

Thermodynamics of cesium complexes formation with 18-crown-6 in ionic liquids

A. G. Vendilo · H. Rönkkömäki · M. Hannu-Kuure · M. Lajunen ·
J. Asikkala · V. G. Krasovsky · E. A. Chernikova · P. Oksman ·
L. H. J. Lajunen · T. Tuomi · K. I. Popov

Received: 20 October 2008 / Accepted: 1 June 2009 / Published online: 18 June 2009
© Springer Science+Business Media B.V. 2009

Abstract Thermodynamic data for cesium complexes formation with 18-crown-6 (18C6, L) $[\text{Cs}(18\text{C}6)]^+$ in N-butyl-4-methyl-pyridinium tetrafluoroborate ($[\text{BMPy}][\text{BF}_4]$, **I**), in 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}][\text{BF}_4]$, **II**) and in 1-butyl-3-methylimidazolium dicyanamide ($[\text{BMIM}][\text{N}(\text{CN})_2]$, **III**) were measured with NMR ^{133}Cs technique at 23–50 °C. The stability of cesium complex in RTILs is estimated to be in the range between water and DMFA. Stability constants for $[\text{Cs}(18\text{C}6)]^+$ are found to

decrease as temperature is increasing. The following values for $\lg K(\text{Cs}+\text{L})$ and $\Delta H(\text{Cs}+\text{L})$ at 23 °C are determined: 2.6 (0.3), $-47(1)$ kJ/mol (RTIL **I**); 2.8(0.3), $-80(3)$ kJ/mol (RTIL **II**) and 3.03 (0.08), $-47(2)$ kJ/mol (RTIL **III**). It is demonstrated that enthalpy change promotes complex formation while the corresponding change of entropy is negative and provides decomposition of $[\text{Cs}(18\text{C}6)]^+$.

Keywords RTIL · Stability constants · Complexes · Cesium · 18-crown-6 · ^{133}Cs NMR

Partly the summary of data is published in Mendeleev Communications (2009), V. 19, p. XX.

A. G. Vendilo
State Research Institute of Reagents and High Purity Substances (IREA), Bogorodskii val 3, 107258 Moscow, Russia

H. Rönkkömäki (✉)
Finnish Institute of Occupational Health, Aapistie 1,
90220 Oulu, Finland
e-mail: hannu.ronkkomaki@ttl.fi

M. Hannu-Kuure · M. Lajunen · J. Asikkala ·
P. Oksman · L. H. J. Lajunen
Department of Chemistry, University of Oulu,
P.O. Box 3000, 90014 Oulu, Finland

V. G. Krasovsky · E. A. Chernikova
Zelinsky Institute of Organic Chemistry RAS,
Leninsky pr. 47, 119991 Moscow, Russia

T. Tuomi
Finnish Institute of Occupational Health, Arinatie 3,
00370 Helsinki, Finland

K. I. Popov
Department of Physical and Colloid Chemistry, Moscow State
University of Food Technologies, Volokolamskoye Sh.11,
125080 Moscow, Russia
e-mail: ki-popov@mtu-net.ru

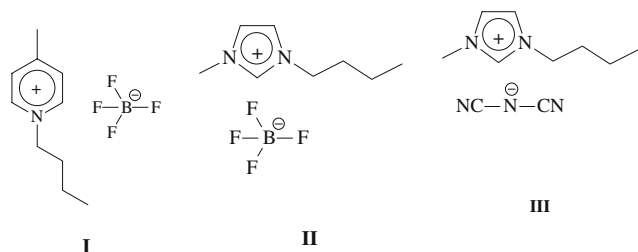
Introduction

Room-temperature ionic liquids (RTILs) are attracting increasing attention in solvent extraction processes due to such important advantages over conventional organic diluents as negligible vapor pressure, low flammability, moisture stability, unusual extraction regularities and possibility to eliminate aqueous phase acidification [1–7]. It is demonstrated, that extraction efficacy of RTIL can be modulated by chelating agent administration. Dai et al. [4], for example, first discovered that highly efficient extraction of strontium ions can be achieved when dicyclohexane-18-crown-6 is combined with RTILs. Visser et al. [3], and Chun et al. [7], reported the extraction of various alkali metal ions with crown ethers in RTIL. Visser and Roberts demonstrated that octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide dissolved in RTILs enhances the extractability of lanthanides and actinides in comparison to conventional organic solvents [8]. 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 [9]. In addition the task-specific RTILs with coordination capacity built in the RTIL cation have been

reported [10, 11]. Recently the efficiency of chelate extraction of 3d-cations with 8-sulfonamidoquinoline [12], Pu(IV) with carbamoylmethylphosphine oxide [13] and uranyl ion with tributylphosphate (TBP) [14] from aqueous phase into RTIL is reported. The higher selectivity of dibenzo-18-crown-6 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 [15].

Besides the issues of target cation, ligand and complex solubility in water and in RTIL, the relative stabilities of complex formation in both phases are of significant importance for extraction selectivity. Unfortunately, almost nothing is known about the numerical values of complex formation constants in RTIL. Some publications report a significant increase of complex stability in a series of RTIL relative to DMSO [16] and to water [15, 17, 18]. As far as we know, no data on the thermodynamic functions have been published in the recent years. Present work aims to diminish this gap by studying the complex formation of cesium ions by 18-crown-6 (L, 18C6) in three hydrophilic RTIL: *N*-butyl-4-methyl-pyridinium tetrafluoroborate ([BMPy][BF₄], **I**), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄], **II**) and 1-butyl-3-methylimidazolium dicyanamide ([BMIM][N(CN)₂], **III**) using ¹³³Cs NMR technique with an emphasis on thermodynamic data (Scheme 1).

