

Extraction of organic impurities using 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆]

Tomasz Koźlecki, Wojciech Sawiński, Adam Sokołowski, Wojciech Ludwig, Izabela Polowczyk

Faculty of Chemistry, Wrocław University of Technology, ul. Norwida 4/6, 50-373 Wrocław, Poland, e-mail: tomasz.kozlecki@pwr.wroc.pl

Extraction of several chloro compounds from water has been examined. As the extracting liquid the 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆], which is common hydrophobic ionic liquid, was used. Additionally, extraction of selected chlorinated compounds from tert-butylmethylether (MTBE) was investigated. The obtained results show the usefulness of [BMIM][PF₆] to remove the organic impurities from water, particularly at the concentration range inappropriate for biological purification plants.

Keywords: liquid-liquid extraction, ionic liquids, industrial wastewater purification.

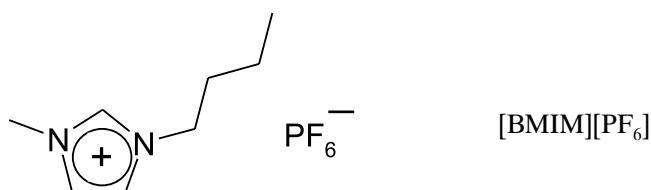
INTRODUCTION

Ionic liquids (ILs) are organic compounds, containing large organic cation (predominantly imidazolium) an organic or inorganic counterion (usually Br⁻, Cl⁻, I⁻, PF₆⁻, BF₄⁻, CH₃OSO₃⁻, NTf₂⁻). The ones, melting at room temperature or below are called room temperature ionic liquids (RTILs)¹. Over the last decade, they have attracted much attention in different areas of chemistry and technology, due to a unique combination of chemical and physical properties, such as negligible vapor pressure, high thermal stability, nonflammability, easy modification of hydrophobicity via the change of alkyl chain and/or counterion, which leads to a controlled solubilization of various organic compounds. Ionic liquids are composed entirely of ions and their vapor pressure can be negligible. For example, vapor pressure of [OMIM][PF₆] at 75°C to be 1.0·10⁻⁶ mbar², thus one can expect that the compound will decompose much below the estimated boiling point.

For the time being, approximately 1500 such compounds are known, 500 of them are commercially available. The number of papers and patents currently being published reflect both the academic and industrial interest in using RTILs in diverse areas, ranging from synthetic and catalytic chemistry to biotechnology, electrochemistry, and materials science. Nowadays, a few commercial processes have been developed: BASF's BASIL (Biphasic Acid Scavenging using Ionic Liquid) process uses ionic liquid to remove acids from reaction mixture; the French Petroleum Institute (IFP) Difasol process employs ionic liquids as reaction solvents for dimerization of butene to octenes. RTILs are investigated in gas separation processes, using both classical devices, as well as membrane contactors³⁻⁵. Another topic investigated is an application of ILs as entrainers for the extractive distillation^{6,7}, and extraction solvents. The initial studies dealt with the miscibility of various ILs with water and organic solvents; on this basis an influence of counter ion on hydrophobicity has been described⁸. The next step was the determination of partition coefficients of various solutes between IL and water^{9,10}, the possibility of extraction of metal ions has been investigated too; however, in the latter case a complexing agent, e.g. crown ether, is necessary¹¹. As a consequence some efforts to synthesize IL with crown ether moiety, as the dedicated metal extractant, have been made¹². This example shows the general topic of the research on ILs – there is a possibility to create dedicated compound, designed to carry out a specific process with the maximum efficiency. An intensive research provided numerous data concerning both the

physico-chemical properties of pure ILs, as well as their mixtures with other compounds. The new aspect is the publication of extraction (the ternary liquid-liquid equilibrium data), necessary for the design of extraction devices¹³⁻¹⁷.

