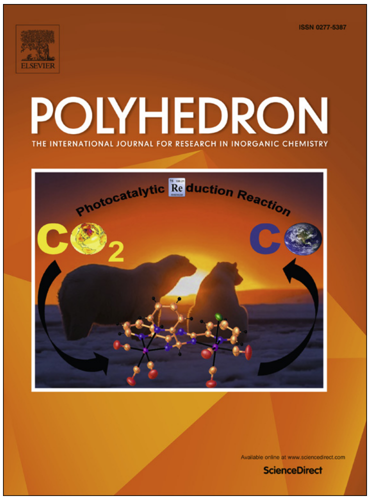

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A cesium-133 nuclear magnetic resonance study of the cesium cation complexation by macrocyclic polyethers in hydrophobic RITLs

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Thermodynamic data for cesium complexes formation with 18-crown-6 (18C6, L) in five hydrophobic room temperature ionic liquids (RTIL): trioctylmethylammonium salicylate ([TOMA][Sal]), tetrahexylammonium dihexylsulphosuccinate ([THA][DHSS]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulphonyl]imide ([BMIM][$N(Tf)_2$]), 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulphonyl]imide ([HMIM][$N(Tf)_2$]) as well as with 12-crown-4 (12C4, L) and 15-crown-5 (15C5, L) in [BMIM][$N(Tf)_2$] are measured with NMR ^{133}Cs technique at 27 to 50 °C. Only $[Cs(18C6)]^+$ complexes are found for [TOMA][Sal], [THA][DHSS], [BMIM][PF_6], while in [BMIM][$N(Tf)_2$] and [HMIM][$N(Tf)_2$] both $[Cs(18C6)]^+$ and $[Cs(18C6)_2]^+$ species are formed. For 12C4 and 15C5 only $[CsL]^+$ species are registered in [BMIM][$N(Tf)_2$]. For [BMIM][$N(Tf)_2$] the log K_1 values are steadily increasing: 12C4 < 15C5 < 18C6. A comparative study of $[Cs(18C6)]^+$ stability in RTILs is estimated to be in the range between water and acetonitrile with constants increasing in the order [THA][DHSS] < [TOMA][Sal] < [BMIM][PF_6] < [BMIM][$N(Tf)_2$] < [HMIM][$N(Tf)_2$]. It is demonstrated that unlike hydrophilic RTIL the entropy change with an exception of [BMIM][PF_6], promotes complex formation while the corresponding enthalpy change is either positive or gives rather small contribution to the complex stability.

Key words: stability constants, complexes, cesium, 18-crown-6, 15-crown-5, 14-crown-4, ^{133}Cs NMR, RTIL

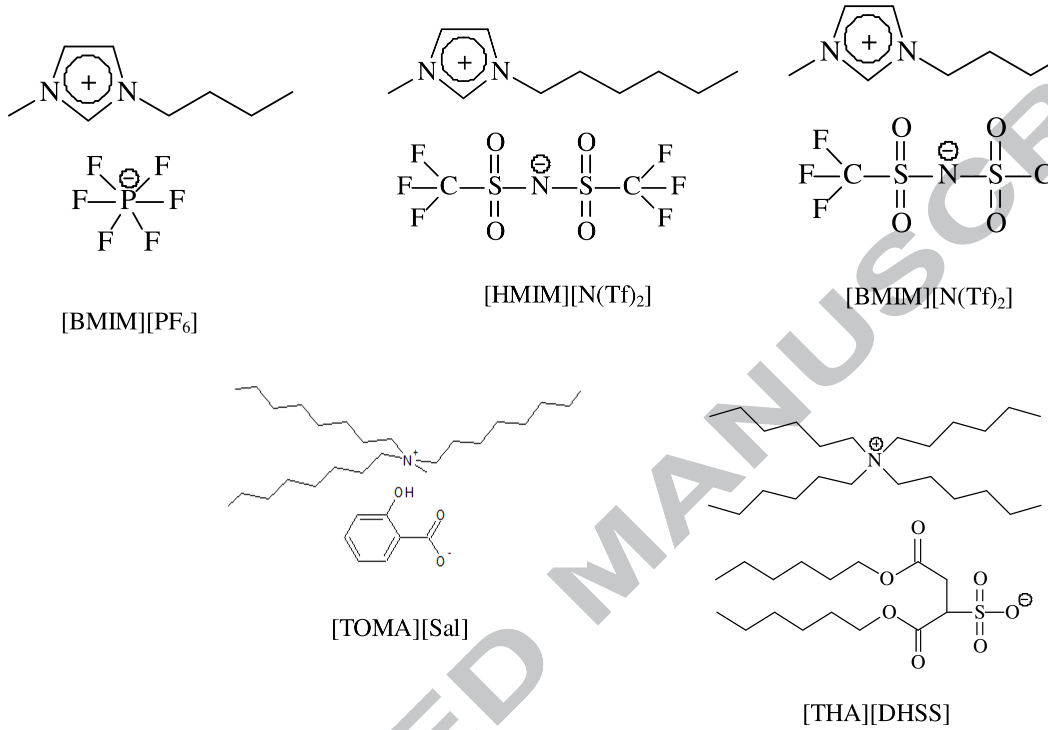
*Partly the preliminary data for 18C6 complexes at 25°C are published in Mendeleev Communications. 20 (2010) 122.