In this study, we focused our attention initially on complex formation thermodynamics for three hydrophilic RTIL, because it was recently demonstrated that some of them can be easily transformed into hydrophobic ones by some salts administration [19]. At the same time unlike hydrophobic RTIL the hydrophilic ones are represented by more broad diversity of cation/anion combinations and are generally cheaper, while the complex stability in homogeneous RTIL/water mixtures represent independent interest. However, the paper on cesium complex formation thermodynamics and extraction in two hydrophobic RTIL is recently also in preparation.



Scheme 1 Structures of RTIL **I**, **II**, **III**

Experimental

Reagents

Cesium nitrate (Merck, reagent purity) was dried at 110 °C for one day before use. 18-crown-6 (Fluka) was dried at 35 °C and used without further purification.

Commercial *N*-butyl-4-methyl-pyridinium tetrafluoroborate sample (Merck) had >98.0% purity with halides content ≤0.1%, and was additionally analysed by ICP-MS for Na (1.6 mg/L), Mg (0.01 mg/L), Ca (0.4 mg/L), Cu (0.007 mg/L), and Cl (<5 mg/L) and then used without additional purification. Water content (K.F.) was <1.0%. ¹H NMR revealed no water signal, pH ~0. As far as there is no ligand protonation and formation of metal hydrolyzed species in the systems studied, thus no any impact of pH on crown ether complex formation equilibrium with alkali metals takes place. We have therefore confined ourselves by a qualitative pH control, operating pH-meter readings maintained with METTLER Toledo 320 pH meter, calibrated by standard aqueous buffer solutions (Oy FF-Chemicals Ab).

1-butyl-3-methylimidazolium tetrafluoroborate was synthesized as described in [20]. Ionic liquid [BMIM][Cl] 14 g (0.081 mol) was dissolved in 200 mL dry acetone, and 9.8 g (0.089 mol) sodium tetrafluoroborate was added. The reaction mixture was stirred at room temperature for 12 h. The precipitated NaCl was filtered, and acetone was evaporated resulting in a yellow viscous liquid. The liquid obtained was dissolved in 100 mL CH₂Cl₂ and washed with water (3 × 10 mL) until the aqueous fraction was detected to be chloride-free by AgNO₃. The dichloromethane solution was mixed with activated charcoal, stirred for 2 h and filtered. The dichloromethane was removed by rotary evaporation. The resulting colourless ionic liquid was dried by heating in vacuo for 36 h at 70 °C (90% yield).

¹H NMR, (300 MHz, CDCl₃); 0.94 (3H, t, NHCH₂CH₂CH₂CH₃), 1.35 (2H, m, NCH₂CH₂CH₂CH₃), 1.84 (2H, p, NCH₂CH₂CH₂CH₃), 3.94 (3H, s, NCH₃), 4.17 (2H, t, NCH₂CH₂CH₂CH₃), 7.27 (1H, s, C(5)H), 7.31 (1H, s, C(4)H), 8.81 (1H, s, C(2)H).

Analysis, found: C 42.69%, H 6.79%, N 12.41, B 4.63%, F 33.56%; calculated for C₈H₁₅N₂BF₄: C 42.51%, H 6.69%, N 12.39%, B 4.78%, F 33.62%. The total sample purity >99.2%. The mole fraction of water constituted 0.7% mass (¹H NMR), pH ~6.

1-Butyl-3-methylimidazolium dicyanamide was synthesized according to [21]. [BMIM][Cl] (4.5 g, 25.8 mmol) was dissolved in CH₂Cl₂, and sodium dicyanamide (1.9 g, 25.3 mol) was added. The reaction mixture was stirred at room temperature approximately 48 h. The reaction mixture was filtered through Kieselguhr. Solvent was evaporated with a rotary evaporator and the product was dried

under high vacuum at 70 °C for 24 h. Yield of [BMIM][N(CN)₂] was 5.2 g, 24.3 mmol, 96%. ¹H NMR (200 MHz, CDCl₃): 0.96 (3H, t, J_{HH} = 7.3 Hz), 1.41 (2H, m), 1.89 (2H, m), 4.13 (3H, s), 4.34 (2H, t, J_{HH} = 7.3 Hz), 7.47 (1H, t, J_{HH} = 1.8 Hz), 7.62 (1H, t, J_{HH} = 1.8 Hz), 10.67 (1H, s).

The total sample purity was found >99.1%, and was proved by mass-spectrometry: MS(ESI+) [m/z (rel. int. (%))]: 139 ([BMIM]), 344 ([BMIM][N(CN)₂][BMIM]). MS(ESI-) [m/z (rel. int. (%))]: 66 (N(CN)₂), 271 ([N(CN)₂][BMIM][N(CN)₂]). The mole fraction of water constituted 0.8% mass (¹H NMR), pH ~ 6.