One of the best-known and described RTILs are the ones containing 1-alkyl-3-methylimidazolium cation and hexafluorophosphate anion. The most widespread example is 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆], of a structure shown below:



As every hexafluorophosphate derivative, [BMIM][PF₆] is hydrophobic and water-insoluble, thus it can be considered as a good candidate to use in the extraction from an aqueous solution. Some properties of [BMIM][PF₆] at 25°C are as follows: surface tension 46.6 mN/m¹⁸, dynamic viscosity 0.207 Pa·s¹⁹, density 1370 kg/m³²⁰ and electrical conductivity 0.146 S/m²¹. It is stable compound, dissolving in solvents with a dielectric constant (ε) higher than 7, except for the water. [BMIM][PF₆] is miscible with propylene carbonate, methanol, acetonitrile, acetone, dichloromethane, tetrahydrofuran and it is immiscible with water, trichloroethylene, carbon disulphide, toluene and hexane¹⁷. Some serious drawback may be caused by the fact that PF₆⁻ anion may undergo hydrolysis to produce HF and PO₄³⁻ in the acidic aqueous phase²².

The aim of this contribution was to investigate the application as a solvent for the removal of halogenated compounds from wastewater. It is a very important subject, particularly when the concentration of contaminants is too high to apply the biological purification systems.

MATERIALS AND METHODS

Materials

[BMIM][PF₆] (99%) was purchased from SynQuest Laboratories Inc. The following materials were purchased from POCH (Poland): MTBE (>99%), 1,1-dichloroethane (>99%), trichloroethane (>99%), 1,1,2,2-tetrachloroethane (>99%), tetrachloroethylene (>99%) and trans-1,2-dichloroethylene

(>99%). The water was purified in our laboratories, and its electrical conductivity at 25°C was below 6 $\mu\text{S}/\text{cm}$.

Procedure

For each run, the measured mass of dry $[\text{BMIM}][\text{PF}_6]$ (ca. 4 g) was placed in a glass flask. $[\text{BMIM}][\text{PF}_6]$ was dried under vacuum at 70°C for 4 h. Next, 10 ml of water solute of halo compound was added. The masses of both phases were precisely measured. The mixture was stirred for 24 h at 25°C in a thermostated shaker. Finally both phases were carefully separated. The same procedure was used for the ionic liquid – MTBE systems.

Analysis

The gas chromatograph GC-14A (Shimadzu) was used to determine the concentration of organic compounds. The water in the ionic liquid phase was determined by the Karl-Fisher titration method with the 701 KF Titino apparatus (Metrohm) coupled with electronic balance (Mettler) using Hydranal Composite 5. The quantity of $[\text{BMIM}][\text{PF}_6]$ in the water phase was measured by the determination of electrical conductivity at 25°C. The calibration curve was determined and it has been proven that the halogenated compounds and contaminants have no significant effect on conductivity.

RESULTS

Chlorinated ethane and ethene derivatives are widely used in commercial applications. Unfortunately, these compounds are recognized as carcinogens; even at very low concentration they can damage the liver. According to EPA, the Maximum Contaminant Level (MCL) in drinking water for tetrachloroethylene is 0.005 mg/l, for trans-1,2-dichloroethylene 0.1 mg/l, 1,1,1-trichloroethane 0.2 mg/l, and for 1,2-dichloroethane 0.005 mg/l. All the above mentioned compounds are hydrophobic, they dissolve weakly in water. Under equilibrium conditions at 25°C mass fractions in the saturated aqueous solution for 1,1,1-trichloroethane, 1,1-dichloroethane, 1,1,2,2-tetrachloroethane, trans-1,2-dichloroethylene and tetrachloroethylene is 0.00129, 0.00504, 0.00283, 0.00452 and 0.00206, respectively.

Together with the LLE data, Table 1 and 2 include the corresponding values for the solute distribution ratio (β) and the selectivity (S), which are widely used parameters to characterize the suitability of a solvent in liquid extraction. Their calculation is easily made from the experimental compositions of the tie-line ends, according to the following expressions:

$$\beta = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \quad (1)$$

$$S = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \cdot \frac{x_1^{\text{I}}}{x_1^{\text{II}}} \quad (2)$$

Figure 1 depicts the equilibrium data for the selected halo compounds in the system containing $[\text{BMIM}][\text{PF}_6]$ – water. As mentioned before, the solubility of halogenated hydrocarbons in water is very low, thus it is possible to depict the data clearly using the standard X-Y plot. The full set of the equilibrium data is presented in Table 1. The highest partition coefficient value has been found for the $[\text{BMIM}][\text{PF}_6]$ – 1,1-dichloroethane – water system ($\beta = 46.33$). It is noteworthy that β values are usually higher at the low concentration of the solute.

