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IMIDAZOLIUM IONIC LIQUIDS IN MINERAL PROCESSING

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Imidazolium ionic liquids (ILs) represent promising potential for industrial and technological applications - considering ILs as a new class of compounds. Usability of ILs in the mineral processing area described in the literature is up to now limited. Their application was indicated for minerals leaching, solvent extraction as well as electrochemical processes showing that these compounds may play an important role in the recovery and purification of high-value metals from water as well as ores. Imidazolium derivatives may be used as either efficient solvents or active compounds promoting separation. Environmental impact and recycling possibilities were also described. Nevertheless, their potential industrial applications in mineral processing require further detailed examination.

key words: imidazolium ionic liquids, minerals leaching, extraction, micelle formation

INTRODUCTION

Majority of chemical processes are carried out mainly in water as generally available solvent. Application of alcohols, halogen derivatives and condensed gases (SO₂, NH₃) has also found application to carry out chemical reactions. Volatile organic solvents (VOC), liquid ammonia are still in common use in the laboratory scale as well as in the chemical industry. There is tendency to eliminate organic solvents by projecting new, environmentally friendly technologies. One of the groups of compounds, which could replace traditional solvents, are ionic liquids (ILs) - organic salts with melting point lower than 100°C. As distinct from organic solvents, ionic liquids are entirely composed of ions. Moreover, conventional salts such as sodium chloride consist of small, close packed cation and anion which form a solid with high melting

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point, that limit their application as a reaction media. On the contrary, ILs are composed of bulky organic cation and small/large anion (Fig. 1). More difficult packing and weaker attractions between ions result in a liquid state of matter (Deetlefs et al., 2006; Blesic et al., 2007).

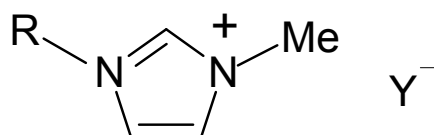


Fig. 1. Chemical structure of 1-alkyl-3-methylimidazolium ionic liquid

Their properties (selectivity, negligible volatility, inflammability, thermal stability ect.) cause that ILs may play promising role as alternative media in a number of industrial applications like catalytical (Welton, 2004; Sheldon, 2001), separation (Visser et al., 2002; Huddleston et al., 1998), electrochemical processes as well in combined reaction-separation processes. ILs are often called designer solvents or task-specific ionic liquids (TSILs) because of possibility to being tailored to fulfil technological demands of the variety applications. IL properties can be significantly adjusted e.g. hydrophobic vs. hydrophilic by interchange of the anion type, or a slight modification of the number or length of alkyl chains in the cation (Visser and Rogers, 2003). Selection of anion may significantly change the miscibility of ILs with water, whereas manipulation in alkyl chain length may have only a slight effect. Moreover, solubility in water might be increased by addition of e.g. short chain alcohols or chaotropes (Welton, 2004; Alfassi et al., 2003; Huddleston et al., 2001).

In this paper we reviewed the literature on ILs application in mineral processing, since ILs may offer potential for development of efficient, environmentally friendly metal recovery technologies from ores and wastes. Some own data on ILs surface properties are also included.

MINERALS LEACHING

The most important step of metallurgical processing is efficient separation of metals from ores followed by metals recovery from concentrate. Depletion of resources leads to using more lean ores and favours the hydrometallurgical approach.

ILs were examined as solvents (either as a neat liquid or as aqueous mixtures) for the leaching of gold, silver, copper and base metals from sulphidic ores (Whitehead et al., 2004; Whitehead et al., 2007). At present, mainly cyanides are used for the commercial hydrometallurgical leaching of gold and silver from ores and concentrates. However, due to the highly toxic nature of cyanide and environmental consequences, the process is very controversial and provokes examination of new leaching species.

$C_4MIM HSO_4$ (1-butyl-3-methyl-imidazolium hydrogen sulphate) and similar compounds in the presence of thiourea (or other S-containing compounds) and iron(III) as oxidant were used to separate gold and silver from ores.