Sample preparation

The exact mass of solid cesium nitrate was mixed with the calculated mass of solid 18C6, and then 1 mL of RTIL was added. Within each series of 9–11 samples, the concentration of cesium was kept constant at a level of 0.005 mol dm⁻³, whereas the concentration of the ligand varied as the ligand-to-metal mole ratio changed steadily from 0 to 10 or to 20. The dissolution process was performed within 3–5 min at 110 °C because sufficient reduction of solvent viscosity was found to occur in this time. The establishment of equilibrium controlled by periodic NMR measurement of some selected samples took 1–2 h. Generally, all samples measured were allowed to equilibrate in closed glass tubes at room temperature for 24 h before NMR measurement. The pH measurements of the samples indicated a pH below the zero for RTIL **I**, and neutral solutions for RTIL **II** and **III**. Control was maintained with METLER Toledo 320 pH meter, calibrated by standard buffer solutions (Oy FF-Chemicals).

The water content in each sample was controlled by ¹H NMR by a comparison of water and RTIL NMR bands integral intensities.

NMR measurements

¹³³Cs NMR was recorded with Bruker DPX400 spectrometer, operating at 52.48 MHz, in a 5 mm diameter sample tube with temperature adjusted to 23, 30, 35, 40, 45 and 50 °C. After each temperature change, the sample was kept in the probehead for 10 min before initiating the measurement. The external standard placed in a 1 mm coaxial inner tube represented a 1:1 vol/vol mixture of aqueous solution of NaCl and CsCl with D₂O (added for lock), which provided a 0.04 mol dm⁻³ concentration of each cation. Downfield shifts are denoted as positive.

Electrospray ionization time-of-flight mass spectrometry

The electrospray ionization time-of-flight mass spectrometry (ESI-ToF MS) was used as a supporting method for a qualitative RTIL solution characterization. ESI-ToF mass spectra have been recorded with Micromass LCT mass spectrometer equipped with a Z-spray electrospray interface. The liquid sample with cesium solution in RTIL with an excess of 18C6 was introduced into the spectrometer by a Harvard Apparatus Model 11 syringe pump at a flow rate of 10 μl min⁻¹. The sample cone voltage was 35 V. The positive and negative ion modes have been acquired using Masslynx NT software.

NMR Data treatment, complex formation constants evaluation

The complex formation study by NMR and ESI-ToF MS revealed only ML complexes in all the systems. The equilibrium can therefore be described by a simple reaction:



An experimentally observed δ_{obs} single time-averaged ¹³³Cs chemical shift of “free” cation and a ligand-bonded cation can be given by an Eq. 2 [17]:

$$\delta_{\text{obs}} = (\delta_{\text{Cs}} + K_1[L]\delta_{\text{CsL}})/(1 + K_1[L]) \quad (2)$$

where

$$[L] = C_L - C_{\text{Cs}}X_{\text{CsL}} \quad (3)$$

$$X_{\text{CsL}} = (\delta_{\text{obs}} - \delta_{\text{Cs}})/(\delta_{\text{CsL}} - \delta_{\text{Cs}}) \quad (4)$$

C_L is a total concentration of the ligand, $[L]$ is a free concentration of the ligand, C_{Cs} is a total concentration of Cs and X_{CsL} is a mole fraction of CsL; δ_{Cs} represents chemical shift of a free cation and δ_{CsL} corresponds to the crown ether coordinated species CsL.

The free ligand concentration $[L]$ was obtained by an iteration method using Eqs. 2, 3 and 4. The stability constant K_1 was calculated by the non-linear curve-fitting program SigmaPlot [22] operating with 9–11 experimental points for a curve. Alternatively the two-step formation scheme was tested by HypNMR software [23], but no evidence of CsL₂ complexes formation was found. All iterations have been performed without fixation of either δ_{CsL} or δ_{Cs} values, treating them equally as any of δ_{obs} experimental points. Thus, calculated and experimental δ_{Cs} values have been obtained, providing additional fitting degree estimate, Table 1. The standard deviation for the measured log K_1 values also meets the requirements for crown ether complexes with alkali cations [24].

Table 1 Stability constants, chemical shifts and thermodynamic quantities ΔG_1 , ΔH_1 , ΔS_1 of cesium complex formation with 18C6 at 23–50 °C

T (°C)	δ_{Mcalc} (ppm)	δ_{Mobs} (ppm)	δ_{MLcalc} (ppm)	Log K_1	ΔG (kJ/mol)	ΔH^a (kJ/mol)	ΔS (kJ/(mol·K))	$T\Delta S^a$ (kJ/mol)
RTIL I								
23	-70.0 ± 6.9	-65.48	-16.5 ± 5.3	2.61 ± 0.31	-14.8	-47	-107	-32
30	-65.4 ± 2.4	-64.97	-16.4 ± 2.9	2.40 ± 0.14	-13.9	-47	-108	-33
35	-65.2 ± 2.3	-64.67	-14.2 ± 3.4	2.26 ± 0.14	-13.3	-47	-108	-33
40	-65.0 ± 2.3	-64.41	-13.8 ± 3.7	2.15 ± 0.13	-12.9	-47	-108	-34
45	-64.6 ± 2.3	-64.06	-11.5 ± 4.8	2.00 ± 0.14	-12.2	-47	-108	-34
50	-64.3 ± 5.3	-63.72	-13.3 ± 5.3	1.93 ± 0.14	-11.9	-47	-107	-35
RTIL II								
23	-68.4 ± 3.7	-66.72	-22.1 ± 4.3	2.76 ± 0.29	-15.7	-80	-220	-65
30	-66.9 ± 2.0	-66.08	-19.8 ± 2.8	2.59 ± 0.05	-15.1	-80	-217	-66
35	-66.7 ± 1.4	-66.01	-17.0 ± 2.5	2.39 ± 0.10	-14.1	-80	-217	-67
40	-66.0 ± 1.3	-65.91	-10.8 ± 3.8	2.09 ± 0.10	-12.6	-80	-218	-68
45	-65.5 ± 1.3	-65.62	-5.56 ± 5.7	1.93 ± 0.12	-11.8	-80	-217	-69
50	-64.7 ± 2.6	-65.33	-16.3 ± 30	1.57 ± 0.32	-9.7	-80	-220	-71
RTIL III								
23	91.4 ± 1.4	91.62	33.7 ± 1.0	3.03 ± 0.08	-17.2	-47	-101	-30
30	89.8 ± 1.1	90.15	33.0 ± 0.9	2.78 ± 0.05	-16.2	-47	-102	-31
35	88.8 ± 1.0	89.19	32.9 ± 0.9	2.66 ± 0.05	-15.7	-47	-102	-31
40	88.0 ± 0.9	88.40	32.5 ± 0.9	2.54 ± 0.04	-15.2	-47	-102	-32
45	87.3 ± 0.9	87.66	32.2 ± 1.0	2.43 ± 0.04	-14.8	-47	-101	-32
50	86.6 ± 0.8	86.86	31.8 ± 1.0	2.32 ± 0.04	-14.4	-47	-101	-33