The selected IL is very selective in this system with S value above 500. For other halo compounds partition coefficient

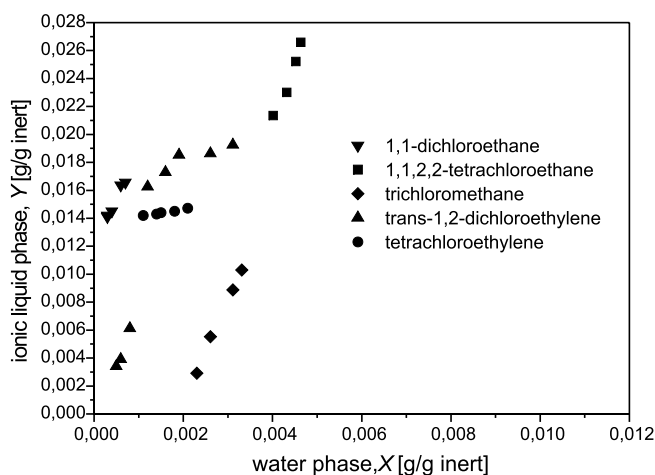


Figure 1. Phase equilibrium of halo compounds in $[\text{BMIM}][\text{PF}_6]$ – water system at 25°C

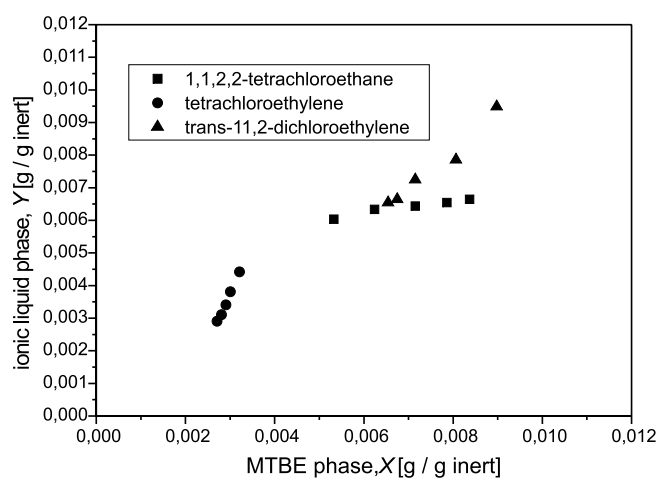


Figure 2. Phase equilibrium of halo compounds in $[\text{BMIM}][\text{PF}_6]$ – MTBE system at 25°C

values were much lower; in the case of trans-1,2-dichloroethylene the highest β obtained was 13.33. In order to compare the behavior of the saturated and unsaturated compounds, a comparison at equal solute concentration has been drawn. In the case of the compounds substituted with two chlorine atoms for $x_2 = 0.0006$ (aqueous phase), the partition coefficient is four times higher for the saturated compound. When the number of chlorine atom increased to 4, the β value decreased, but for all compounds it varies between 5 and 13. The selectivity of $[\text{BMIM}][\text{PF}_6]$ versus other ethane derivatives ($S > 200$) makes it suitable for their separation. Additionally, it can be applied for the separation of chloroform from the aqueous solution. The structure of this widespread compound is very specific due to the presence of only one carbon atom. In the $[\text{BMIM}][\text{PF}_6]$ – water system, the partition coefficient decreases from 3.09 (for $x_2 = 0.0033$) to 1.26 (for $x_2 = 0.0023$), thus it is the system which operates much less efficiently at a high concentration of chloroform.

In the present contribution, the equilibrium for the $[\text{BMIM}][\text{PF}_6]$ – halogenated compound – MTBE has been determined as well (Figure 2, Table 2). Tert-butylmethylether (MTBE) is a commonly used solvent. Our experiments have been carried out using three compounds behaving similarly with water. In all the cases the β value was close to 1; for trans-1,2-dichloroethylene when $x_2 < 0.0081$, in MTBE phase $\beta = 1$.

For two other systems, some small deviations have been observed: for 1,1,2,2-tetrachloroethane initially $\beta < 1$, but the

decrease of the solute concentration causes β to increase, while for tetrachloroethylene an opposite effect is observed. Comparison of the selectivity indicates that [BMIM][PF₆] can be used in these systems, but S -values are one order of magnitude lower than in the case of water. It is also possible to carry out a reverse process, i.e. the removal of the chlorinated compound from the ionic liquid using MTBE.