The extraction of gold was achieved to be >85% from synthetic oxidic ore as well as natural sulphidic ore at 20-50°C using ionic liquid as a solvent. Gold extraction was close to results achieved for aqueous system H_2SO_4 /thiourea/ $Fe_2(SO_4)_3$, whereas recovery of silver from the natural sulphidic ore was significantly higher ($\geq 60\%$) for the neat IL compared with an aqueous acid solution (<10%) as presented in Fig. 2. Moreover, high selectivity for the extraction of gold and silver was reported, with minimal selectivity of other metals (Cu, Zn, Pb and Fe).

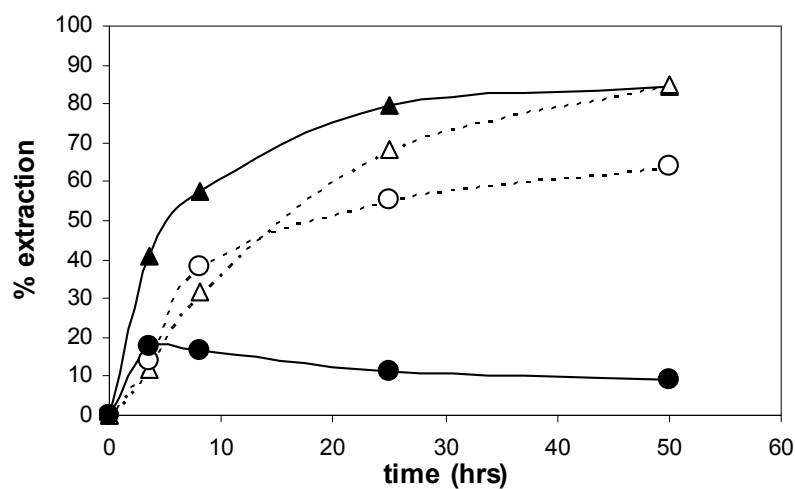


Fig. 2. Comparative leaching of gold and silver from ore using aqueous H_2SO_4 or $C_4MIM HSO_4$ in presence of $Fe_2(SO_4)_3$ and thiourea

Extension of n-alkyl chain length in imidazolium cation resulted in decreasing extraction efficiency of gold and silver, that might result from the increasing viscosity of ILs. The analysis of leaching results obtained for ILs with varied chain length and different types of anions showed that $C_4MIM HSO_4$ was the most effective medium that is important taking into account relatively low price of this compound.

Table 1. Effect of $C_4MIM HSO_4$ concentration on copper extraction from chalcopyrite at 70°C (Whitehead et al., 2007)

$C_4MIM HSO_4$ [%w/w]	Cu extracted [%]
10	55.7
20	58.1
50	82.2
100	86.6
1 M H_2SO_4	23.2

Copper extraction from chalcopyrite showed selective extraction of copper towards iron in the ionic liquid medium at 70 °C. Application of neat IL was more efficient (efficiency 87% of copper) than its solution (55% for 10%w/w) as shown in Table 1. Moreover, the recycling ability of C₄MIM HSO₄ by separation of gold and silver on activated charcoal was proposed without decomposition or significant change in the structure of IL (Whitehead et al., 2004; Whitehead et al., 2007).

MINERALS BENEFICIATION

One of the most important beneficiation processes is froth flotation of minerals, which requires hydrophobicity of the mineral particle. Only a few minerals naturally possess hydrophobic surface, hence, variety of reagents (collectors) providing hydrophobicity of the surface are used (Drzymała, 2001; Fuerstenau et al., 1985). The difficulty in the recovery of oxide-containing minerals causes that search of the new collectors is of utmost importance. So far some research involved application of pyridinium salts (which are also described as ionic liquids) in potash ores, phosphate rock, sulphide, oxide, silicate ores and coal (Madaan et al., 2008). Similarities in the composition of pyridinium and imidazolium salts allow assuming that imidazolium ILs may also behave like cationic collectors being suitable for oxide ores. ILs may form films at the surface of negatively charged particles by ion-ion interaction or interact by free electron pair of the nitrogen atom in cation with the ore surface that might increase hydrophobicity of ore particles. However, there is lack of research including application of the imidazolium ILs in flotation.