^a The accuracy of ΔH and $T\Delta S$ values is: ± 1 (RTIL I), ± 3 (RTIL II), ± 2 (RTIL III) kJ/mol

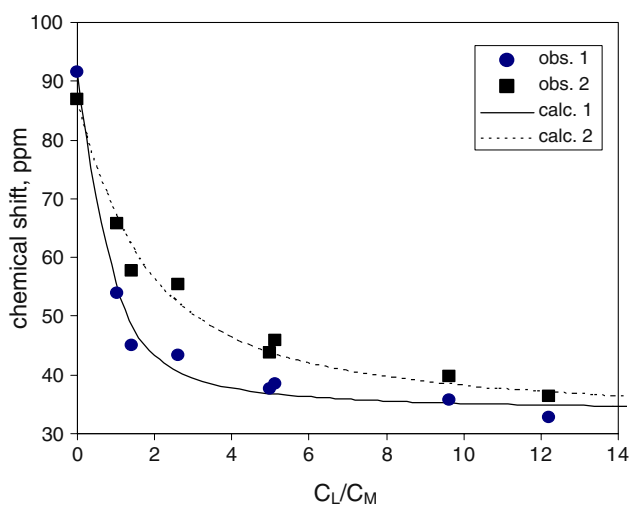


Fig. 1 Variation of ^{133}Cs NMR chemical shift versus ligand-to-cesium mole ratio (C_L/C_M) in RTIL I at 35 °C (1); and 50 °C (2). Solid line represents the least square fit using Eq. 2

The typical titration curves are presented at Fig. 1. Values of calculated $\ln K_1$ were then plotted versus $1/T$. A linear relationship was obtained, indicating the constancy of ΔH_1 within the temperature range 23–50 °C, Fig. 2. Then the values ΔH_1 , ΔG_1 , $T\Delta S_1$ were calculated. The experimental results are presented in Tables 1, 2 and 3.

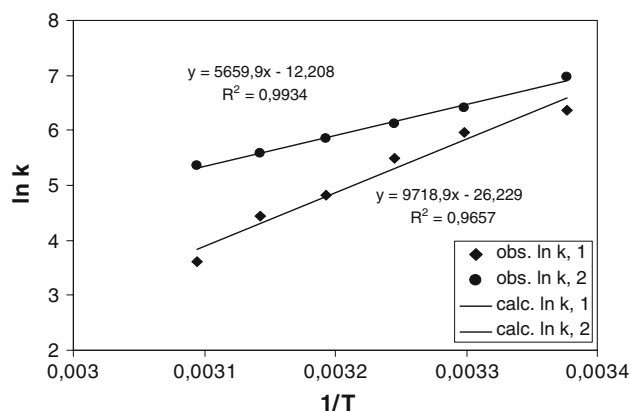


Fig. 2 The dependence of $\ln K_1$ versus $1/T$ for cesium complexes in RTIL I (2) and II (1)

Results and discussion

At room temperature ^{133}Cs resonances reveal a single time averaged signal for all solutions studied indicating the fast exchange of “free” and coordinated metal species even for highly viscous solutions. At the same time ^{133}Cs chemical shifts demonstrate different features depending on particular RTIL. The δ_{Cs} values are observed to be negative and rather close to each other for RTIL I and II, whereas those for RTIL III are found to be positive. An increase of crown

Table 2 Chemical shifts and stability constants of cesium complex with 18C6 at 23 °C

Solvent	DN ^f	δ_{Cs} calc	δ_{CsL} calc	$\delta_{\text{CsL}2}$ calc	LogK ₁	Reference
1,2-Dichloroethane	0	–	–	–	7.98	[29]
RTIL IV ^d		–32.60	–6.46 (0.6)	–46.5 (1.2) ^c	~4 ÷ 5	[26]
Acetonitrile	14.1	24.1 ^c	14.8 ^c	–53 (7) ^c	4.8 (0.2)	[24] ^a
Propylene carbonate	15.1	–36.5 ^a	–8.1 (0.2) ^a	–44.5 (0.3) ^a	4.50	[24] ^a
Acetone	17.0	–35.8 ^c	–6.4 ^c	–47 (9) ^c	4.51 (0.04)	[24] ^a
DMFA	26.6	–0.8 ^c	3.37 ^c	–48.2 (0.8) ^c	3.64 (0.02)	[24] ^a
DMSO	29.8	68.0 ^c	23.6 ^c	–49 (2.4) ^c	3.04 (0.02)	[24] ^a
RTIL III		91.4 (1.4)	33.7 (1.4)	–	3.03 (0.08)	Present work
RTIL II		–68.4 (3.7)	–22.1 (4.3)	–	2.8 (0.3)	Present work
RTIL I		–70 (7)	–16 (5)	–	2.6 (0.3)	Present work
RTIL V ^e		23.26 (0.48)	–7.0 (4.6)	–	1.20 (0.13)	[24]
Water	33	~0	–	–	0.96 (0.03)	[24] ^a

