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Formation of Complexes in RTIL and Ion Separations

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1. Introduction

Room temperature ionic liquids (RTILs) are gaining an increasing interest as a unique medium for a complex formation and development of new inorganic materials (Cocalia et al, 2006; Billard et al, 2003; Yan et al, 2010; Vendilo et al, 2010; Nockemann et al, 2009; Nockemann et al, 2008; Murding & Tang, 2010; Billard & Gaillard, 2009; Taubert, 2004; Tang et al, 2008). Among the most promising fields the RTIL-based lithium batteries (Lewandowski & Swiderska-Mocek, 2009; Rosol et al, 2009) and recent applications of ionic liquids in the separation technology (Dundan & Kyung, 2010; Dietz, 2006) can be considered as a “hot” research topic. The present review is therefore focused on the role of cation complexes in RTIL-based metal ion separations, while the other important aspects of inorganic salt behaviour in RTILs are excellently summarised in another chapter of this book (Nockemann, 2011).

RTILs are intensively studied in solvent extraction processes due to such important advantages over conventional organic diluents as negligible vapor pressure, low flammability, moisture stability, relatively high radiation stability, different extraction properties and possibility to eliminate aqueous phase acidification (Cocalia et al, 2006a; Visser et al, 2000; Dai et al, 1999; Luo et al, 2006; Chen, 2007; Chun et al, 2001; Visser & Rogers, 2003). It is demonstrated that extraction efficacy of RTIL can be also modulated by a chelating agent administration. Dai *et al.* (Dai et al, 1999), for example, first discovered that highly efficient extraction of strontium ions can be achieved when dicyclohexane-18-crown-6 (DC18C6) is combined with RTILs. Visser *et al.* (Visser et al, 2000) reported the extraction of various alkali metal ions with crown ethers in RTILs. Visser and Rogers demonstrated that octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide dissolved in RTILs enhanced the extractability of lanthanides and actinides in comparison to conventional organic solvents (Visser & Rogers, 2003). The extraction of silver ions was found to be greatly enhanced by a combined application of RTIL and calyx[4]arene compared to that of

chloroform (Shimojo & Goto, 2004). In addition, the task-specific RTILs with coordination capacity built in the RTIL cation have been reported (Visser, et al, 2002; 2001a). Recently the efficiency of chelate extraction of 3d-cations with 8-sulfonamidoquinoline (Ajioka et al, 2008), Pu(IV) with carbamoylmethylphosphine oxide (Lohithakshan & Aggarwal, 2008) and uranyl ion with tributylphosphate (TBP) (Dietz & Stepinski, 2008) from aqueous phase into RTILs was reported. The higher selectivity of dibenzo-18-crown-6 (DB18C6) to K^+ over Na^+ in *N*-octadecylisoquinolinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate compared with that in molecular solvents suggests that RTIL provides a unique solvation environment for the complexation of crown ethers with the ions (Nishi et al, 2006). These research results provided numerous analytical applications of RTILs (Berton & Wuilloud, 2010; Ning et al, 2010; Manzoori, et al, 2009; Lertlapwasin et al, 2010). This Chapter is intended to present a review of data on complex formation of cations in hydrophilic and hydrophobic RTILs, (Table 1) in relevance to the extraction and separation processes.

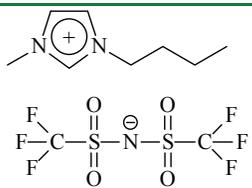
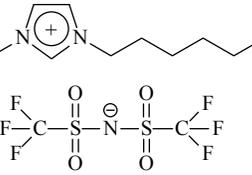
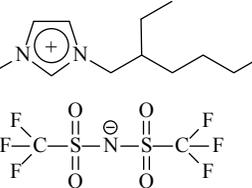
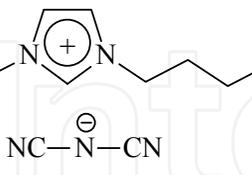
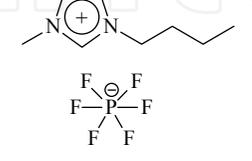
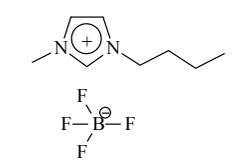
Chemical formula	Abbreviation	Name, Comment
	[BMIM][N(Tf) ₂]	1-butyl-3-methylimidazolium bis[trifluoromethyl]sulphonyl]imide; hydrophobic RTIL
	[HMIM][N(Tf) ₂]	1-hexyl-3-methylimidazolium bis[trifluoromethyl]sulphonyl]imide; hydrophobic RTIL
	[EtHMIM][N(Tf) ₂]	1-(2-ethylhexyl)-3-methylimidazolium bis[trifluoromethyl]sulphonyl]imide; hydrophobic RTIL
	[BMIM][N(CN) ₂]	1-butyl-3-methylimidazolium dicyanamide; hydrophilic RTIL
	[BMIM][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate; hydrophobic RTIL
	[BMIM][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate; hydrophilic RTIL

Table 1. Chemical formulae and abbreviations of RTILs commonly used in a present review

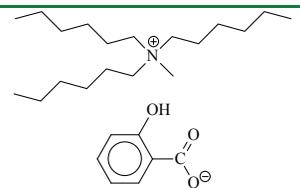
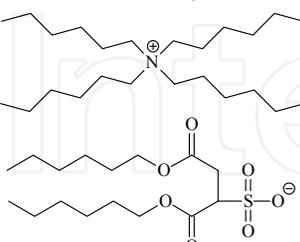
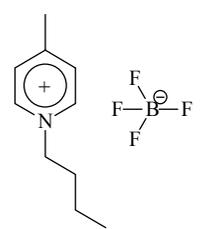
Chemical formula	Abbreviation	Name, Comment
	[TOMA][Sal]	trioctylmethylammonium salicylate; task-specific hydrophobic RTIL
	[THA][DHSS]	Tetrahexylammonium dihexylsulfosuccinate; task-specific hydrophobic RTIL
	[BMPy][BF ₄]	N-butyl-4-methyl-pyridinium tetrafluoroborate; hydrophilic RTIL

Table 1. (Continued) Chemical formulae and abbreviations of RTILs commonly used in a present review

2. Thermodynamics of complex formation in RTIL

Inorganic salts usually have poor solubility in both hydrophobic and hydrophilic RTILs at a level of 0.05-0.005 mol/dm³ (Yan et al, 2010; Seddon et al, 2000; Rosol et al, 2009; Djigailo, 2010), although in some cases (LiClO₄ in [BMIM][SCN]) it may exceed 4 mol/dm³ at ambient temperature (Rosol et al, 2009). Thus for a successive extraction of cations from aqueous solution into a hydrophobic RTIL some complexing agents are required (Cocalia et al, 2006a; Visser et al, 2000) as well as in the case of conventional organic solvents. These agents are either added to RTIL or are synthetically included into the RTIL's anion or cation structure (task-specific RTILs). This in turn requires a knowledge of particular complexes participating the extraction equilibria and chemical speciations.

However, the number of reports on the complex composition, equilibrium constants and thermodynamics of complex formation is surprisingly small relative to that of conventional molecular solvents, Table 2. The data on ΔH and ΔS of complex formation are even less common (Vendilo et al, 2010a; 2010c; 2009a).

It should be noted that all the constants mentioned in Table 2 represent co-called "conditional" equilibrium constants defined as:

$$\beta_n = [\text{ML}_n][\text{M}]^{-1}[\text{L}]^{-n} \quad (1)$$

where [M], [L] and [ML_n] represent the concentrations of cation M, ligand L and complex species ML_n (electrostatic charges are omitted for simplicity).

In a same way:

$$K_n = [\text{ML}_n][\text{ML}_{n-1}]^{-1}[\text{L}]$$

Cation	Ligand	RTIL	Method	Ref.
UO ₂ ²⁺	NO ₃ ⁻	[BMIM][N(Tf) ₂]	UV-Vis, 18.5 °C	Georg et al, 2010
Ag ⁺	Cryptand 222	[EMIM][BF ₄],[BMIM][BF ₄] [EMIM][CF ₃ SO ₃] [EMIM][N(Tf) ₂] [BMIM][N(Tf) ₂] [BMIM][N(Tf) ₂] [BMIM][N(Tf) ₂] [MPPyr][N(Tf) ₂] [BMPyr][N(Tf) ₂]	Potentiom.; Ag-electrode 25 °C	Lewandowski et al, 2005;
H ⁺ ,Li ⁺ , Na ⁺ K ⁺ , Rb ⁺ , Cs ⁺ , NH ₄ ⁺	Valinomycin	[TDMA][TFPB] ^a	Cyclic voltammetry; 25 °C	Langmaier & Samec, 2009
Li ⁺ , Na ⁺ K ⁺ , Rb ⁺	DB-18-crown-6	[ODIQ][TFBP] ^b	Cyclic voltammetry; 56 °C	Nishi et al, 2006 ;
Li ⁺	12-crown-4 15-crown-5 18-crown-6 Bz-15-crown-5	The binary molten salt mixture: 55/45 mol. % 1- methyl-3-ethylimidazolium chloride and AlCl ₃	⁷ Li ⁺ NMR, 1- 22 °C	Eyring et al, 1993
Li ⁺ Cs ⁺	OH ⁻ 18-crown-6	[THA][DHSS] [BMIM][BF ₄], [THA][DHSS] [BMIM][N(Tf) ₂], [BMPy][BF ₄] [BMIM][PF ₆], [TOMA][Sal] [BMIM][N(CN) ₂] [BMIM][CF ₃ SO ₃] [HMIM][N(Tf) ₂] [EtHMIM][N(Tf) ₂]	NMR,25 °C ¹³³ Cs NMR, 25 - 50 °C in a water saturated RTIL	Djigailo, 2010 Popov et al, 2007; Vendilo, et al, 2010a,c; Vendilo et al, 2009, 2009a
Cs ⁺	DB-18-crown-6	[BMIM][N(Tf) ₂] [THA][DHSS],[TOMA][Sal]	NMR ¹³³ Cs, 25 - 50 °C	Djigailo, 2010
Na ⁺ , Cs ⁺	18-crown-6; DB-18-crown-6	[BMPy][BF ₄]/ water solvent	mixed NMR ¹³³ Cs, ²³ Na; 25 °C	Popov et al, 2007
Sr ²⁺	Dichloromethylene- bis(phosphonic acid) triisopropyl ester	[BMIM][N(CN) ₂]	NMR ³¹ P, 25 °C	Vendilo, 2010d
Ni ²⁺ , Pb ²⁺	2-aminothiophenol	[BMIM][PF ₆]	25 °C, extraction;	Lertlapwasin et al, 2010
Cu ²⁺	ethylenediamine	[BPy][NO ₃] ^c	UV-Vis; 25-45 °C	Song et al, 2005