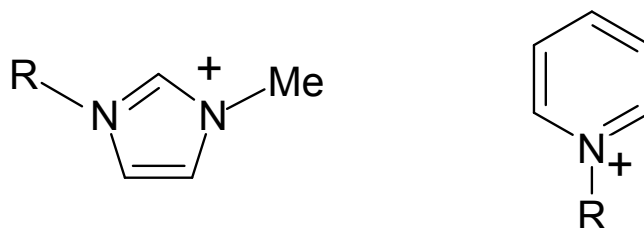


Fig. 3. Comparison of the structures of 1-alkyl-3-methylimidazolium and alkyipyridinium cation

SOLVENT EXTRACTION OF METAL IONS FROM AQUEOUS SOLUTION

Another consideration is given to application of ionic liquids in separations in order to replace organic solvents used in traditional liquid-liquid extraction of metal

ions from aqueous solutions. Some properties which make ILs attractive as alternative media in extraction processes are tunability, negligible vapour pressure, good thermal stability, and a wide liquid range. Since the partitioning of metal ions from aqueous solutions into ionic liquids is inefficient as a result of the tendency of the metal cations to remain hydrated in the aqueous phase, additional extractants, type of crown ethers (Dai et al., 1999; Chun et al., 2001), calixarenes (Luo et al., 2004), ditizone ditizone (Wei et al., 2003) and others (Visser and Rogers, 2003) were used. These species significantly enhance the partitioning of metal ions by forming complexes. The variety of tests were carried out in regard to extract heavy metals (Dai et al., 1999; Wei et al., 2003), alkali metals (Chun et al., 2001), actinides (Visser and Rogers, 2003) and lanthanoid ions (Kozonoi et al., 2007).

Modification of commonly used ILs by including a metal ion-ligating functional group in structure of one of the ions provides TSILs which play dual role of both hydrophobic solvents and extractants. Visser presented new thiourea, urea and thioether derivative of ILs designed to extract heavy metal ions (e.g. Hg^{2+} and Cd^{2+}) (Visser et al., 2001; Visser et al., 2002). According to the literature, preliminary research indicates that the application of ILs as an alternative solvent to replace traditional organic solvents in liquid - liquid extraction of metal ions is very promising.

ILs may also offer potential for the development of efficient processing of nuclear materials. The method for treating or reprocessing spent nuclear fuel using ionic liquids, and in particular to recover uranium and plutonium, was patented (Thied et al., 1999).

OTHER APPLICATIONS

We have also indicated several applications of ILs which not necessarily refer to mineral processing, however, are important in neighbouring technological areas such as metal electrowinning and waste material recycling. ILs may have potential to reduce energy consumption due to their low melting point.

Preliminary research on ILs in the electrorefining and electrowinning technologies pertains mainly aluminium processing (Nogrady, 2006; Kamavaram et al., 2003). The possibilities of aluminium refining is limited due to a strong affinity to oxygen, and cannot be electrolyzed in an aqueous solution due to its negative reduction potential (Zhang et al., 2003). Aluminium production through electrodeposition needs dissolution of alumina in molten cryolite (Na_3AlF_6) bath. To keep cryolite liquid the temperature of 1000°C is needed consuming large amounts of energy. Application of ILs instead of cryolite might diminish energy demand in a significant way. Electrorefining of aluminium alloy in acidic $\text{C}_4\text{MIM AlCl}_4$ (1-butyl-3-methylimidazolium tetrachloroaluminate) was carried out, resulting in obtaining high purity aluminum (99.89%). Energy consumption was estimated to be about 3 kWh/kg-Al in comparison to 17-18 kWh/kg-Al for the existing industrial refining process (Kamavaram et al., 2003).

Moreover, aluminium was also recovered from waste aluminium metal matrix composite by electrolysis in $C_4MIM AlCl_4$ at $103^\circ C$. A high purity product ($>98\% Al$) was obtained (Kamavaram et al., 2005). What is characteristic for electrolysis in ILs is high purity of metal deposits obtained, high current densities possible as well as low energy consumption.

The possibility of application of ILs in processing of copper sulfide ores and base metal sulfides supported by preliminary findings in the use of ionic liquids in the electrorefining of chalcopyrite ($CuFeS_2$) was also indicated (McCluskey et al., 2001).