^a log K_1 values for 25 °C, $I = 0\text{--}0.1$ mol/dm³, IUPAC selection

^b Estimated in RTIL/water mixed solvent by extrapolation to zero water content

^c Chemical shifts from [25] are reported with a correction related to the reference treatment in our paper

^d RTIL **IV**—1-Butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide

^e RTIL **V**—N-butylpyridinium methylsulfate

^f Donor number from ref. [28]

Table 3 Thermodynamic quantities ΔG_1 , ΔH_1 , ΔS_1 of cesium complex formation with 18C6 at 23 °C

Solvent	ΔG_1 (kJ/mol)	ΔH_1 (kJ/mol)	$T\Delta S_1$ (kJ/mol)	Reference
Acetonitrile	–27.3	–17 (1)	10.3	[24] ^a
Propylene carbonate	–25.7	–43.3	–17.6	[24] ^a
Acetone	–25.6	–52.8 (0.4)	–27.2	[24] ^a
DMFA	–20.8	–49.2 (0.8)	–28.4	[24] ^a
RTIL III	–17.2 (0.8)	–47 (2)	–30 (2)	Present work
RTIL II	–15.7 (0.8)	–80 (3)	–65 (3)	Present work
RTIL I	–14.8 (0.8)	–47 (1)	–32 (1)	Present work
Water	–5	–17 (1)	–12	[24] ^a

^a 25 °C, $I = 0\text{--}0.1$ mol/dm³, IUPAC selection

ether concentration resulted in the corresponding monotonous increase of δ_{obs} for RTIL **I** and **II**. By contrast the chemical shifts of ¹³³Cs decreased as 18C6 was added to the RTIL **III** solution. Thus, complex formation diminishes the differences in Cs⁺ environment and makes chemical shifts δ_{CsL} more close to each other for all three RTIL, relative to δ_{Cs} . 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.

Generally, chemical shift of ¹³³Cs seems to depend rather on an anion's nature of 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 [Cs18C6]⁺ are almost the same in RTIL **I** and **II**. This is consistent with formation of similar species [Cs·n[BF₄]]^{1–n} and [Cs(18C6)·(n–x)[BF₄]]^{1–n+x} in both RTIL. Meanwhile for RTIL **III** the chemical shifts of δ_{Cs} and δ_{CsL} are definitely different, demonstrating different environment of cesium in both species relative to those for RTIL **I** and **II**. At the same time the chemical shift values at high excess of 18C6 in all RTIL studied are sufficiently different from those found for sandwich type complexes [Cs(18C6)₂]⁺ registered for molecular solvents [25] and for RTIL **IV** [26], Table 2. This is a serious argument for the lack of [Cs(18C6)₂]⁺ in RTIL **I–III**.

It is interesting to note that chemical shifts of $[\text{Cs}(\text{18C6})]^+$ are essentially independent of solvent nature, Table 2. 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 $[\text{Cs}(\text{18C6})]^+$ are strongly solvent dependent both in RTIL and in molecular solvents.

It should be noted that for RTIL **I** and **II** cesium resonances got sufficiently broadened relative to the reference signal as 18C6 was added and the metal-to-ligand ratio constituted $\sim 0.5 \div 2$. Particularly, in RTIL **I** at 23 °C the line width of a narrow band of Cs^+ increased up to 760 Hz at $[\text{18C6}]/[\text{Cs}] = 1.8$ and then again decreased to the same value as that of reference resonance when the excess amount of 18C6 was increased. The sample heating resulted in decrease of the line width. The similar, but less pronounced effect was also registered in RTIL **II**. This observation could be explained by a superposition of several phenomena: (i) relatively high solution viscosities of RTIL **I** and **II**; (ii) low symmetry of $[\text{Cs}(\text{18C6})]^+$ complex and (iii) the decrease of ligand (metal) exchange rates when no excess of either cation or L relative to CsL composition is present. Indeed, in presence of water molecules the viscosity of RTIL **I** was found to be low, and no line broadening is registered [17]. At the same time RTIL **III** was characterised by the lowest viscosity and the lack of line broadening, while the viscosity of RTIL **I** was the highest among the solvents studied.

The chemical shifts change of ^{133}Cs depend on 18C6 concentration for RTIL **I** and **II** in a very similar way with those observed for the same complexes in acetone, DMFA and pyridine [25], while those for RTIL **III** are similar to DMSO and acetonitrile. In all the systems studied the change of chemical shift was monotonic, indicating the existence of only a single 1:1 ML complex, and the absence of ML_2 species. Otherwise the change in chemical shift direction for an opposite one at 1:1 metal-to-ligand mole ratio is normally observed [25, 26]. Qualitatively this conclusion was supported by ESI-ToF MS, which revealed presence of ML species, but not of ML_2 for all three RTIL. The lack of ML_2 was ascertained by increasing the excess of L and increasing the sensitivity of detection by focusing the scan only to ML_2 ions. Besides CsL^+ ions also BMIM^+ (base peak at m/z 139), and impurities of NaL^+ have been detected. The molecular composition of these ions was checked by an accurate mass measurement.