^a Tridodecylmethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; ^bN-octadecyl-isoquinolinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; ^cN-butylpyridinium nitrate

Table 2. Complexes in RTIL, characterized by stability constants

Complex formation studies in aqueous solutions require the ionic strength control (Popov & Wanner, 2005), which is normally provided by an inert supporting electrolyte added in amounts that several orders of magnitude exceed the content of reagents participating in the equilibrium. Therefore the correct comparison of the equilibrium data is possible when they are referred to an equal ionic strength values.

In the case of RTILs the ionic strength is provided by the solvent itself. Thus the ionic strength I depends on a density and molar mass of a RTIL and varies in a rather wide range. For example, $I = 5.35 \text{ mol} \cdot \text{dm}^{-3}$ for [BMIM][BF₄], 4.83 for [BMIM][PF₆], and 2.91 for [BMIM][N(Tf)₂]. In our review we have used the “conditional” constants in the form they have been published, although these can be transformed into thermodynamic constants.

Unfortunately up to now there are no systems studied by at least two independent research groups. At the same time, the stability constants published evidently have different quality. For example, all constants presented in (Eyring et al, 1993) have too high SD to be treated by IUPAC even as provisional. Indeed, $\log K_1$ values for Li⁺ complexes with 12-crown-4, 15-crown-5, benzo-15-crown-5 (Bz-15-crown-5) and 18-crown-6 (18C6) in a mixture of RTILs are reported to be 3.1 ± 2.3 , 4.1 ± 3.5 , 3.5 ± 2.9 and 1.8 ± 0.6 respectively (Eyring et al, 1993).

The constants presented in (Lertlapwasin et al, 2010) are not actually the stability constants, but are some effective ones. Those published for valinomycin (Langmaier & Samec, 2009) seem to be overestimated, as far as they exceed any known constants for this ligand in any solvent by several orders of magnitude. However, the data that are reported for Ag⁺ seem to be reliable, as the presented by this group value for DMSO fits in very well with the corresponding data of several independent research groups. Some of the $\log K$ values for RTILs are presented in Tables 3-5 along with the stability of the same complexes in some molecular solvents (Ruas et al, 2006; Ikeda et al, 2008; Danil de Namor et al, 1995; Arnaud-Neu et al, 2003; Bessiere & Lejaille, 1979; Ernst & Jezowska-Trzebiatowska, Jezowska-Trzebiatowska & Chmielowska, 1961; Chmielowska, 1961; Kikuchi & Sakamoto, 2000).

As could be seen from Table 3 the stability of such different species as [UO₂(NO₃)₂], [Ag(Cryptand 2.2.2)]⁺ and [Cs(18C6)]⁺ in a “classical” RTIL [BMIM][N(Tf)₂], is generally higher than in water, but lower than in the less polar molecular solvents. The same result we recently got for complexes of Sr²⁺ with dichloromethylene-bis(phosphonic acid) triisopropyl ester: $\log K_1 = 3.5$ in [BMIM][N(CN)₂], while in water $\log K_1 = -0.37$ (Vendilo, 2010d). Only for Li⁺ complex with OH⁻ in [THA][DHSS], $\log K_1 = -0.22$ is comparable within the error with the value obtained for water: -0.1 (Djigailo, 2010).

This trend can be observed clearly for [Cs(18-crown-6)]⁺ stability in a number of hydrophobic and hydrophilic RTILs, Table 4. The only one exception registered up to now is a case of task-specific RTIL [THA][DHSS], in which an anion of ionic liquid competes for Cs⁺ with 18-crown-6 and therefore diminishes the $\log K_1$ of [Cs(18-crown-6)]⁺ complex. This conclusion is of importance for extraction of cations from aqueous solutions.

It was noted, that the $\log K_1$ values for RTILs fall inside, but not outside the range of those for molecular solvents, with location between acetonitrile and water (Vendilo et al, 2010). At the same time, the $\log K_1$ values for an alkali metal cation with crown ether in molecular solvents is correlated (Mei et al, 1977; Smetana & Popov, 1980) with donor number (DN) of the solvent (Reichardt, 2005), Table 5, although some exceptions for [Cs(18C6)]⁺ are known (pyridine: DN 33.1; $\log K_1 = 5.7$ (Mei et al, 1977)). In this sense, the $\log K_1$ value presented in Table 5 suggest that hydrophobic RTILs [HMIM][N(Tf)₂], [BMIM][N(Tf)₂], [BMIM][PF₆], [TOMA][Sal] as well as hydrophilic [BMIM][N(CN)₂] [BMPy][BF₄] [BPy][MeSO₄] have DN between 33 (water) and 14 (acetonitrile), e.g. span the same range that polar molecular

solvents do, but are rather far from such nonpolar solvent as 1,2-dichloroethane (DN 0 (Kikuchi & Sakamoto, 2000)). This observation spreads out the data reported by Nishi *et al.* for Li⁺, Na⁺, K⁺ and Rb⁺ complexes with dibenzo-18-crown-6 in a hydrophobic RTIL *N*-octadecylisoquinolinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, which is demonstrated to have DN between 4.4 (nitrobenzene) and 0 (1,2-dichloroethane).

Complex	log β _i				
	[BMIM][N(Tf) ₂]	H ₂ O	Acetonitrile	DMSO	MeOH
[UO ₂ NO ₃] ⁺	4.8 ^a	0.30 ^b	7.9 ^c		
[UO ₂ (NO ₃) ₂]	8.3 ^a	0.31 ^b	15.0 ^c		^d
[UO ₂ (NO ₃) ₃] ⁻	12.2 ^a		20.0 ^c		
[Ag(Cryptand 222)] ⁺	10.0 ^e ;	9.6 ^f	9.01 ^j	8.4 ^e	12.3 ^f
[Cs(18-crown-6)] ⁺	3.4 ^h	0.91 ⁱ	4.8 ⁱ	3.04 ⁱ	4.6 ⁱ
[Cs(18-crown-6) ₂] ⁺	1.29 ^h		0.6 ⁱ		2.06 ⁱ

^a (Georg *et al.*, 2010); ^b (Ruas *et al.*, 2006); ^c (Ikeda *et al.*, 2008); ^d log K₂ = 3.67 (Ernst & Jezowska-Trzebiatowska, 1966) and 3.4 (Jezowska-Trzebiatowska & Chmielowska, 1961); ^e (Lewandowski *et al.*, 2005); ^f (Bessiere & Lejaille, 1979); ^j (Danil de Namor *et al.*, 1995); ^h (Vendilo *et al.*, 2010); ⁱ (Arnaud-Neu *et al.*, 2003); all data for 23-30 °C.

Table 3. Stability constants of complexes in [BMIM][N(Tf)₂] and in molecular solvents

M ⁺	RTIL / L (Nishi <i>et al.</i> , 2006)	log K ₁	RTIL / L (Langmaier & Samec, 2009)	log K ₁
Li ⁺	[TDMA][TFPB]/DB18C6	5.0	[TDMA][TFPB]/valinomycin	11.1
Na ⁺	[TDMA][TFPB]/DB18C6	7.0	[TDMA][TFPB]/ valinomycin	12.8
K ⁺	[TDMA][TFPB]/DB18C6	8.2	[TDMA][TFPB]/ valinomycin	17.2
Rb ⁺	[TDMA][TFPB]/DB18C6	7.3	[TDMA][TFPB]/ valinomycin	15.7
Cs ⁺	[BMIM] [N(Tf) ₂]/ DB18C6	3.47 ^a	[TDMA][TFPB]/ valinomycin	15.1
NH ₄ ⁺			[TDMA][TFPB]/ valinomycin	14.7

^a Ref. (Djigailo, 2010); for Li⁺, Na⁺, K⁺ and Rb⁺ complexes with DB18C6 in 1,2-dichloroethane log K₁: 11.3; 11.2; 9.9; 8.3; in nitrobenzene: 4.8; 7.3; 7.2; 5.2; in DMFA: 3.0; 3.34; 3.54, 3.54; for Na⁺, K⁺ and Rb⁺ in water: 1.16; 1.67; 1.08 and in methanol: 4.40; 5.05 and 4.23 respectively (Nishi *et al.*, 2006); for Cs⁺ complex with valinomycin in methanol log K₁=3.90, for K⁺ 4.48-4.90; for NH₄⁺ 1.67; Na⁺ 0.67-1.1; Rb⁺ 4.81 (IUPAC, 2007)

Table 4. Stability constants of alkali metal complexes with DB18C6 and valynomycine in RTIL at 25 °C

There is also some qualitative agreement of the log K₁ values and a solvent polarity derived from E^N_T scale (Reichardt, 2005) (empirical scale based on solvatochromic pyridinium *N*-phenolate betaine dye), Table 5. An examination of Table 5 reveals that the polarity of RTILs with a range of 0.60 – 0.65 fits well into the existing empirical solvent polarity scale for molecular solvents characterizing them not as “superpolar”, but as quite normal polar solvents (Reichardt, 2005). In this respect it is interesting to note, that the water content in RTIL strongly affects both stability constants (Popov *et al.*, 2007) and E^N_T values (Reichardt, 2005). As far as all log K₁ values in Table 5 correspond to a water saturated samples, this might be a reason of a far not ideal correlation between E^N_T and stability constants.