The possibility of electrolytic purification and electrowinning is a results of the immiscibility of selected ionic liquids with water and some organic solvents and their electrical conductivity. Especially wide electrochemical windows make ILs predominant towards conventional aqueous and organic electrochemistry in the electrodeposition of certain metals (Nogrady, 2006).

POSSIBILITY OF RECYCLING

Despite a number of advantages successful commercialization of ILs will depend on price and possibilities of recycling. Due to chemical stability and negligible volatility, ionic liquids are amenable to multiply recycling which allows decreasing the cost of a process. Solubility contributes most likely to the transport in environment and resulting spreading of contaminates. However, the loss of ILs into aqueous solution during e.g. solvent extraction will be important factor in process cost estimation (Alfassi et al., 2003). It was shown, that supercritical as well as relatively low-pressure gaseous CO_2 can be used to separate ILs from organic mixtures and water (Scurto et al., 2003; Blanchard and Brennecke, 2001). Additionally, the ionic liquid can be recycled following separation of metals e.g. gold or silver on activated carbon (Whitehead et al., 2004).

Presently ILs are very expensive, however, when production on a mass scale will start the price of ILs is expected to drop significantly.

ENVIRONMENTAL IMPACT

The wide range of possible industrial applications requires an evaluation of ionic liquids with respect to their (eco)toxicity. The impact should be assessed before they enter the environment as a part of sustainable development of chemical production.

Toxicity of the common class of imidazolium ionic liquids was measured using the variety of bioassay tests including bacteria, algae, mammalian cell lines (Ranke et al., 2005; Zhao et al., 2007) as well as their biodegradability using activated sludge (Garcia et al., 2005; Gathergood et al., 2006). Imidazolium derivatives were found to be more toxic than selected organic solvents (acetone, acetonitrile, metha-

nol), poorly biodegradable and relatively resistant to photodegradation (Stepnowski and Zalewska, 2004). Increasing toxicity with elongation of alkyl chain length was also observed. The high level of biodegradability was achieved by the incorporation of an ester in the side chain of the imidazolium cation and combination with octylsulfate anion (Gathergood et al., 2006). As an effective disposal method for difficult biodegradable ionic liquid cations - the electrochemical wastewater treatment was proposed. The electrolysis results in complete destruction of 1-butyl-3-methylimidazolium cation to easily biodegradable products (Stolte et al., 2008).

SURFACE ACTIVITY

Imidazolium ionic liquids with long chain are generally seen to behave as amphiphilic compounds, displaying interface interaction. Likewise surfactants, ionic liquids also depend on chain length regarding the interface ordering phenomena (Blesic et al., 2007; Miskolczy et al., 2004; Vanyur et al., 2007; Jungnickel et al., 2008). Amphiphilic ILs possess significant promise in miscellaneous industrial applications, where high surface areas, modification of the interfacial activity or stability of colloidal systems are required. However, the state of knowledge of ILs structure and behaviour in an aqueous solution is so far limited. The phenomena of ILs self-organization in aqueous solutions are currently under investigation by our group as well as other authors (Vanyur et al., 2007; Inoue et al., 2007; Łuczak et al., 2007). The length of the alkyl chain substituents, the degree of substitution, type of counterion as well as temperature were found to have vital effect on the CMC values of ILs. There is lack of studies concerning more composed systems including e.g. electrolytes or cosurfactants.

In our previous research we have determined CMC of 1-alkyl-3-methylimidazolium ionic liquids with alkyl chain lengths 4 -18 and chloride anion (C_nMIM Cl) by surface tension and electrical conductivity measurements. The results of the surface tension measurements for the aqueous solutions as a function of the ILs concentration are presented in Fig. 4.

Discontinuities are observed only for compounds possessing the alkyl chain equal or longer than 8 carbon atoms, suggesting that only these imidazolium derivatives may be able to form micelles at 298K. The CMCs for [C₄MIM] Cl and [C₆MIM] Cl were not observed, even though the surface tension measurements of high concentrated solutions were conducted. The micelle formation in these ILs cannot be positively confirmed in the current conditions of measurements (298 K) that might result from their composition - too short alkyl chain in cation or high Krafft point of these compounds. The experimental results of the break points indicating CMCs are presented in Table 2.