Our attempts to treat the experimental NMR data as a superposition of CsL and CsL_2 by HypNMR have failed. This is also an argument in favor of only one type of complex formation: CsL. Thus, complexes CsL_2 if any, are very weak in the systems studied. Our observations make RTIL similar to such solvents as water, DMSO and DMFA,

where also no any formation of CsL_2 complex was found [25].

The stability constants of cesium complexes demonstrate much less difference than chemical shifts, although some analogy can definitely be detected. The $\log K_1$ values for CsL in RTIL **I**, **II** and **III** at 23 °C were evaluated to be 2.6; 2.8 and 3.03 respectively, and are found to be rather close to each other. It is interesting to note, that the magnitude of $\log K_1$ for all three RTILs falls inside, but not outside the range of those for molecular solvents, with location between DMFA and water. The $\log K_1$ value for a cation with crown ether in molecular solvents is correlated [25, 27] with donor number (DN) of the solvent [28], Table 2, although some exceptions for $[\text{Cs}(\text{18C6})]^+$ are known (Pyridine: DN 33.1; $\log K_1 = 5.7$ [25]). In this sense, the $\log K$ values obtained in the present study suggest that hydrophilic RTIL **I**, **II**, **III** and **V** have DN between 33 and 29, while hydrophobic RTIL **IV** has DN between 0 and c.a. 16 (1,2-dichlorethane [29] and acetone/acetonitrile, respectively). This observation is in a good agreement with Nishi et al. [15] for Li, Na, K, Rb and Cs complexes with dibenzo-18-crown-6 in a hydrophobic RTIL *N*-octadecylisoquinolinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, which is reported to have DN between 4.4 (nitrobenzene) and 0 (1,2-dichlorethane).

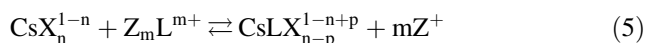
It should be noted, that the direct measurement of $\log K_1$ in RTIL **I** in present work gave the value in a very good agreement with our earlier estimation [17], obtained in RTIL/water mixed solvent by extrapolation to zero water content, Table 2.

An increase of temperature decreases the stability constants of CsL in all three RTIL. However, the degree of such a decrease is different. The linear plots of $\ln K_1$ versus $1/T$ gave the possibility to estimate ΔH_1 values, Fig. 2. The thermodynamic quantities for the formation of $[\text{Cs}(\text{18C6})]^+$ in RTIL are summarized in Table 3 together with those in molecular solvents. As far as 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 differences in metal-solvent contribution are expected to be more exothermic in RTIL than in water, Eq. 5.

Generally, it can be seen that enthalpy change promotes complex formation in RTIL, whereas the corresponding change of entropy is negative and results in decomposition of $[\text{Cs}(\text{18C6})]^+$. However, the thermodynamic quantities indicate clearly, that the contributions to the overall stability of CsL complex may differ rather significantly. The reaction enthalpies and entropies, reveal greater differences, than $\log K_1$ depending on RTIL composition. The complexation of Cs^+ is the most exothermic in RTIL **II**. Moreover, the observed ΔH 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 2 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 (5) is more complicated than that one in molecular solvents [30, 31]. 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:



The NMR chemical shift data indicate that crown ether does not substitute all RTIL anions X^- in coordination sphere of cesium in 1:1 complexes. This observation agrees well with X-ray structural data for cesium complexes with 18-crown-6 in solid state [32, 33] and aqueous solution [34], and with classical molecular dynamics simulations [35]. In all these structures cesium is located above mean oxygen plane of the crown-ether ring since its size is larger than the cavity size of 18C6 (170 and 130 pm respectively [24]).

Thus the exposed part of Cs^+ may strongly interact with RTIL anions making coordination number equal to 8 or 9 as it is observed crystallographically for molecular solvents.

On the other hand, a strong influence of the ionic liquid cation, Z^+ , on $\log K_1$, ΔH and ΔS values of complex formation is observed when one compares RTIL **I** and **II**, indicating Z^+ -crown ether interactions of various intensity. Such an interaction has also analogues among molecular solvents. For example, for AN, nitromethane (NM) and even for chloroform 18-crown-6 · 2AN, 18-crown-6 · 2NM and 18-crown-6 · 2CH₂Cl₂ solvates have been isolated and their structures have been determined by X-Ray crystallography [36–39]. Hence, both cation and anion of RTIL have an impact on the resultant stability constant of chelated compound.

The stability constants for the formation of 18-crown-6 complexes in RTIL are all larger than in water. The reaction thermodynamic quantities, however, differ much among the solvents. The complexation is sufficiently more exothermic in RTIL **I** to **III** than in water. On the other hand, the reaction entropies are more negative than in water.

In conclusion, the complexation of 18-crown-6 with cesium ion mainly reflects the different solvation of 18-crown-6 and also the different degree of solvent structure. In general, RTILs provide good promises of complex stability contribution in cesium extraction processes.

Acknowledgements The authors would like to thank the Russian Foundation for Basic Research (Grant 07-08-00246) and the Academy of Science of Finland for their financial support of the work. We also wish to express our gratitude to Päivi Joensuu for assistance in sample analysis.