A tendency to form ML_2 complexes decreases sybatic with DN, or antibatic with E^{N_T} . Cs^+ forms therefore only ML complexes with 18-crown-6 in water (E^{N_T} 10), DMSO (E^{N_T} 0.45) and [BMIM][PF₆], [TOMA][Sal], [BMIM][BF₄] (E^{N_T} 0.66-0.67), while in a weakly solvating solvents 1,2-dichloroethane (E^{N_T} 0.3 for CH₂Cl₂), acetone (E^{N_T} 0.35), DMFA (E^{N_T} 0.4) and [HMIM][NTf₂] (E^{N_T} 0.654), [BMIM][NTf₂] (E^{N_T} 0.596) also ML_2 species are registered. The $\log K_2$ values for [EtHMIM][N(Tf)₂], [HMIM][N(Tf)₂] and [BMIM][N(Tf)₂] appeared to be 2 to 3 log units lower then $\log K_1$, Table 5. These values correspond well to those found for molecular solvents, and for UO₂²⁺ complexes with NO₃⁻ in [BMIM][N(Tf)₂], Table 3.

Solvent	DN ^b	E^{N_T} ^c	$\log K_1$	$\log K_2$	Reference
1,2-Dichloroethane	0		7.98	2.58	Kikuchi & Sakamoto, 2000
Acetonitrile	14.1		4.8	0.6	Arnaud-Neu et al, 2003; Mei et al, 1977
Propylene carbonate	15.1		4.50	1.0	Arnaud-Neu et al, 2003; Mei et al, 1977
Acetone	17.0	0.35	4.51	1.5	Arnaud-Neu et al, 2003; Mei et al, 1977
[HMIM][N(Tf) ₂]		0.654	4.4	1.13	Vendilo et al, 2010
DMFA	26.6	0.40	3.64	0.4	Arnaud-Neu et al, 2003; Mei et al, 1977)
[EtHMIM][N(Tf) ₂]			3.4	1.16	Vendilo et al, 2010
[BMIM][N(Tf) ₂]		0.596	3.4	1.29	Vendilo et al, 2010
DMSO	29.8	0.45	3.04		Arnaud-Neu et al, 2003
[BMIM][N(CN) ₂]			3.03		Popov, 2007a
[BMIM][BF ₄]		0.673	2.8		Popov, 2007a
[BMPy][BF ₄]		0.630	2.6		Popov, 2007a
[BMIM][PF ₆]		0.667	2.4		Vendilo et al, 2010
[TOMA][Sal]			1.43		Vendilo et al, 2010
[BPy][MeSO ₄]			1.20		Vendilo et al, 2008
Water	33	1.0	0.96	-	Arnaud-Neu et al, 2003
[THA][DHSS]			0.76		Vendilo et al, 2010

^a For molecular solvents $\log K_1$ values are given for $I = 0 - 0.1 \text{ mol/dm}^3$; ref. (Arnaud-Neu et al, 2003) indicates IUPAC selection; ^b Ref. (Gutmann & Vichera, 1966); ^c Ref. (Reichardt, 2005)

Table 5. Stability constants of cesium complexes with 18C6 in RTILs and in molecular solvents at 25 °C.

Indeed N(Tf)₂-anion has a very weak solvating ability, being easily substituted in coordination sphere of UO₂²⁺ even by nitrate ion, which in turn demonstrates a very high stability. For a long time it was believed that N(Tf)₂⁻ does not form complexes, unless the crystal structures of [PMIM][Eu(N(Tf)₂)₄], [BMIM][Eu(N(Tf)₂)₄], [BMPy]₂[Eu(N(Tf)₂)₅] (Tang et al, 2008) and [mppy]₂[Yb(N(Tf)₂)₅], where PMIM indicates 1-propyl-3-methylimidazolium and mppy - 1-methyl-1-propylpyrrolidinium (Murding, et al 2005), have demonstrated that it can coordinate as a bidentate ligand via oxygen atoms forming either 6-membered or 4-membered rings:



Similar structures have been found for alkaline earth metals: [mppy_r]₂[Ca(N(Tf)₂)₄], [mppy_r]₂[Sr(N(Tf)₂)₄] and [mppy_r][Ba(N(Tf)₂)₃] (Babai & Murding, 2006). Even the alkali ions are found to form weak bonds with N(Tf)₂⁻ (Yan et al, 2010). An X-Ray structure of [K(18C6)][N(Tf)₂] revealed that bistriflimide anion forms an asymmetric bridge between two [K(18C6)]⁺ units. One has a monodentate bond with an oxygen atom of one Tf fragment of N(Tf)₂⁻ anion. Another Tf arm is coordinated via two oxygen atoms with a formation of a chelate ring with K⁺ to the second [K(18C6)]⁺ unit. The potassium ions have therefore the coordination numbers 7 and 8.

A saturation of RTILs with water leads generally to a decrease of stability constant value for alkali metal complexes with crown ethers. For [Cs(18C6)]⁺ in [BMPy][BF₄]/water mixed solvents a linear dependence of logK₁ on RTIL content was observed (Popov et al, 2007). This behavior is similar to that in water/ethanol mixtures (Arnaud-Neu et al, 2003).

An increase of temperature decreases the stability constants of CsL for [HMIM][N(Tf)₂], [BMIM][N(Tf)₂] and [BMIM][PF₆], but increases them for [TOMA][Sal] and [THA][DHSS]. The thermodynamic quantities for the formation of [Cs(18C6)]⁺ in RTIL are summarized in Table 6 together with those for molecular solvents.

With an exception of [THA][DHSS] and [TOMA][Sal], the cesium nitrate solubility in RTIL is much less than in water, the metal-solvent interaction is likely to be stronger in water, than in RTIL, *i.e.* less energy is needed for breaking the metal-(RTIL anion) bonds. Thus the

Solvent	ΔH_1 , kJ/mol	ΔS_1 , J/(mol K)	ΔH_2 , kJ/mol	ΔS_2 , J/(mol K)	Reference
Acetonitrile	-17 (1)	35			Arnaud-Neu et al, 2003
Propylene carbonate	-43.3	-17.6			Arnaud-Neu et al, 2003
Methanol	-47.2	-70.5	-13.9	-7.1	Arnaud-Neu et al, 2003
Acetone	-52.8 (0.4)	-27.2			Arnaud-Neu et al, 2003
DMFA	-49.2 (0.8)	-28.4			Arnaud-Neu et al, 2003
[EtHMIM][N(Tf) ₂]	9 (18)	100 (60)	-17.5 (0.3)	-36.5 (1.0)	Vendilo et al, 2010
[HMIM][N(Tf) ₂]	-9.5 (0.4)	53 (15)	-17.8 (0.3)	-38.3 (0.9)	Vendilo et al, 2010
[BMIM][N(Tf) ₂]	-6.8 (1.9)	41.5 (6.1)	-41.3 (0.7) ^b	-114 (1) ^b	Vendilo et al, 2010
[BMIM][N(CN) ₂]	-47 (2)	-30 (2)			Popov et al, 2007a
[BMIM][BF ₄]	-80 (3)	-65 (3)			Popov et al, 2007a
[BMIM][PF ₆]	-21.0 (1.4)	-25.4 (4.5)			Vendilo et al, 2010
[BMPy][BF ₄]	-47 (1)	-32 (1)			Popov et al, 2007a
[TOMA][Sal]	3.85 (0.25)	40.3 (0.7)			Vendilo et al, 2010
Water	-17 (1)	-39			Arnaud-Neu et al, 2003
[THA][DHSS]	2.1 (0.3)	21.6 (1.1)			Vendilo et al, 2010

^a Ref. (Arnaud-Neu et al, 2003), corresponds to 25 °C and $I = 0 - 0.1$ mol/dm³, IUPAC selection; ^b Ref. (Vendilo et al, 2008).

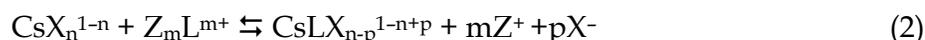
Table 6. Thermodynamic Quantities ΔH_1 , ΔS_1 , ΔH_2 and ΔS_2 of Cesium Complexes Formation with 18C6 in RTIL and in molecular solvents at 25 °C ^a.

differences in metal-solvent interactions are expected to make complex formation more exothermic in RTIL than in water. Indeed, for CsL formation ΔH_1 is negative for all hydrophilic RTILs, [HMIM][N(Tf)₂], [BMIM][N(Tf)₂], [BMIM][PF₆] and almost for all polar molecular solvents.