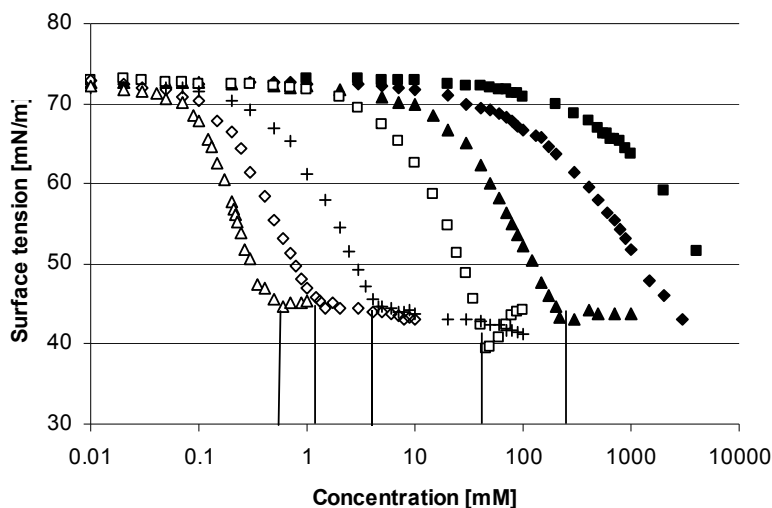


Fig. 4. Surface tension data versus IL concentration isotherms measured at 298 K for aqueous solutions of [C₄MIM] Cl (■), [C₆MIM] Cl (◆), [C₈MIM] Cl (▲), [C₁₀MIM] Cl (□), [C₁₄MIM] Cl (+), [C₁₆MIM] Cl (◇) and C₁₈MIM Cl (Δ)

Table 2. Comparison of CMC results of C_nMIM Cl and literature data of C_nMIM Br, cationic surfactants of the alkyltrimethylammonium chlorides and bromides and sodium alkylsulphates in 298K

Nr of C atoms	C _n MIM Cl	C _n MIM Br	C _n TAC	C _n TAB	SAS*
8	220 ^[1] 234 ^[1]	150 ^[2]		225 ^[3]	140 ^[4] 139 ^[5]
10	59.9 ^[1] 53.8 ^[1]	41 ^[7]	94.7 ^[6] 96 ^[9]	62 ^[3] 62.7 ^[11] 60.2 ^[11]	33 ^[4] 33 ^[5]
12		9.8 ^[7] 9.5 ^[8]	22.2 ^[6] 22 ^[9]	14.3 ^[3] 14.8 ^{[12]**} 15.7 ^{[12]**}	8.6 ^[4] 8.59 ^[5]
14	3.38 ^[1] 3.15 ^[1]	2.5 ^[7] 2.6 ^[8]	5.63 ^[6] 5.5 ^[9]	4.08 ^{[12]**} 3.94 ^{[12]**}	2.2 ^[4] 2.12 ^[5]
16	1.26 ^[1] 1.14 ^[1]	0.61 ^[7] 0.65 ^[8]	1.3 ^{[10]**}	0.93 ^{[12]**} 0.92 ^{[12]**}	0.58 ^[4] 0.58 ^[5]
18	0.40 ^[1] 0.45 ^[1]				0.23 ^[4] 0.16 ^[5]

[1]our previous work (Jungnickel et al.,2008)

[2] (Goodchild et al., 2007)

[3] (D'errico et al., 2001)

[4] (Shaw, 1992)

[5] (Huibers et al., 1997)

[6] (Perger and Bester – Rogac, 2007)

[7] (Vanyur et al., 2007)

[8] (Inoue et al., 2007)

[9] (Hayami et al., 1998)

[10] (Blesic et al., 2007)

[11] (Chakraborty and Moulik, 2007)

[12] (Basu Ray et al., 2005)

*313 K, **296 K

Described results show that elongation of the carbon chain decreases the CMC meaning that increasing the hydrophobic part of the IL cations favours micelle formation - as has been shown in the literature (Hunter, 1989). For homologous series of 1-alkyl-methylimidazolium chlorides, linear relationship between the logarithm of CMC and the number of carbon atoms in the alkyl chain of the cation has been found to be:

$$y = 4.5 - 0.28x \text{ (logCMC = } A - Bx \text{)}$$

where A , B are constants for a particular homologous series and temperature, and x is number of carbon atoms in the hydrocarbon chain. Constant A varies with the nature and number of hydrophilic groups while B is a constant which reflects the effect of each additional methylene group on the CMC. This equation is in good agreement with the relationship calculated for values published by Belsic ($y = 4.7 - 0.29x$) (Belsic et al., 2007).