The most widespread factor describing the behavior of an organic liquid contacted with water is the 1-octanol/water partition coefficient (K_{ow}), defined as the ratio of molar concentrations of chemicals in 1-octanol and water in the dilute solution. The 1-octanol-water partition coefficient is a measure of bio-concentration and soil sedimentation tendencies of the chemical in a hydrologic cycle. Choua et al.²³ found for [BMIM][PF₆] $\log K_{ow} = -1.70$, thus it depicts low bio-concentration and soil sedimentation tendencies. On contrary, for trichloromethane $\log K_{ow} = 1.97$, 1,1-dichloroethane $\log K_{ow} = 1.81$, 1,1,2,2-tetrachloroethane $\log K_{ow} = 2.39$, tetrachloroethane $\log K_{ow} = 2.88$ and trans-1,2-dichloroethane $\log K_{ow} = 2.09$ ²⁴. This coefficient can be also compared with the value for the system containing water and studied solvent, e.g. for trichloromethane $\log K_{iw} = 0.63$, 1,1-dichloroethane $\log K_{iw} = 1.81$, 1,1,2,2-

tetrachloroethane $\log K_{iw} = 0.86$, tetrachloroethane $\log K_{iw} = 1.25$ and trans-1,2-dichloroethane $\log K_{iw} = 1.27$. It is clearly visible that [BMIM][PF₆] is comparable with 1-octanol only for 1,1-dichloroethane, for other chloro derivatives values of the partition coefficient are one order of magnitude lower than for 1-octanol.

Considering the potential application of [BMIM][PF₆] as a solvent in a classical extractor, one can see that for the aqueous feed the favorable difference of densities is observed (ca. 370 kg/m³), as well as the low interfacial tension (our measurements suggest the values ca. 1 mN/m); the latter result is expected, because ionic liquids have the amphiphilic structure. One important drawback is the high viscosity of [BMIM][PF₆], but an increase of water content drastically decreases it, according to the equation:

$$\eta = \eta_0 \cdot 10^{(-\chi_w/0.19)} \quad (3)$$

where η and η_0 are the [BMIM]PF₆ viscosity of actual and pure ionic liquid, respectively, and χ_w is the water mole fraction.

The increase of temperature decreases viscosity as well. The reduction of viscosity is most important in mem-

Table 1. The composition of the experimental tie-line ends and the values of the solute distribution ratio (β) and the selectivity (S) for ternary systems (water + halo compound- + [BMIM][PF₆])

water - rich phase			ionic liquid - rich phase			β	S
x_1	x_2	x_3	x_1	x_2	x_3		
(water + 1,1-dichloroethane + [BMIM][PF ₆])							
0.9750	0	0.0250	0.0230	0	0.9770		
0.9744	0.0003	0.0253	0.0298	0.0139	0.9563	46.33	1515.01
0.9740	0.0003	0.0257	0.0322	0.0140	0.9538	46.67	1411.59
0.9738	0.0004	0.0258	0.0361	0.0143	0.9496	35.75	964.36
0.9731	0.0006	0.0263	0.0365	0.0161	0.9474	26.83	715.38
0.9717	0.0007	0.0276	0.0377	0.0163	0.9460	23.29	600.18
(water + 1,1,2,2-tetrachloroethane + [BMIM][PF ₆])							
0.9750	0	0.0250	0.0230	0	0.9770		
0.9613	0.0040	0.0347	0.0231	0.0209	0.9560	5.23	217.44
0.9600	0.0043	0.0357	0.0242	0.0225	0.9536	5.23	210.18
0.9592	0.0045	0.0363	0.0242	0.0246	0.9512	5.47	216.68
0.9585	0.0046	0.0369	0.0243	0.0259	0.9498	5.62	221.61
(water + tetrachloroethylene + [BMIM][PF ₆])							
0.9750	0	0.0250	0.0230	0	0.9770		
0.9544	0.0011	0.0445	0.0321	0.0140	0.9539	12.73	378.41
0.9477	0.0014	0.0509	0.0318	0.0141	0.9541	10.07	300.15
0.9425	0.0015	0.0560	0.0319	0.0142	0.9539	9.47	279.70
0.9328	0.0018	0.0654	0.0314	0.0143	0.9543	7.94	236.01
0.9189	0.0021	0.0790	0.0316	0.0145	0.9539	6.90	200.78
(water + trans-1,2-dichloroethylene + [BMIM][PF ₆])							
0.9750	0	0.0250	0.0230	0	0.9770		
0.9735	0.0005	0.0260	0.0305	0.0034	0.9661	6.80	217.04
0.9731	0.0006	0.0263	0.0316	0.0039	0.9645	6.50	200.16
0.9719	0.0008	0.0273	0.0335	0.0061	0.9604	7.63	221.22
0.9687	0.0012	0.0301	0.0397	0.0160	0.9443	13.33	315.34
0.9678	0.0016	0.0306	0.0411	0.0170	0.9419	10.63	250.19
0.9644	0.0019	0.0337	0.0418	0.0182	0.9400	9.58	221.00
0.9597	0.0026	0.0377	0.0420	0.0183	0.9397	7.04	160.83
0.9456	0.0031	0.0423	0.0432	0.0189	0.9379	6.10	134.72
(water + trichloromethane + [BMIM][PF ₆])							
0.9750	0	0.0250	0.0230	0	0.9770		
0.9691	0.0023	0.0286	0.0237	0.0029	0.9734	1.26	51.56
0.9684	0.0026	0.0290	0.0241	0.0055	0.9704	2.12	85.00
0.9647	0.0031	0.0322	0.0250	0.0088	0.9662	2.84	109.54
0.9622	0.0033	0.0345	0.0255	0.0102	0.9643	3.09	116.63