Generally, it can be seen that enthalpy change promotes complex formation in hydrophilic RTIL, whereas the corresponding change of entropy is negative and provides the decomposition of [Cs(18C6)]⁺. However, this is not the case of hydrophobic RTILs [HMIM][N(Tf)₂], [BMIM][N(Tf)₂], [TOMA][Sal] and [THA][DHSS], that reveal a positive entropy change like acetonitrile. Moreover, the entropy change gives the dominating contribution to [Cs(18C6)]⁺ stability in [BMIM][N(Tf)₂], [TOMA][Sal] and [THA][DHSS]. Only one hydrophobic RTIL ([BMIM][PF₆]) demonstrates the same behavior as hydrophilic RTILs and polar molecular solvents.

Thus, the thermodynamic quantities clearly indicate, that the contributions to the overall stability of CsL complex may differ rather significantly. The reaction enthalpies and entropies, show greater diversity, than $\log K_1$ depending on RTIL composition. The complexation of Cs⁺ is the most exothermic in [BMIM][BF₄]. Moreover, the observed ΔH_1 value is the highest known for CsL in both molecular solvents and RTIL. At the same time the corresponding entropy change for this solvent is also the highest, diminishing the enthalpy contribution to the $\log K_1$. The data listed in Table 6 obviously indicate, that both cation and anion of RTIL affect the complex formation stability and thermodynamic functions change.

This is not simply explained in terms of the solvation of the cesium ion and 18C6. The tentative scheme of complex formation in RTIL (2) is more complicated than that in molecular solvents (Ohtsu & Ozutsumi, 2003; Ozutsumi et al, 1994). In general, both ions forming the ionic liquid (its cation Z⁺ and anion X⁻) may react with cesium complex constituents. Z⁺ is competing with cesium for the ligand, while X⁻ solvates cesium, resisting complex formation:



In this respect ¹³³Cs NMR study can be considered as a very sensitive probe. The NMR chemical shift data, Table 7, indicate that crown ether does not substitute all RTIL anions X⁻ in coordination sphere of cesium in [Cs(18C6)]⁺ complexes, even in triflimide-based RTILs. This observation agrees well with X-ray structural data for cesium complexes with 18-crown-6 in solid state (Gjikaj & Adam, 2006; Ellerman et al, 1998) and in an aqueous solution (Ozutsumi et al, 1989), as well as with classical molecular dynamics simulations (Dang, 1995). In all these structures cesium is located above the mean oxygen plane of the crown ether ring since its size is larger than the cavity size of 18C6 (170 and 130 pm, respectively (Arnaud-Neu et al, 2003)). Thus the exposed part of Cs⁺ may interact with RTIL anions making coordination number equal to 8 or 9 as it is observed crystallographically for molecular solvents. This supposition is also in a good agreement with the structural data for [K(18C6)][N(Tf)₂] (Yan et al, 2010).

¹³³Cs NMR chemical shifts of Cs⁺ cation in RTILs span a very broad range from - 90 ppm ([BMIM][PF₆]) to 90 ppm ([BMIM][N(CN)₂]) clearly indicating their dependence on the RTIL's anion nature, but not of the cation's one. Indeed, for all three [N(Tf)₂]-based RTILs the chemical shifts of Cs⁺ are the same within the experimental error. At the same time the highly negative shift for [BMIM][PF₆] is rather close to those observed for [BMPy][BF₄] and [BMIM][BF₄] (~ - 70 ppm).

Solvent	¹³³ Cs NMR chemical shift, ppm			Reference
	δ_{Cs}	δ_{CsL}	δ_{CsL_2}	
Acetonitrile	24.1	14.8	-53 (7)	Mei et al, 1977
Propylene carbonate	-36.5	-8.1 (0.2)	-44.5 (0.3)	Mei et al, 1977
Acetone	-35.8	-6.4	-47 (9)	Mei et al, 1977
[HMIM][N(Tf) ₂]	-30.7 (0.6)	-5 (1.0)	-50 (4)	Vendilo et al, 2010
DMFA	-0.8	3.37	-48 (1)	Mei et al, 1977
[EtHMIM][N(Tf) ₂]	-30.6 (0.2)	-3.9 (0.2)	-51 (4)	Vendilo et al, 2010
[BMIM][N(Tf) ₂]	-29.6 (0.5)	-5; -6.5	-47 (1)	Vendilo et al, 2010
DMSO	68.0	23.6	-49 (2)	Mei et al, 1977
[BMIM][N(CN) ₂]	91 (1)	34 (1)	-	Popov et al, 2007a
[BMIM][BF ₄]	-68 (4)	-22 (4)	-	Popov et al, 2007a
[BMPy][BF ₄]	-70 (7)	-16 (5)	-	Popov et al, 2007a
[BMIM][PF ₆]	-91 (2)	-7 (14)	-	Vendilo et al, 2010
[TOMA][Sal]	31 (0.7)	-29 (1)	-	Vendilo et al, 2010
[BPy][MeSO ₄]	23.3 (0.5)	-7 (5)	-	Vendilo et al, 2008
[THA][DHSS]	22.5 (0.3)	-47 (2)	-	Vendilo et al, 2010

^a All ¹³³Cs NMR chemical shifts are reported relative to external reference CsCl solution in D₂O. Down field shifts are denoted as positive.

Table 7. ¹³³Cs NMR chemical shifts for [Cs(18C6)] and [Cs(18C6)₂] complexes at 22-25 °C^a

An increase of crown ether concentration in RTIL up to 1:1 cation/ligand molar ratio resulted in the corresponding monotonous increase of δ_{obs} for [BMIM][N(Tf)₂], [HMIM][N(Tf)₂], [EtHMIM][N(Tf)₂] and at a higher ligand excess for [BMIM][PF₆] up to ~ -5 ppm, which corresponded to [Cs(18C6)]⁺ species. By contrast, the chemical shifts of ¹³³Cs decreased as 18C6 was added to the [TOMA][Sal] and [THA][DHSS] solution. Thus, complex formation diminishes the differences in Cs⁺ environment and makes chemical shifts δ_{CsL} more close to each other for all RTIL, relative to δ_{Cs} . This observation is consistent with the fact that in all solvents 18C6 occupies the major part of cesium coordination sphere in more or less similar way. However, the resonances of ¹³³Cs in [CsL]⁺ still remain different in values and signs indicating different solvation and/or different ligand conformation of a complex, Table 7.

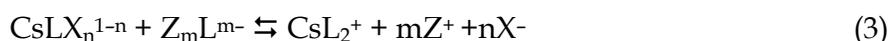
For [BMIM][N(Tf)₂], [HMIM][N(Tf)₂], [EtHMIM][N(Tf)₂] an excess of 18C6 over [Cs][L] 1:1 molar ratio leads to decrease of a chemical shift indicating the CsL₂ complex formation. The upfield shift followed by a sharp break and a downfield shift which gradually approaches an almost the same limiting value for all three N(Tf)₂-based RTILs can be explained by the formation of a strong CsL complex followed by addition of a second molecule of a ligand to form a "sandwich" CsL₂ complex. A similar break was also found for such molecular solvents as propylene carbonate, acetonitrile, and DMFA (Mei et al, 1977).

It is interesting to note that chemical shifts of [Cs(18C6)₂]⁺ are essentially independent of solvent's nature, Table 7, providing almost the same values for RTIL and for molecular solvents. This observation indicates that in a "sandwich"-type complex the two crown ether molecules effectively shield the cesium ion from interaction with solvent. By contrast, the chemical shifts of [Cs(18C6)]⁺ are strongly solvent dependent both in RTIL and in molecular solvents.

Generally, chemical shift of ^{133}Cs seems to depend rather on an anion's nature in RTIL, than on the cation's one. This can be expected reasonably, as the co-ordination sphere of Cs^+ in RTIL is formed by anions. These anions are partly substituted by 18C6 due to complex formation, while the remaining ones provide the cause for differences in the chemical shifts of complexes. Indeed, the chemical shifts of Cs^+ and $[\text{Cs}18\text{C}6]^+$ are almost the same in $[\text{BMIM}][\text{BF}_4]$ and $[\text{BMPy}][\text{BF}_4]$ as well as in $[\text{BMIM}][\text{N}(\text{Tf})_2]$, $[\text{HMIM}][\text{N}(\text{Tf})_2]$ and $[\text{EtHMIM}][\text{N}(\text{Tf})_2]$. This is consistent with formation of similar species $[\text{Cs} \cdot (\text{BF}_4)_n]^{1-n}$ and $[\text{Cs}(18\text{C}6) \cdot (\text{BF}_4)_{n-x}]^{1-n+x}$ in both $[\text{BF}_4]$ -based RTIL, as well as $\{\text{Cs} \cdot [\text{N}(\text{Tf})_2]_m\}^{1-m}$ and $\{\text{Cs}(18\text{C}6) \cdot [\text{N}(\text{Tf})_2]_{m-x}\}^{1-m+x}$ in those $[\text{N}(\text{Tf})_2]$ -based. Meanwhile, for $[\text{BMIM}][\text{N}(\text{CN})_2]$ and $[\text{THA}][\text{DHSS}]$ the chemical shifts of δ_{Cs} and δ_{CsL} are definitely different, demonstrating a different environment of cesium in both species relative to those mentioned above.