Comparison of CMC data of imidazolium derivatives with the common surfactants let to conclude that we can observe similar CMC vs. number of carbon atoms in chain relationships between ILs and surfactants. The CMC values of $[C_n\text{MIM}][\text{Cl}]$ ionic liquids were found to locate between those of $C_n\text{TAC}$ and SAS possessing alkyl moiety with the analogical number of carbon atoms. An analogical relationship was also found for $[C_n\text{MIM}][\text{Br}]$, $C_n\text{TABr}$ and SAS, as shown in Fig. 5. The lower CMC values of ILs in comparison to the alkyltrimethylammonium salts might be attributed to the structure of the imidazolium head group which has weaker affinity to the hydrogen bond formation with water. On the other hand, IL as salt possessing some ionic strength may have tendency to stronger salting-out effect. Moreover, it may be also the result of interactions between anion and aromatic ring in imidazolium derivatives which did not occur in the case of typical surfactants. The lower values for compound with Br^- than Cl^- anions can be explained by the influence of the anion size. The larger ion is, the weaker hydration occurs. The weaker hydrated anions are easily adsorbed on the surface of the micelles which decreases electrostatic repulsion and in this way facilitates aggregation (Hunter, 1989).

A linear relationship between the CMC values and carbon atoms number for mentioned ILs as well as surfactants is presented in Fig. 5.

As mentioned before, the CMC determination may strongly depend on the solubility of surfactant. For ionic surfactants, there is a temperature called the Krafft temperature (K_T), below which the solubility decreases dramatically. It is necessary to measure the CMC of surfactants above the Krafft temperature since there is no micelle formation below the K_T . With rising the temperature the solubility slowly increases until at the Krafft temperature CMC is reached. The Krafft temperature and CMC of the surfactants provide information about the conditions at which the compound acts as an amphiphile (Hunter, 1989; Holmberg, 2002).

Fig. 6 presents an exemplary result of Krafft temperature determination by the conductivity method. During temperature transition the electrical conductivity increases with the increasing temperature, due to larger dissolution of the IL until the K_T



is reached. After K_T the conductance increases slowly due to the increase in ionic mobility.

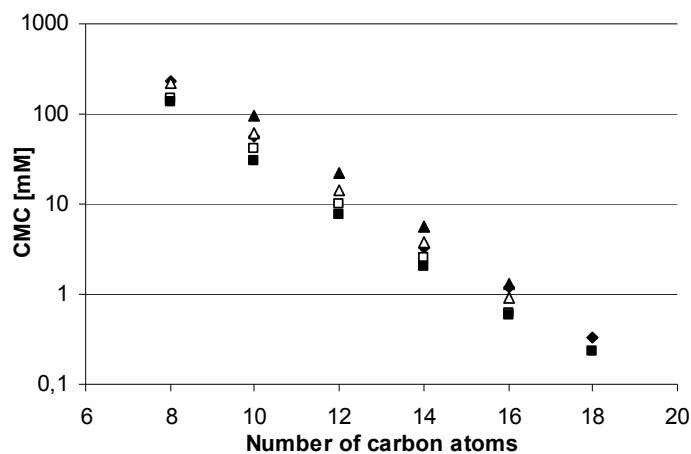


Fig. 5. CMC dependence on alkyl chain length in 298 K: C_nMIM Cl (◆), C_nMIM Br (□), C_nTAC (▲), C_nTAB (Δ) and SAS (■)