*) The weight fractions of the water, halogenated compound, and [BMIM][PF₆] are denoted by x_1 , x_2 and x_3 , respectively

Table 2. The composition of the experimental tie-line ends and the values of the solute distribution ratio (β) and the selectivity (S) for ternary systems (MTBE + halo compound + [BMIM][PF₆])

MTBE-rich phase			ionic liquid-rich phase			β	S
x_1	x_2	x_3	x_1	x_2	x_3		
(MTBE + 1,1,2,2-tetrachloroethane + [BMIM][PF ₆])							
0.9749	0.0053	0.0198	0.0165	0.0060	0.9775	1.13	66.89
0.9734	0.0062	0.0204	0.0183	0.0063	0.9754	1.02	54.05
0.9720	0.0071	0.0209	0.0189	0.0064	0.9747	0.90	46.36
0.9710	0.0078	0.0212	0.0194	0.0064	0.9741	0.83	41.71
0.9695	0.0083	0.0222	0.0201	0.0066	0.9733	0.80	38.35
(MTBE + tetrachloroethylene + [BMIM][PF ₆])							
0.9753	0.0027	0.0220	0.0220	0.0029	0.9751	1.07	47.62
0.9751	0.0028	0.0221	0.0232	0.0031	0.9737	1.11	46.53
0.9749	0.0029	0.0222	0.0251	0.0034	0.9715	1.17	45.54
0.9747	0.0030	0.0223	0.0278	0.0038	0.9684	1.27	44.41
0.9745	0.0032	0.0223	0.0313	0.0044	0.9643	1.38	42.81
(MTBE + trans-1,2-dichloroethylene + [BMIM][PF ₆])							
0.9785	0.0065	0.0150	0.0630	0.0065	0.9305	1.00	15.53
0.9772	0.0067	0.0161	0.0663	0.0066	0.9271	0.99	14.52
0.9761	0.0071	0.0168	0.0715	0.0072	0.9213	1.01	13.84
0.9752	0.0080	0.0168	0.0779	0.0078	0.9143	0.98	12.21
0.9742	0.0089	0.0169	0.0935	0.0094	0.8971	1.06	11.00

*) The weight fractions of the MTBE, halogenated compound, and [BMIM][PF₆] are denoted by x_1 , x_2 and x_3 , respectively

brane contactors, where mass transfer surface is limited by the internal diameter of capillary. It seems that the use of membrane contactors, rather than the classical extraction devices is very favorable. The application of an appropriate membrane material reduces the loss of IL significantly, passing to an aqueous phase. Table 1 shows that under equilibrium conditions the IL content in an aqueous phase is as high as 3 wt%, for tetrachloroethylene even 5 wt%. The reduction of IL losses is clearly a priority when the technological process is devised, because extraction is rarely the last operation of the process; low concentration of chloro compounds prevents their full recovery. One must consider some way to completely remove the contaminant from the IL to prevent the contamination of the atmosphere. Yang and Dionysiou²⁵ proved the possibility to carry out the photodegradation of chlorophenols in the solution of [BMIM][PF₆]; the problem of the solute recovery was also investigated by Li et al.²⁶, for the extraction of dyes with [BMIM][PF₆].