On the other hand, a strong influence of the ionic liquid cation, Z^+ , on $\log K_1$, ΔH_1 and ΔS_1 values of complex formation is observed when $[\text{BMIM}][\text{BF}_4]$ and $[\text{BMPy}][\text{BF}_4]$ are compared, indicating Z^+ -crown ether interactions of various intensity. Such interaction has also analogues among molecular solvents. For example, for AN, nitromethane (NM) and even for chloroform 18-crown-6 $\cdot 2\text{AN}$, 18-crown-6 $\cdot 2\text{NM}$ and 18-crown-6 $\cdot 2\text{CH}_2\text{Cl}_2$ solvates have been isolated and their structures have been determined by X-ray crystallography (de Boer et al, 1982; Rogers et al, 1988; Garrell et al, 1988; Jones et al, 1994). Hence, both cation and anion of RTIL have an impact on the resultant stability constant and thermodynamic quantities of chelated compound.

For ML_2 complexes in hydrophobic RTIL the situation is significantly different from that for ML complexes: ΔH_2 is more negative than ΔH_1 , at the same time ΔS_2 is negative, while ΔS_1 is positive. For the second crown ether molecule coordination in $[\text{BMIM}][\text{N}(\text{Tf})_2]$, $[\text{HMIM}][\text{N}(\text{Tf})_2]$ and $[\text{EtHMIM}][\text{N}(\text{Tf})_2]$, (3):



a possible explanation could be associated with a very weak X^- bonding in the CsLX_n^{1-n} species. An extreme case, when $n = 0$, is also possible. This is consistent with poor coordinating ability of the $\text{N}(\text{Tf})_2^-$ anion towards alkali and alkaline earth cations (Jensen et al, 2002). Alternatively, in $[\text{BMIM}][\text{PF}_6]$, $[\text{BMIM}][\text{BF}_4]$, $[\text{BMPy}][\text{BF}_4]$ and $[\text{BMIM}][\text{N}(\text{CN})_2]$, the solvent's anion X^- is bound to cesium more tightly and prevents CsL_2^+ complex formation. Such interpretation is supported by a much better extraction of CsNO_3 from water into RTIL for $[\text{TOMA}][\text{Sal}]$, $[\text{THA}][\text{DHSS}]$ and $[\text{BMIM}][\text{PF}_6]$ relative to $[\text{BMIM}][\text{N}(\text{Tf})_2]$, $[\text{HMIM}][\text{N}(\text{Tf})_2]$ and $[\text{EtHMIM}][\text{N}(\text{Tf})_2]$ in an absence of 18C6. Therefore a complex formation plays an important role in extraction processes.

3. Chelating agent assisted extraction of inorganic cations from water into RTIL

Solvent extraction represents a significant separation technique in both metal ion or organic compounds separations with numerous advantages over competing techniques. However, liquid-liquid extraction usually employs water-immiscible organic solvents, many of which are toxic, flammable and volatile (Dundan & Kyung, 2010; Dietz, 2006). Ionic liquids exhibit some properties that make them an attractive alternative to the conventional organic solvents: a good thermal stability, low vapor pressure, an ability to solubilize a wide range of solutes, low flammability, a wide liquid range and a very high tunability (Dietz, 2006).

Indeed, for the separations of gases, organic molecules and biomolecules (e.g. amino acids) the distribution coefficients have been found to exceed those of conventional solvents. At the same time, the situation with inorganic cation extraction is not so clear.

One of the first communications on Sr^{2+} extraction from water into a series of dialkylimidazolium-based RTILs in the presence of dicyclohexane-18-crown-6 reported $\log D > 4$ (Dai et al, 1999), while most of molecular solvents revealed a very low extraction degree under same conditions. Moreover, this work has demonstrated that the extraction degree is tunable by varying either RTILs anion or a cation. Since this report an intensive research of RTILs extraction ability, selectivity and extraction mechanisms for inorganic cations separation was undertaken worldwide (Cocalia et al, 2006; Vendilo et al, 2010; Dundan & Kyung, 2010; Dietz, 2006; Visser et al, 2000; Chun et al, 2001; Visser & Rogers, 2003; Murding & Tang, 2010; Egorov et al, 2010; Davis, 2005; Djigailo, 2010; Manzoori, et al, 2009; Lertlapwasin et al, 2010). Within these the two distinct directions can be identified.

The first one is associated with attempts to vary the combination of a RTIL with an indifferent complexing ability and a complexing agent dissolved in a ionic liquid to enhance the target cation's solubility in order to obtain either a maximal D value or a higher extraction selectivity (Dietz, 2006; Cocalia et al, 2006a; Visser et al, 2000). This research area may be subdivided into two: the use of extractant systems employing neutral extractants (e.g., crown ethers, calixarenes, tri-*n*-butylphosphate) and acidic or anionic ones (e.g., organophosphorus acids, pseudohaloids, 2-thenoyltrifluoroacetone, etc.).

Another path assumes to gain the same objective by a modification of either a cation or an anion of RTIL's in such a way that they get an ability to form complexes with extracted substrates ("task-specific" RTILs) (Dietz, 2006; Egorov et al, 2010; Davis, 2005; Luo et al, 2006). In turn, the second area may also be subdivided into synthetic implementation of a complexing agent fragment in a RTIL's cation or in its anion. In some cases an anion itself can initially possess a sufficient complexing ability (e.g., [THA][DHSS], [TOMA][Sal]).

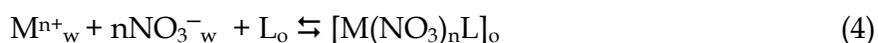
Recently the use of neutral extractants has received the most attention as they have played an important role in cation separations based on conventional solvents and therefore the direct comparison is possible (Dietz, 2006). Over a past decade some important peculiarities, advantages and drawbacks of RTILs relative to conventional solvents have been found.

An extraction efficiency of RTILs over conventional solvents was definitely observed for a series of cations in presence of neutral complexing agents (Dietz, 2006; Murding & Tang, 2010). At the same time, unlike for molecular solvents the D_M values for alkali and alkaline earth cations M in numerous RTIL/water systems in the presence of different crown ethers declined as HNO_3 concentration in aqueous phase increased, then the D_M dependence passed a minimum at c.a. 1 mol/dm^3 concentration and started to increase as nitric acid concentration increased up to 3 mol/dm^3 (Dietz, 2006; Egorov et al, 2010). Our group has demonstrated that the pH-dependence of crown-ether assisted extraction from water into RTIL phase correlates well with the relative distribution of a crown (Vendilo, et al, 2009), Fig. 1, 2.

Such a behavior can be treated positively if an extraction from neutral aqueous solutions is considered. Then the elimination of the strong aqueous phase acidification usually needed for extraction enhancement by a molecular liquid is a definite advantage of RTILs. Meanwhile, the same effect becomes a disadvantage for some real liquid nuclear waste treatment, which is known to be initially highly acidic (Dietz, 2006; Djigailo, 2010).

Another important peculiarity is a different extraction mechanism. For the conventional solvents an extraction of neutral species of a cation M^{n+} is required, e.g., if it is present in

aqueous solution in the form of nitrate, then its partitioning into the organic phase promoted by a neutral (nonionized) complexing agent L can be presented by a general equation (4):



where indexes "w" and "o" indicate aqueous and organic phase respectively.

Quite a different and a more complicated situation of ion exchange was observed for the extraction of metal ion nitrates from water into common RTILs, e.g., [BMIM][PF₆] and [BMIM][N(Tf)₂] (Dietz, 2006; Djigailo, 2010), equation (5):



where Z⁺ and X⁻ denote the cation and anion of a RTIL, respectively. A partitioning mechanism (5) in which metal ion transfer is accompanied by a loss of a RTIL's cation to an aqueous phase indicates a serious problem in potential applications of ionic liquids in liquid-liquid extraction. First of all, this mechanism questions the RTILs as "green" extractants. Indeed, solving the problem of air pollution by conventional solvents, RTILs give rise to an aqueous phase pollution by their cations. At the same time this process leads to the RTIL decomposition, shortens the number of extraction cycles and therefore makes the process more expensive.

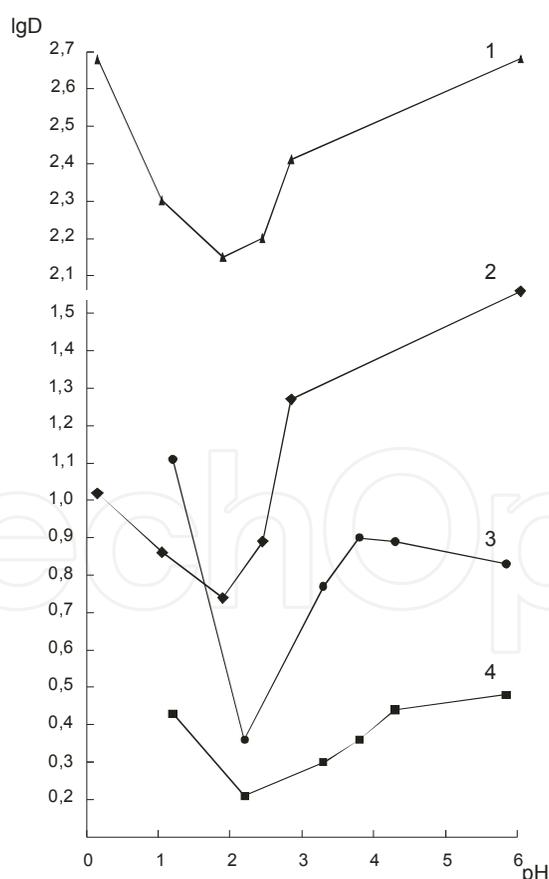


Fig. 1. pH profile of DB18C6 and 18C6 assisted cesium extraction (2) and (3) respectively, and of 18C6 (4) and DB18C6 (1) extraction from water into [TOMA][Sal] at 22 °C (Djigailo, 2010).

