High Selective Water/Butan-1-ol Separation on Investigation of Limiting Activity Coefficients with $[P_{8,8,8,8}][NTf_2]$ Ionic Liquid. Fluid Phase Equilib. 449: 1-9.
18. Freire MG, Neves CMSS, Marrucho IM, Canongia-Lopes JN, Rebelo LPN, et al. (2010). High-Performance Extraction of Alkaloids Using Aqueous Two-phase Systems with Ionic Liquids. Green Chem. 12: 1715-1725.
19. Fan Y, Dong X, Li Y, Zhong Y, Miao J, et al. (2015). Extraction of l-Tryptophan by Hydroxyl-functionalized Ionic Liquids. Ind Eng Chem Res. 54: 12966-12973.
20. Ventura SPM, E Silva FA, Quental MV, Mondal D, Freire MG, et al. (2017). Ionic-liquid-mediated Extraction and Separation Processes for Bioactive Compounds: Past, Present, and Future Trends. Chem Rev. 117: 6984-7052.
21. Louros LSC, Cláudio AFM, Neves CMSS, Freire MG, Marrucho IM, et al. (2010). Extraction of Biomolecules Using Phosphonium-based Ionic Liquids + K_3PO_4 Aqueous Biphasic Systems. Int J Mol Sci. 11: 1777-1791.
22. Gorke J, Srienc F, Kazlauskas R. (2010). Toward Advanced Ionic Liquids. Polar, Enzyme- friendly Solvents for Biocatalysis. Biotech Bioproc Eng. 15: 40-53.
23. Domańska U, Wiśniewska A, Dąbrowski Z, Więckowski M. (2018). Ionic Liquids as Efficient Extractants for Quercetin from Commercial Red Anion (Allium cepa L.). J Appl Sol Chem Model. 7: ?.
24. Wlazło M, Zawadzki M, Domańska U. (2018). Separation of Water/Butan-1-ol Based on Activity Coefficients at Infinite Dilution in 1,3-Didecyl-2-methylimidazolium Dicyanamide Ionic Liquid. J Chem Thermodyn. 116: 316-322.
25. Passos H, Trindade MP, Vaz TSM, da Costa LP, Freire MG, et al. (2013). The Impact of Self-aggregation on the Extraction of Biomolecules in Ionic-liquid-based Aqueous Two-phase Systems. Sep Pur Techn. 108: 174–180.
26. Thierry R, Lionel M, Olivier-Bourbigou H, Gilbert B. (2009). A Comparison of the Acidity Levels in Room-Temperature Ionic Liquids. J Electrochem Soc. 156: F115-F121.
27. Driver G, Johnson KE. (2003). 3-Methylimidazolium bromohydrogenates(I): a room-temperature ionic liquid for ether cleavage. Green Chem. 5: 163-169.

28. Xing H, Wang T, Zhou Z, Dai Y. (2007). The sulfonic acid-functionalized ionic liquids with pyridinium cations: Acidities and their acidity–catalytic activity relationships. J Mol Catal A: Chem. 264: 53-59.
29. Magna L, Bildé J, Olivier-Bourbigou H, Robert T, Gilber B. (2009). About the Acidity-Catalytic Activity Relationship in Ionic Liquids: Application to the Selective Isobutene Dimerization. Oil Gas Sci Technol. 64: 669-679.