The RTILs are a new group of solvents, which are still under investigation. Despite their growing production, it is hard to expect that it will reach the same scale as for the classical solvents; this will make them rather expensive. The economical aspects limit their application to specific processes of high industrial importance. Extensive research should provide a general outline for their application; the target-oriented design of the structure will provide the ILs most appropriate for the specific applications.

ACKNOWLEDGMENTS

The work was supported by the Polish Committee for Scientific Research (KBN) within the grant No. 3 T09B 10027.

SUMMARY

– We have examined the possibility to extract the halogenated organic compounds from water using the hydro-

phobic ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆]. Our data clearly show the applicability of this compound for such purpose.

– The highest partition coefficient value has been found for the [BMIM][PF₆] – 1,1-dichloroethane – water system ($\beta = 46.33$).

– For other chlorinated compounds the values of β are lower, usually between 5 and 13, except for chloroform where $1.3 < \beta < 3$.

– Generally, the β values for the saturated halo compounds are higher than for the unsaturated ones. For the compounds with two chlorine atoms the difference is four-fold, an increase of the substitution decreases the gap.

– Extraction of the halogenated compounds from tert-butylmethylether (MTBE) has been examined as well. In this case the partition coefficient values are around 1; the system can be used to extract the chlorinated compounds from the MTBE or IL phase.

– [BMIM][PF₆] can be applied in membrane contactors, because its viscosity can be greatly reduced by an increase of water content and/or temperature.

– The most important economical problem is the loss of IL due to the some solubility in water. Diminishing this will greatly improve the economy of extraction.

SYMBOLS

- x – weight solute / weight feed solvent in raffinate phase, -
- y – weight solute / weight extraction solvent in extract, -
- β – solute distribution ratio, -
- S – selectivity, -
- K_{ow} – 1-octanol/water partition coefficient, -
- K_{ilw} – ionic liquid/water partition coefficient. -