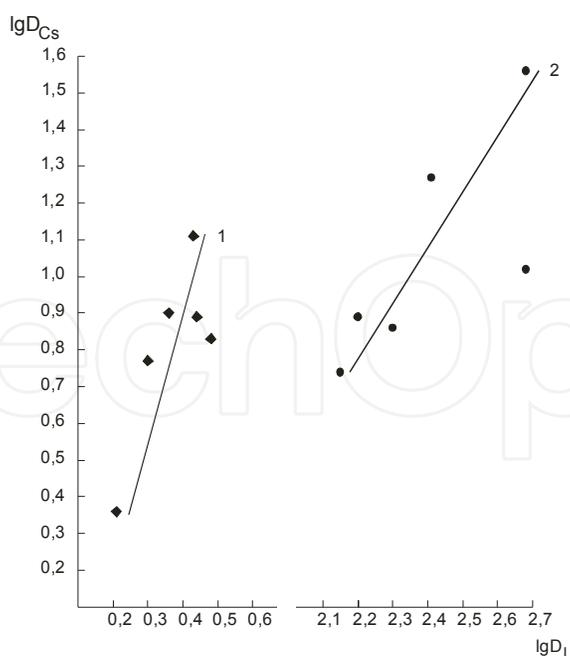
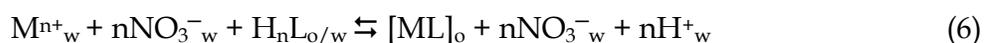


Fig. 2. Correlations between distribution coefficients of Cs^+ and crown ethers in [TOMA][Sal]: $\log D_{\text{Cs}^{18\text{C}6}}$ and $\log D_{18\text{C}6}^{\text{Cs}}$ (1); $\log D_{\text{Cs}^{\text{DB}18\text{C}6}}$ and $\log D_{\text{DB}18\text{C}6}^{\text{Cs}}$ (2)

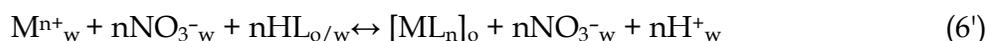
The solution of this problem is possible if an ion exchange is somehow suppressed in favor of traditional extraction. Recently three approaches to diminish an ion exchange mechanism contribution have been described (Dietz, 2006): (i) an increase of alkyl chain length in 1-alkyl-3-methylimidazolium cation of RTIL; (ii) fluorination of this alkyl chain and (iii) use of a sacrificial cation exchanger.

For the series of [RMIM][N(Tf)₂] it was demonstrated that the partitioning mode of Sr^{2+} into RTIL in presence of DC18C6 shifts from Scheme (5) to an equation (4) as R changes from pentyl to decyl, e.g. as the hydrophobicity of a RTIL cation increases (Dietz et al, 2003). Indeed, an increase of the alkyl chain length makes the transfer of [RMIM]⁺ into aqueous phase more difficult and therefore shifts the balance of a relative contribution of ion exchange mechanism and of a neutral complex extraction in favor of the latter. However, the total extraction efficiency in this case decreases significantly. A similar result was obtained by fluorination of R (Dietz, 2006). Therefore both approaches (i) and (ii) seem to be the dead end. An alternative approach (iii) does not influence ion exchange mechanism, but simply aims to reduce the losses of imidazolium cations at the expense of specially added to a RTIL “sacrificial” cation. This cation partitions the aqueous phase instead of a RTIL’s cation. For this purpose sodium tetraphenylborate was found to reduce [BMIM]⁺ losses by 24% as Cs^+ was extracted into [BMIM][N(Tf)₂] by “BOB-CalixC6” without any decrease of D_{Cs} values (Luo et al, 2004). This approach looks better, but does not seem to become a universal and satisfactory solution. Anyhow, its further research is needed.

More advantageous looks the use of anionic complexing agents. Then the general extraction scheme may eliminate the ion exchange mechanism if a polydentate chelating agent H_nL is properly selected in order to form zerocharged species $[\text{ML}]^0$, equation (6):



or for a ligand HL of a lower denticity and basicity:



Here the index "o/w" indicates the presence of L in both organic and aqueous phases. For example, for Zr^{4+} , U^{4+} and Pu^{4+} an ethylenediaminetetraacetic acid (EDTA, H_4edta), which forms the neutral complexes $[M(IV)edta]^o$ might be a good choice, while for Am^{3+} and Ln^{3+} EDTA is undesirable, but the dialkyl ester of diethylenetriaminepentaacetic acid (DTPA, H_5dtpa) - H_3R_2dtpa is expected to form the same zero charged species: $[Ln(R_2dtpa)]^o$, where R indicated some alkyl.

Indeed it was demonstrated that for such d-metal ions as Ni^{2+} , Cu^{2+} and Pb^{2+} an extraction by RTILs in the presence of β -diketonates (HL) proceeds in the same way as in chloroform, nitrobenzene or toluene as a neutral hydrated complex $[ML_2(H_2O)_n]^o$, where $n=1,2$ (Hirayama et al, 2005). A similar observation was reported for none chelating inorganic ligands: CN^- , OCN^- , SCN^- and halide ions (Visser et al, 2001).

At the same time an improper selection of an anionic ligand for a particular cation (Visser et al, 2001) can lead to an anionic complex formation, which has the same disadvantages of ion exchange mechanism as with neutral ligands. In fact it was demonstrated (Jensen et al, 2003) that Eu^{3+} with 2-thenoyltrifluoroacetone (Htta) forms besides the neutral species $[Eu(tta)_3]^o$ also $[Eu(tta)_4]^-$ and an undesirable anion exchange mechanism of $[Eu(tta)_4]^-$ for $[N(Tf)_2]^-$ prevails at a water/[BMIM][N(Tf)₂] interface. This example indicates an importance of stability constant-based speciations of complexes formed by a ligand with a target cation both in aqueous and RTIL phases.

The data for aqueous solutions are generally available in the most comprehensive IUPAC Stability Constants Database (IUPAC, 2007), which embraces over 400 000 of stability constants measured for different solvents, including RTILs. Unfortunately, the number of published $\log K$ values for RTILs is still rather poor, Table 2.

Solvent	W, % ^e	$\log\beta_{2(1)}$	$\log D_{Cs}$	$\log D_{Cs^{18C6}}$	$\log D_{18C6^{Cs}}$	$\log[D_{Cs^{18C6}}/ (D_{Cs}D_{18C6})]$
[HMIM][N(Tf) ₂]	1.3	5.57	-1.24	0.82	0.25	1.81
[EtHMIM][N(Tf) ₂]	0.7	4.56	-0.81	0.56	-0.27	1.64
[BMIM][N(Tf) ₂]	0.5	4.69	-0.67	1.56	0.77	1.46
[BMIM][PF ₆]	1.9	2.4	-0.59	-0.20	0.13	0.26
[TOMA][Sal]	7.6	1.45	0.69	0.83	0.49	-0.38
[THA][DHSS]	4.4	0.77	1.21	0.25	-0.12	-0.84
1,2-dichloroethane		10.56 ^b	-7.7 ^f	0.8 ^c	0.03 ^d	6.93

^a Extraction data for RTIL are taken from (Vendilo, et al, 2009) for 25 °C, $pH_{water}=7$; $[Cs]_o=0.0015$ mol/L, $[18C6]_o=0.15$ and phases volume ratio $V_{water}/V_{RTIL}=10$; $D_{Cs}=[Cs]_{RTIL}/[Cs]_{water}$; $D_{Cs^{18C6}}=[Cs]_{RTIL}/[Cs]_{water}$ in presence of 0.15 mol/L 18C6 in RTIL; $D_{18C6}=[18C6]_{RTIL}/[18C6]_{water}$; $\beta_{2(1)}=K_1$ if no CsL_2 complexes are formed, and $\beta_{2(1)}=K_1K_2$ if CsL_2 complex exists in a particular RTIL; ^b Ref. (Kikuchi & Sakamoto, 2000), ^c Ref. (Abramov, 2000), picrate salt; ^d Ref. (Takeda et al, 1998), ^e W -equilibrium water content in RTIL phase after extraction in presence of 18C6, mass %; ^f Ref. (Levitskaia et al, 2007), picrate salt.

Table 8. Stability constants of cesium complex formation with 18C6 in RTIL and extraction efficacy from water at 25 °C^a.

However, for Cs^+ some comments are possible. Formation of crown ether complexes promotes cesium extraction (Vendilo, et al, 2009) into hydrophobic RTIL from water if the complex stability in RTIL is higher than in water, Table 8. Indeed for [BMIM][N(Tf)₂], [HMIM][N(Tf)₂], [EtHMIM][N(Tf)₂], [BMIM][PF₆] and [TOMA][Sal] $\log K_1^{RTIL} > \log K_1^{water}$

and cesium content in RTIL increases due to 18C6 administration. For [THA][DHSS] $\log K_1^{\text{RTIL}} < \log K_1^{\text{water}}$ and crown ether decreases cesium content in RTIL. The $\log D_{\text{Cs}}^{18\text{C6}}$ values have the same order of magnitude for RTILs, 1,2-dichloroethane and other volatile organic diluents (Abramov, 2000; Takeda et al, 1998; Levitskaia et al, 2007), while the hazardous properties of the latter are much higher.