References

1. Earle, M.J., Seddon, K.R.: Ionic liquids. Green solvents for future. *Pure Appl. Chem.* **72**, 1391–1398 (2000)
2. Cocalia, V.A., Holbray, J.D., Gutowski, K.E., Bridges, N.J., Rogers, R.D.: Separations of metal ions using ionic liquids: the challenges of multiple mechanisms. *Tsinghua Sci. Technol.* **11**, 188–193 (2006)
3. Visser, A.E., Swatloski, R.P., Reichert, W.M., Griffin, S.T., Rogers, R.D.: Traditional extractants in nontraditional solvents: Groups 1 and 2 extraction by crown ethers in room temperature ionic liquids. *Ind. Eng. Chem. Res.* **39**, 304–3596 (2000)
4. Dai, S., Ju, Y.H., Barnes, C.E.: Solvent extraction of strontium nitrate by crown ether using room-temperature ionic liquids. *J. Chem. Soc., Dalton Trans.* **120**, 1–1202 (1999)
5. Luo, H., Dai, S., Bonnesen, P.V., Buchana, A.C.: Separation of fission products based on ionic liquids containing aza-crown ether fragment. *J. Alloy Compd.* **418**, 195–199 (2006)
6. Chen, P.-Y.: The assessment of removing strontium and cesium cations from aqueous solutions based on the combined methods of ionic liquid extraction and electrodeposition. *Electrochim. Acta* **52**, 5484–5492 (2007)
7. Chun, S., Dzyuba, S.V., Bartsch, R.A.: Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction. *Anal. Chem.* **73**, 3737–3741 (2001)
8. Visser, A.E., Roberts, R.D.: Room-temperature ionic liquids: new solvents for f-element separations and associated solution chemistry. *J. Solid State Chem.* **171**, 109–113 (2003)
9. Shimajo, K., Goto, M.: Solvent extraction and stripping of silver ions in room-temperature ionic liquids containing calixarenes. *Anal. Chem.* **76**, 5039–5044 (2004)
10. Visser, A.E., Swatloski, R.P., Reichert, W.M., Mayton, R., Sheff, S., Wierzbicki, A., Davies, J.H., Rogers, R.D.: Task-specific ionic liquids incorporating novel cations for the coordination and extraction of Hg^{2+} and Cd^{2+} : synthesis, characterization and extraction studies. *Environ. Sci. Technol.* **36**, 2523–2529 (2002)
11. Visser, A.E., Swatloski, R.P., Reichert, W.M., Mayton, R., Sheff, S., Wierzbicki, A., Davis Jr, J.H., Rogers, R.D.: Task-specific ionic liquids for extraction of metal ions from aqueous solution. *Chem. Commun.* **13**, 5–136 (2001)
12. Ajioka, T., Oshima, S., Hirayama, N.: Use of 8-sulfonamidoquinoline derivatives as chelate extraction reagents in ionic liquid extraction system. *Talanta* **74**, 903–908 (2008)
13. Lohithakshan, K.V., Aggarwal, S.K.: Solvent extraction studies of Pu(IV) with CMPO in 1-octyl-3-methyl imidazolium hexafluorophosphate (C8mimPF6) room temperature ionic liquid (RTIL). *Radiochim. Acta* **96**, 93–97 (2008)
14. Dietz, M.L., Stepinski, D.C.: Anion concentration-dependent partitioning mechanism in the extraction of uranium into room-temperature ionic liquids. *Talanta* **75**, 598–603 (2008)
15. Nishi, N., Murakami, H., Imakura, H., Kakiuchi, T.: Facilitated transfer of alkali-metal cations by dibenzo-18-crown-6 across the electrochemically polarized interface between an aqueous solution and a hydrophobic room-temperature ionic liquid. *Anal. Chem.* **78**, 5805–5812 (2006)