LITERATURE CITED

1. Friemantle, M. (2007). New frontiers for ionic liquids. *Chem. Eng. News*. 85, 23 – 26.

2. Blanchard, L.A., Gu, Z. & Brennecke, J.F. (2001). High-pressure phase behavior of ionic liquid/CO₂ systems. *J. Phys. Chem. B.* 105, 2437 – 2444.
3. Scovazzo, P., Kieft, J., Finan, D.A., Koval, C., DuBois, D. & Noble R. (2004). Gas separation using non-hexafluorophosphate [PF₆]⁻ anion supported ionic liquid membranes. *J. Membrane Sci.* 238, 57 – 63.
4. Yokozeki A. & Shiflett M.B. (2007). Hydrogen purification using room-temperature ionic liquids. *Appl. Energy.* 84, 351 – 361.
5. Lee, B.-C. & Outcalt, S.L. (2006). Solubilities of gases in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data.* 51, 892 – 897.
6. Arlt, W., Seiler, M., York, C. & Scheider, T. Ionic liquids as selective additives for the separation of close-boiling or azeotropic mixtures. PTC Int. Appl., 2002, WO 0274718 A2.
7. York, C., Seiler, M., Beste, Y.A. & Arlt, W. (2004). Influence of ionic liquids on the phase behavior of aqueous azeotropic systems. *J. Chem. Eng. Data.* 49, 852 – 857.
8. Olivier-Bourbigou, H. & Magna, L. (2002). Ionic liquids: perspectives for organic and catalytic reactions. *Journal of Molecular Catalysis A: Chem.* 182 – 183, 419 – 437.
9. Abraham, A., Zissimos, A.M., Huddleston, J.G., Willauer, H.D., Rogers, R.D. & Acree jr, W.E. (2003). Some novel liquid partitioning systems: water – ionic liquids and aqueous biphasic systems. *Ind. Eng. Chem. Res.* 42, 413 – 418.
10. Li, C., Xin, B., Xu, W. & Zhang, Q. (2007). Study on the extraction of dyes into a room-temperature ionic liquids and their mechanism. *J. Chem. Technol. Biotechnol.* 82, 196 – 204.
11. Visser, A.E., Swatowski, R.P., Reichert, W.M., Griffin, S.T. & Rogers, R.D. (2000). Traditional extractants in nontraditional solvents: groups 1 and 2 extraction by crown ether in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* 39, 3596 – 3604.
12. Luo, H., Dai, S., Bonnesen, P.V. & Buchanan III, A.C. (2006). Separation of fission products based on ionic liquids: task-specific ionic liquids containing an aza-crown ether fragment. *J. Alloys Comp.* 418, 195 – 199.
13. Arce, A., Rodríguez, O. & Soto, A. (2004). Experimental determination of liquid equilibrium using ionic liquids: tert-amyl ethyl ether + ethanol + 1-octyl-3-methylimidazolium chloride system at 298.15 K. *J. Chem. Eng. Data.* 49, 514 – 517.
14. Lechter, T.M., Deenadayalu, N., Soko, B. & Ramjugernath, D. (2003). Ternary liquid-liquid equilibria for mixtures of 1-methyl-octylimidazolium chloride + and alkanol + an alkane at 298.2 K and 1 bar. *J. Chem. Eng. Data.* 48, 904 – 907.
15. Arce, A., Rodríguez, O. & Soto, A. (2006). A comparative study on solvents for separation of tert-amyl ethyl ether and ethanol mixtures. New experimental data for 1-ethyl-3-methyl imidazolium ethyl sulfate ionic liquid. *Chem. Eng. Sci.* 61, 6929 – 6935.
16. Deenadayalu, N., Ngongo, K.C., Lechter, T.M. & Ramjugernath, D. (2006). Liquid-liquid equilibria for ternary mixture (an ionic liquid + benzene + heptane or hexadecane) at T=298.2 K and atmospheric pressure. *J. Chem. Eng. Data.* 51, 988 – 991.
17. Arce A., Earle M.J., Rodríguez H. & Seddon K.R. (2007). Separation of benzene and hexane by solvent extraction with 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ionic liquids: effect of the alkyl-substituent length. *J. Phys. Chem. B.* 111, 4732 – 4736.
18. Koel, M. (2000). Physical and chemical properties of ionic liquids based on the dialkylimidazolium cation. *Proc. Estonian Acad. Sci., Chem.* 49, 145 – 155.
19. Baker, S.N., Baker, G.A., Kane, M.A. & Bright F.V. (2001). The cybotactic region surrounding fluorescent probes dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate: Effects of temperature and added carbon dioxide. *J. Phys. Chem. B.* 105, 9663 – 9668.
20. Huddleston, J.G., Willauer, H.D., Swatowski, R.S., Visser, A.E. & Rogers, R.D. (1998). Room temperature ionic liquids as novel media for 'clean' liquid-liquid extraction. *Chem. Commun.* 1765 – 1766.
21. McEwen, A.B., Ngo, H.L., LeCompte, K. & Goldman, J.L., (1999). Electrochemical properties of imidazolium salt electrolytes for electrochemical capacitor applications. *J. Electrochem. Soc.* 146, 1687 – 1695.
22. Swatowski, R.P., Holbrey, J.D. & Rogers, R.D. (2003). Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem.* 5, 361 – 363.
23. Choua, C.-H., Perng, F.-S., Wong, D.S.H. & Su W.C. 1-Octanol/water partition coefficient of ionic liquids, 15 Symposium on Thermophysical Properties, Boulder, USA, 22-27.06.2003.
24. <http://www.dfm.com.tw/member/chemical/cas/108-88-3.htm>.
25. Yang, Q. & Dionysiou, D.D. (2004). Photolytic degradation of chlorinated phenols in room temperature ionic liquids. *J. Photochem. Photobiol. A: Chem.* 165, 229 – 240.
26. Li, C., Xin, B., Xu, W. & Zhand Q. (2007). Study in the extraction of dyes into a room-temperature ionic liquid and their mechanisms. *J. Chem. Technol. Biotechnol.* 82, 196 – 204.