It should be noted that the complex stability in RTIL increases as the RTIL ability to extract cesium without 18C6 (D_{Cs}) decreases, Fig.3. Meanwhile, there are no simple relationships between $\log K_1$ ($\log \beta_{1,2}$) and crown ether assisted extraction efficiency ($D_{\text{Cs}}^{18\text{C6}}$), Table 8. This happens due to a superposition of at least two phenomena: the relative stability of complexes is superimposed on a relative solubility of the crown ether and its complexes in the RTIL/water systems. However, when the ligand's extraction (D_{L}) and D_{Cs} are taken into account then a perfect linear relationship between $[\log D_{\text{Cs}}^{18\text{C6}} - \log D_{\text{Cs}} - \log D_{\text{L}}]$ and $\log \beta_{1,2}$ is observed, Fig 4.

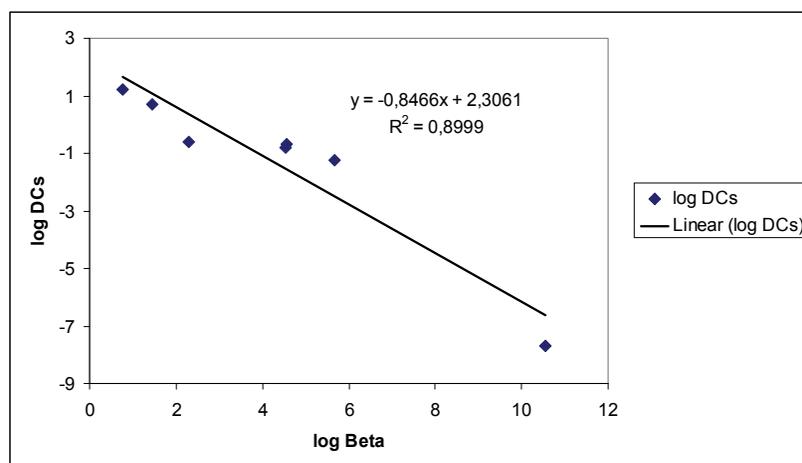


Fig. 3. Plot of $\log D_{\text{Cs}}$ vs. $\log \beta_{1,2}$ for [TOMA][Sal], [THA][DHSS], [BMIM][PF₆], [BMIM][N(Tf)₂], [HMIM][N(Tf)₂], [EtHMIM][N(Tf)₂] and 1,2-dichlorethane at 25 °C (Vendilo, et al, 2010a,c)

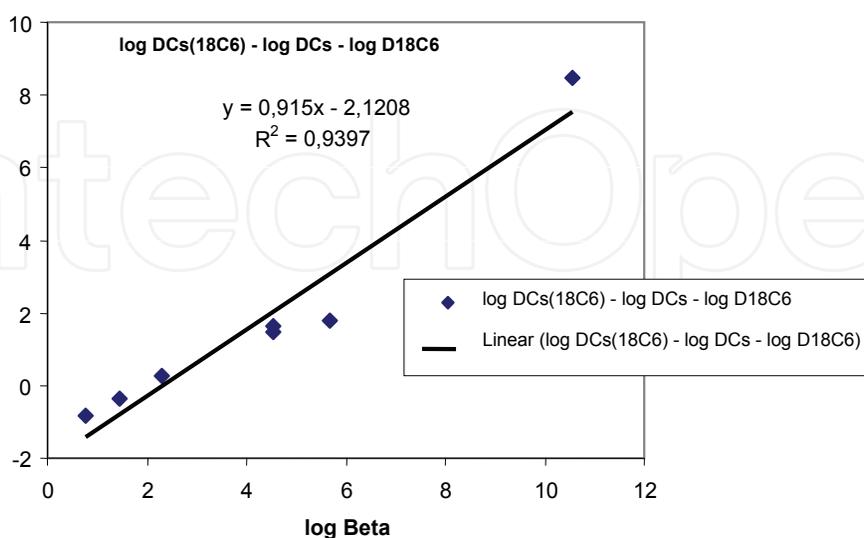


Fig. 4. Plot of $[\log D_{\text{Cs}}^{18\text{C6}} - \log D_{\text{Cs}} - \log D_{18\text{C6}}]$ vs. $\log \beta_{1,2}$ for [TOMA][Sal], [THA][DHSS], [BMIM][PF₆], [BMIM][N(Tf)₂], [HMIM][N(Tf)₂], [EtHMIM][N(Tf)₂] and 1,2-dichlorethane at 25 °C (Vendilo, et al, 2010a,c).

This linearity has a certain background. When an aqueous phase of cesium nitrate is in equilibrium with a RTIL organic phase containing crown ether L, the distribution ratio ($D_{Cs^{18C6}}$) for such RTILs as [TOMA][Sal], [THA][DHSS] and [BMIM][PF₆], where only CsL species are formed is represented by a simple equation (7):

$$D_{Cs^{18C6}} = ([Cs]^{RTIL} + [CsL]^{RTIL}) / ([Cs]^w + [CsL]^w) \quad (7)$$

where the superscripts "RTIL" and "w" denote organic and aqueous phase, respectively. When the total concentration $[L]^t \gg [Cs]^t$ and the stabilities of complexes in both phases are high enough ($\log K_1^{RTIL} \geq 2$; $\log K_1^w \geq 2$), then $[Cs]^{RTIL} \ll [CsL]^{RTIL}$ and $[Cs]^w \ll [CsL]^w$. In this case the equilibrium concentrations of $[Cs]^{RTIL}$ and $[Cs]^w$ in (7) can be neglected. The equation (7) is therefore transformed into (8):

$$D_{Cs^{18C6}} = [CsL]^{RTIL} / [CsL]^w \quad (8)$$

or

$$D_{Cs^{18C6}} = (K_1^{RTIL} [Cs]^{RTIL} [L]^{RTIL}) / (K_1^w [Cs]^w [L]^w) \quad (9)$$

as far as $[Cs]^{RTIL} / [Cs]^w = D_{Cs}$ and $[L]^{RTIL} / [L]^w = D_L$, then

$$D_{Cs^{18C6}} = K_1^{RTIL} D_{Cs} D_L / K_1^w \quad (10)$$

or

$$\log D_{Cs^{18C6}} = \log K_1^{RTIL} + \log D_{Cs} + \log D_L - \log K_1^w \quad (11)$$

Thus the plot of $(\log D_{Cs^{18C6}} - \log D_{Cs} - \log D_L)$ versus $\log K_1^{RTIL}$ should be linear with a slope 1. For [BMIM][N(Tf)₂], [HMIM][N(Tf)₂], [EtHMIM][N(Tf)₂] the equations (7), (9), (10) and (11) become more complicated due to formation of CsL₂ complexes and the lack of such complexes in water. For a molecular solvent 1,2-dichloroethane the equation (7) and its derivatives additionally have to involve the formation equilibrium for neutral complexes CsL(NO₃) in both RTIL and aqueous phases. However, surprisingly all seven solvents fit equation (11) with a slope 0.92 and a correlation coefficient R²=0.94.

This indicates clearly an importance of complex stability contribution for hydrophobic RTILs in extraction processes. At the same time this trend is strongly modulated by a relative solubility of the chelating agent, its complex with a target cation and a metal nitrate in water and in a RTIL phase. Our group has found that a more hydrophobic DB18C6 reveals better extraction of Cs⁺ into [BMIM][NTf₂], [TOMA][Sal] and [THA][DHSS] than 18C6, while the stability constants of complex formation are approximately the same (Djigailo, 2010).

Among other issues that make challenge for researchers in the field of RTIL extraction is the problem of an extracted cation regeneration from ionic liquid and therefore a RTIL regeneration. The low vapor pressure becomes here an evident disadvantage as far as RTIL can not be removed via evaporation like conventional solvents. However it was demonstrated that, for lanthanides the stripping from [BMIM][PF₆] in the presence of *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphane oxide (CMPO) can be accomplished by using aqueous solutions of guanidine carbonate with either DTPA or EDTA (Levitskaia et al, 2007). For Am(III) complex with CMPO in [BMIM][N(Tf)₂] more than 95% of americium was stripped by using 1.0 M oxalic acid (Nakashima et al, 2003).

Recovery of metal ion from ionic liquid could be also achieved by simply lowering pH (see (Murding & Tang, 2010) and references there), or by a back extraction by a supercritical CO₂ (Murding & Tang, 2010). It should be noted, that the extraction can be combined with an electrochemical recovery, as it was demonstrated for UO₂²⁺ and Sm³⁺ (Murding & Tang, 2010) or by electrodialysis (Vendilo et al, 2010), see below. At the same time it is reasonable to note, that for some RTIL's the distillation is possible (Earle et al, 2006).

It is also important that RTILs can generally withstand α - and γ -radiation (Murding & Tang, 2010; Allen et al, 2002), although in some cases irradiation of RTIL and of a chelating agent can diminish the radioactive cation partitioning (Chao et al, 2010).

Recently a broad application of RTILs in extraction processes is limited by their relatively high cost, yet unclear toxicity and long-term stability. The first publications on the toxicity issues have appeared not long ago (Docherty et al, 2005; Jastorff et al, 2003) and a lot of work in this field is still ahead. The same situation refers to the RTILs solubility in water, which is critical for their recyclability and their time-of-life. The solubility data are available only for a small number of ionic liquids. At the same time, the cost of some recently developed RTILs, e.g. of [TOMA][Sal] is about an order of magnitude lower, then for those as [BMIM][N(Tf)₂] and can be diminished if the production increases on the demand of the market.