16. Lewandowski, A., Osinska, M., Stepniak, I.: Stability of Ag^+ complexes with cryptand 222 in ionic liquids. *J. Inclusion Phenom. Macrocycl. Chem.* **52**, 237–240 (2005)
17. Popov, K., Rönkkömäki, H., Hannu-Kuure, M., Kuokkanen, T., Lajunen, M., Vendilo, V., Oksman, P., Lajunen, L.H.J.: Stability of crown-ether complexes with alkali-metal ions in ionic liquid-water mixed solvents. *J. Inclusion Phenom. Macrocycl. Chem.* **59**, 377–381 (2007)
18. Popov, K.I., Rönkkömäki, H., Hannu-Kuure, M., Kuokkanen, T., Lajunen, M., Vendilo, A., Glazkova, I.V., Lajunen, L.H.J.: Stability constant of the sodium complex with dibenzo-18-crown-6 in mixed water-ionic liquid solvent. *Russ. J. Coord. Chem.* **33**, 393–395 (2007)
19. Djigailo, D.I., Smirnova, S.V., Torocheshnikova, I.I., Vendilo, A.G., Popov, K.I., Pletnev, I.V.: Extraction of nitrates of alkali and alkaline earth metals with crown ether into hydrophilic ionic liquid in presence of salting-out agent. *Vestn. Mosk. Univ. (Moscow University Bull.) Ser. 2* **50**, 164–168 (2009)
20. Farmer, V., Welton, T.: The oxidation of alcohols in substituted imidazolium ionic liquids using ruthenium catalysts. *Green Chem.* **4**, 97–102 (2002)
21. Asikkala, J. Application of ionic liquids and microwave activation in selected organic reactions. PhD Theses. Acta Universitatis Oulunensis, A 502, Oulu University Press, Oulu (2008)
22. Sigmaplot for Windows, Version 4.0, 1986–1997 SPSS Inc.
23. Frassinetti, C., Alderighi, L., Gans, P., Sabatini, A., Vacca, A., Ghelli, S.: Determination of protonation constants of some fluorinated polyamines by means of ^{13}C NMR data processed by the new computer program HypNMR2000. Protonation sequence in polyamines. *Anal. Biochem.* **376**, 1041–1052 (2003)
24. Arnaud-Neu, F., Delgado, R., Chaves, S.: Critical evaluation of stability constants and thermodynamic functions of metal complexes of crown ethers. *Pure Appl. Chem.* **75**, 71–102 (2003)
25. Mei, E., Popov, A.I., Dye, J.L.: Complexation of the cesium cation by macrocyclic polyethers in various solvents. A cesium-133 Nuclear Magnetic Resonance study of the thermodynamics and kinetics of exchange. *J. Phys. Chem.* **81**, 1677–1681 (1977)
26. Vendilo, A.G., Rönkkömäki, H., Hannu-Kuure, M., Lajunen, M., Asikkala, J., Petrov, A.A., Krasovsky, V.G., Chernikova, E.A., Oksman, P., Lajunen, L.H.J., Popov, K.I.: Stability constants of cesium complexes with 18-crown-6 in ionic liquids. *Koord. Khim.* **34**, 645–650 (2008); [*Russ. J. Coord. Chem.* **34**, 635–640]
27. Smetana, A.J., Popov, A.I.: Lithium-7 Nuclear Magnetic Resonance and calorimetric study of lithium crown complexes in various solvents. *J. Solut. Chem.* **9**, 183–196 (1980)
28. Gutmann, V., Vichera, E.: Coordination reactions in non aqueous solutions—the role of the donor strength. *Inorg. Nucl. Chem. Lett.* **2**, 257–260 (1966)
29. Kikuchi, Y., Sakamoto, Y.: Complex formation of alkali metal ions with 18-crown-6 and its derivatives in 1, 2-dichloroethane. *Anal. Chim. Acta* **403**, 325–332 (2000)
30. Ohtsu, K., Ozutsumi, K.: Thermodynamics of solvation of 18-crown-6 and its alkali-metal complexes in various solvents. *J. Inclusion Phenom. Macrocycl. Chem.* **45**, 217–224 (2003)
31. Ozutsumi, K., Ohtsu, K., Kawashima, T.: Thermodynamics of complexation of 18-crown-6 with sodium, potassium, rubidium caesium and ammonium ions in N, N-dimethylformamide. *J. Chem. Soc. Faraday Trans.* **90**, 127–131 (1994)
32. Gjickaj, M., Adam, A.: Complexation of alkali triflates by crown ethers: synthesis and crystal structure of $\text{Na}(12\text{-crown-4})_2$ $[\text{SO}_3\text{CF}_3]$, $\text{Na}(15\text{-crown-5})[\text{SO}_3\text{CF}_3]$, $[\text{Rb}(18\text{-crown-6})] [\text{SO}_3\text{CF}_3]$ and $[\text{Cs}(18\text{-crown-6})] [\text{SO}_3\text{CF}_3]$. *Z. Anorg. Allg. Chem.* **632**, 2475–2480 (2006)
33. Ellerman, J., Bauer, W., Schuetz, M., Heinemann, F.W., Moll, M.: Chemie Polyfunktioneller Moleculer 130 Mitt.[1]: Spaltprodukte, Kristallstrukturen und Festkoerper-NMR-Spektern. *Monatshefte fur Chemie* **129**, 547–566 (1998)
34. Ozutsumi, K., Natsuhara, M., Ohtaki, H.: An X-ray diffraction study on the structure of 18-crown-6 ether complexes with alkali metal ions in aqueous solutions. *Bull. Chem. Soc. Jpn.* **62**, 2807–2818 (1989)
35. Dang, L.X.: Mechanism and thermodynamics of ion selectivity in aqueous solutions of 18-crown-6 ether: a molecular dynamic study. *J. Am. Chem. Soc.* **117**, 6954–6969 (1995)
36. de Boer, J.A.A., Reinhoudt, D.N., Harkema, S., van Hummel, G.J., de Jong, F.: Thermodynamic constants of complexes of crown ethers and uncharged molecules and X-ray structure of the 18-crown-6 $\cdot (\text{CH}_3\text{NO}_2)_2$. *J. Am. Chem. Soc.* **104**, 4073–4076 (1982)
37. Rogers, R.D., Richards, P.F., Voss, E.J.: Neutral solvent/crown ether interactions, 4. Crystallization and low temperature (-150°C) structural characterization of 18-Crown-6 $\cdot 2(\text{CH}_3\text{CN})$. *J. Inclusion Phenom.* **6**, 65–71 (1988)
38. Garrell, R.L., Smyth, J.C., Fronczek, F.R., Gandour, R.D.: Crystal structure of the 2:1 acetonitrile complex of 18-crown-6. *J. Inclusion Phenom.* **6**, 73–78 (1988)
39. Jones, P.G., Hiemisch, O., Blaschette, A.: Bildung und Kristallstruktur des Komplexes $[(18\text{-Krone-6})(\text{CH}_2\text{Cl}_2)_2]$. *Z. Naturforsch.* **49b**, 852–854 (1994)