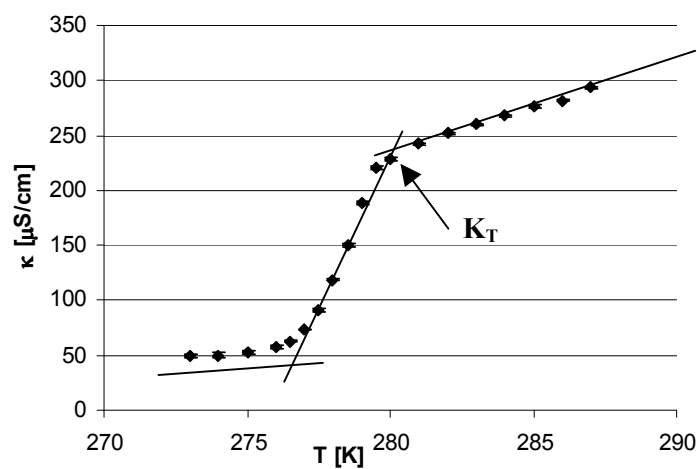


Fig. 6. The Krafft temperature determination of [C₁₆MIM]Cl

The Krafft temperatures listed in Table 5 show that determination of K_T by this method was only possible for ILs possessing more than 16 carbon atoms in chain length. The K_T for the rest of the compounds could not be determined as there was no visible turbidity even at a few degrees below 0°C. In Table 3 we report the Krafft temperatures for 1-alkyl-3-methylimidazolium chlorides, alkyltrimethylammonium bromide as well as sodium alkyl sulphates compounds. Results show that the Krafft

temperatures of ILs are lower than those of the C_n TAB and much lower than SAS homologues, presenting behaviour opposite to CMC dependence, meaning that imidazolium derivatives behave like surfactants at lower temperatures.

Table 3. The Krafft temperatures of imidazolium ILs and alkyltrimethylammonium bromides compounds

Number of Carbon atoms	8	10	12	14	16	18
C_n MIM Cl	< 273	< 273	< 273	< 273	279.5	297
C_n TAB	< 273 ^[1]	< 273 ^[1]	< 273 ^[1]	~273 ^[1]	297 ^[2]	308-309 ^[1]
SAS		281 ^[3]	289 ^[3]	303 ^[3]	318 ^[3]	329 ^[3]

[1] (Davey et al., 1989)

[2] (Adam and Pankhurst, 1946)

[3] (Shaw, 1992)

CONCLUSIONS

The application of imidazolium ionic liquids as media for separation (e.g. leaching) is growing promptly mainly because of the adjustable nature of both cation and anion. The separation possibilities are very wide including recovery of valuable metals from waste waters, ores as well as organic molecules and gases. Moreover, they offer potential to projecting and developing processes with reduced energy consumption as a result of their low melting point.

Ionic liquids are considered as promising compounds mainly thanks to their negligible vapour pressure, hence, there is no loss of ILs through evaporation. However, most of ILs described nowadays in literature for catalysis, electrochemical and separation processes consist of halogen containing anions which might be toxic and corrosive. Therefore, it is important to find methods to take advantage of the nonvolatile nature of ionic liquids that is untypical for wide used liquid media.

For the sake of many advantageous properties and successful initial experiments considering potential applications projecting of inherently non-toxic, hydrolysis stable and biodegradable compounds is crucial.

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Łuczak, J., Joskowska, M., Hupka J., *Imidazoliowe ciecze jonowe w mineralurgii*, Physicochemical Problems of Mineral Processing, 42 (2008), 223-236 (w jęz. ang)

Imidazoliowe ciecze jonowe (ILs) stanowią nową klasę związków o szerokich możliwościach przemysłowego zastosowania. Z przeglądu dostępnej literatury wynika, że ILs mogłyby zostać wykorzystane do odzysku i oczyszczania metali ze środowiska wodnego oraz rud w procesach ługowania, ekstrakcji rozpuszczalnikowej oraz w procesach elektrochemicznych. Pochodne imidazoliowe mogą być wykorzystywane zarówno jako rozpuszczalniki jak i aktywne czynniki separujące. W pracy uwzględniono także wpływ na środowisko oraz możliwości odzysku ILs. Wykazano, że potencjalne zastosowanie w mineralurgii wymaga dalszych systematycznych badań.

słowa kluczowe: imidazoliowe ciecze jonowe, ługowanie mineralne, ekstrakcja, formowanie miceli