4. Cation separations by RTIL based liquid membranes and supported liquid membranes

The separations of inorganic cations can be provided by liquid-liquid extraction, the use of RTIL-based liquid membranes and supported membranes. It was observed, that the partitioning of lanthanides in [BMIM][PF₆] in the presence of CMPO was higher and with better selectivity than that in dodecane (Levitskaia et al, 2007). The reversed extraction selectivity in RTILs relative to isooctane for a series of lanthanides in the presence of *N,N,N',N'*-tetra(*n*-octyl)diglycolamide was reported (Murding & Tang, 2010). The separation of Sc³⁺ from a mixture of Sc³⁺, La³⁺, Y³⁺ and Yb³⁺ in an aqueous phase by Cyanex 925 into octylimidazolium hexafluorophosphate has been registered (Sun et al, 2007), while some task-specific RTILs provided almost quantitative uranyl ion extraction (Srnecik et al, 2009).

The use of RTILs-based liquid membranes for cation separations is less common. Our group has tested Cs⁺ transfer from its nitrate salt aqueous solution from the anode chamber to a cathode chamber filled with water under voltage gradient through [BMIM][N(Tf)₂] layer with 18C6 (Vendilo et al, 2010d), Fig. 5, 6. In the absence of crown ether c.a. 50 % of Cs⁺ has been accumulated in a RTIL phase within 4 hours. The process seems to stop when 50% of a cation still remains in the initial solution. At the same time no any increase of cesium concentration at anode was observed, Fig.5. This clearly indicates the formation of either neutral or anionic species of cesium with RTIL's anions, e.g. [CsN(Tf)₂]⁰, [Cs{N(Tf)₂}]⁻, etc., and is in a good agreement with NMR data (Vendilo et al, 2010d). The neutral or negatively charged species do not strip into the anode compartment and partly stay in the RTIL's phase in equilibrium with anode compartment when the voltage gradient becomes compensated by the concentration gradient.

When 18C6 was added to the ionic liquid phase, then 90% of cesium placed initially in the anode chamber, move both to RTIL's phase (44 %) and to cathode compartment (46 %) within the same period of time, Fig.6. This is also consistent with the stability constants and NMR-based chemical speciation model which assumes the formation of cationic species in

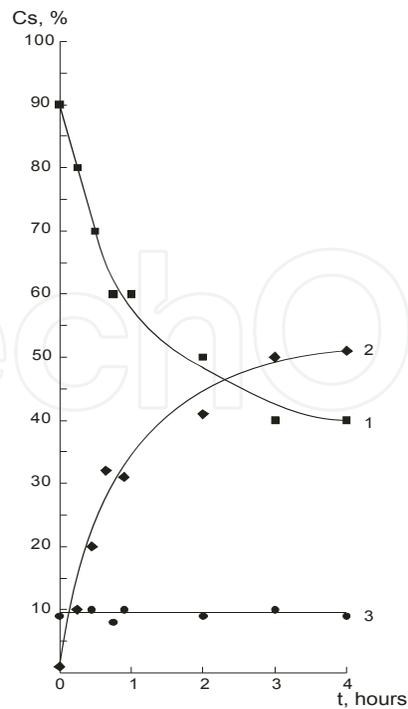


Fig. 5. Cs⁺ distribution in the electrokinetic cell: anode compartment (1), [BMIM][N(Tf)₂] based liquid membrane (2) and cathode compartment (3). Initial cesium concentration: 0.005 mol/L in anode chamber; the solution equilibrated 24 hours at E=0 V; then 1 V/cm gradient was applied

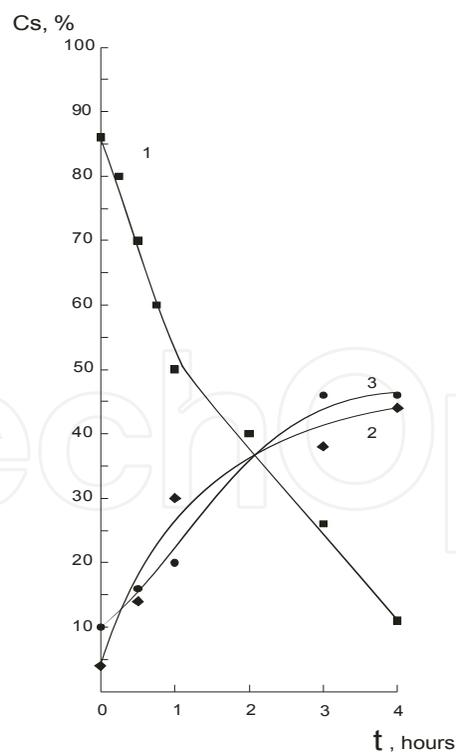


Fig. 6. Cs⁺ distribution in the electrokinetic cell: anode compartment (1), [BMIM][N(Tf)₂] based liquid membrane with 0.15 mol/L 18C6 (2) and cathode compartment (3). Initial cesium concentration: 0.005 mol/L in anode chamber; the solution equilibrated 24 hours at E=0 V; then 1 V/cm gradient was applied.

the presence of 18C6 excess: $[\text{Cs}(\text{18C6})_2]^+$. Therefore there are no obstacles for a cationic complex to strip into cathode compartment.

An application of chemical speciations makes the situation clearer, Fig. 7. Indeed, for the stability levels of 18C6 complexes with Cs^+ in $[\text{BMIM}][\text{N}(\text{Tf}_2)]$ the 1000-fold excess of 18C6 over Cs^+ is needed to provide an absolute $[\text{Cs}(\text{18C6})_2]^+$ species domination (93%). When only a 100-fold excess takes place as it happens after 4 hours of power supply, then almost 44% of cesium exist in either $[\text{CsN}(\text{Tf}_2)]^0$ or $[\text{Cs}\{\text{N}(\text{Tf}_2)_2\}^-$ forms ("free" Cs), which are not capable to move to the cathode compartment and the process intensity declines.

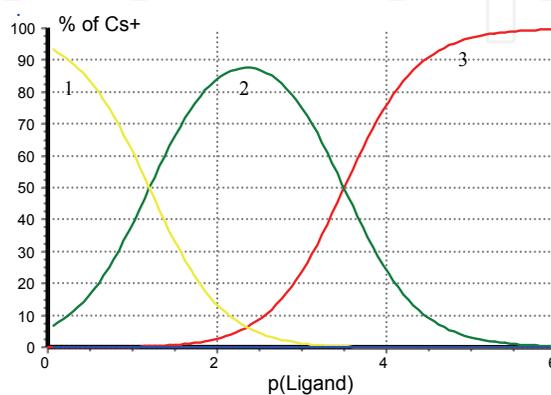


Fig. 7. Chemical speciations of 0.001 mol/L Cs^+ in $[\text{BMIM}][\text{N}(\text{Tf}_2)]$ as a function of 18C6 concentration, $p[\text{18C6}]$: $[\text{Cs}(\text{18C6})]^+$ (1), $[\text{Cs}(\text{18C6})_2]^+$ (2) and "free" Cs^+ (3); Species, Academic Software (IUPAC, 2007).

It is worthwhile to note that the separation process can be significantly enhanced if different chelating agents are added at once into a RTIL phase and into anode compartment. We have recently got positive results when to a mixture of Cu^{2+} and Cs^+ in anode chamber an aqueous solution of EDTA was added ($\text{pH} \sim 5$), while 18C6 was dissolved in the RTIL's phase. The speciation scheme clearly demonstrates that under the experimental conditions copper forms negatively charged species $[\text{Cu}(\text{edta})]^{2-}$, while Cs^+ ions do not interact with EDTA. Thus Cs^+ strips into membrane and then into cathode compartment, while copper is retarded in the anode one.

The main problem in such process is a RTIL's decomposition due to its slow dissolution in water in both chambers. A possible solution could be associated with a fixation of a RTIL on some solid porous frame. Our preliminary experiments with porous Al_2O_3 filled with $[\text{BMIM}][\text{N}(\text{Tf}_2)]$ indicate this path to be a promising one. Various forms of RTIL's immobilization on solid phase are recently reported (Martinis et al, 2009; Gallardo et al, 2008; Vincent et al, 2008; Campos et al, 2008; Campos et al, 2008a; Guibal et al, 2008; Vincent et al, 2008a; Venkatesan et al, 2007).

The facts listed above indicate that ionic liquids are very promising solvents for liquid - liquid extraction of a variety of metal ions. At the same time a lot of physicochemical data on the properties of complexes formed in this medium has to be obtained before the practical application of RTILs in this field becomes real.

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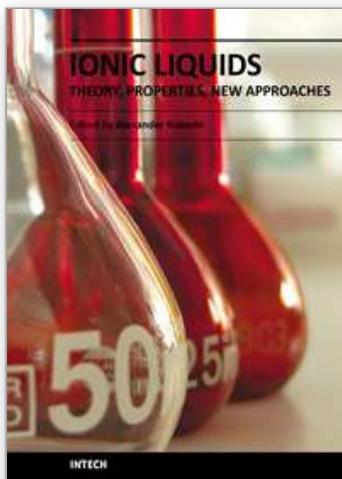
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Ionic Liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. This book, consisting of 29 chapters gathered in 4 sections, reviews in detail and compiles information about some important physical-chemical properties of ILs and new practical approaches. This is the first book of a series of forthcoming publications on this field by this publisher. The first volume covers some aspects of synthesis, isolation, production, modification, the analysis methods and modeling to reveal the structures and properties of some room temperature ILs, as well as their new possible applications. The book will be of help to chemists, physicists, biologists, technologists and other experts in a variety of disciplines, both academic and industrial, as well as to students and PhD students. It may help to promote the progress in ILs development also.

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