1. Introduction

Since 1967 crown ethers have been intensively studied and successfully applied for metal ion extraction in water/molecular liquid separations. It has been demonstrated that the cation-selective nature of crown ethers facilitates their implementation in the removal of Cs^+ and Sr^{2+} from liquid nuclear wastes. The development of a new class of hydrophobic solvents – room-temperature ionic liquids (RTILs) has given a new impulse to the crown ether enhanced separations [1-7], and provided a unique medium for complexes formation [8-10]. 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, and a possibility to eliminate aqueous phase acidification. Besides the issues of 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 cesium complex formation constants in RTILs [11-13]. The data on the thermodynamic quantities for cesium complexes formation have been published in the recent years only for hydrophilic RTIL [13].

Present work aims to diminish this gap by studying the complex formation of cesium ions with 18-crown-6 (L, 18C6) in five hydrophobic RTILs (Scheme 1): trioctylmethylammonium salicylate ([TOMA][Sal]), tetrahexylammonium dihexylsulphosuccinate ([THA][DHSS]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), 1-butyl-3-methylimidazolium bis[trifluoromethyl)sulphonyl]imide ([BMIM][$N(Tf)_2$]), 1-hexyl-3-

methylimidazolium bis[trifluoromethyl)sulphonyl]imide ([HMIM][N(Tf)$_2$]) and with 14-crown-4 (L, 14C4), 15-crown-5 (L, 15C5) in [BMIM][N(Tf)$_2$] operating ^{133}Cs NMR technique with an emphasis on thermodynamic data. Two of RTIILs under the study ([TOMA][Sal], ([THA][DHSS]) represent task –specific ionic liquids.



Scheme 1. Structures of RTILs.

Experimental

2.1. Reagents

Cesium nitrate (Merck, reagent purity) was dried at 110 °C for one day before use, 18-crown-6, 15-crown-5 and 12-crown-4 (Sigma-Aldrich) have been dried at 35 °C and used without further purification.

Trioctylmethylammonium salicylate ([TOMA][Sal]). Aliquat® 336 (Aldrich; the 2:1 mol/mol mixture of methyltrioctyl- and methyltridecylammonium chloride) was mixed with 30% excess of sodium salicylate in 200 mL of chloroform. The mixture was shaken for 4 hr and then was rinsed with a large amount of distilled water. The solvent was evaporated and the liquid residue was heated up to 100 °C under reduced pressure for 5 hr. After cooling to room temperature a white solid matter was obtained with a density 0.943 g·cm^{-3}; T_{melt}=32.8±0.4 °C, T_f=14±2 °C. Yield: 90%. The NMR spectra indicated: ^{1}H NMR (500 MHz, Bruker DRX500, solvent $CDCl_3$, TMS) 0.88 (9 H), 1.24 (30 H), 1.59 (6 H), 3.19 (3 H), 3.27 (6 H), 7.20 (1 H), 7.92 ppm (1 H); ^{13}C NMR (126 MHz, solvent DMSO-D_6, TMS) 13.80 (C^*H_3), 21.93 ($C^*H_2CH_3$), 21.25, 25.68, 28.27, 28.32, 31.04 (various CH_2CH_2 fragments); 47.41 (CH_3N); 60.50 (CH_2N); 115.35, 115.62, 120.73, 129.73, 130,88 (aromatic C); 163.17 (COH); 171.00 ppm (COO). Analyses**,** found: C, 76.06; H, 11.64; N: 2.62; calc.: C, 76.49; H, 11.89; N: 2.62.

After equilibration with water at ambient temperature, the solid product transformed into a slightly yellowish viscous liquid with the density of 0.942 g·cm^{-3} and a freezing point below −18 °C. Water content measured by Karl Fisher titration constituted 0.18% wt (0.09 mol·dm^{-3}) for a solid product and 4.83% wt (2.52 mol·dm^{-3}) for RTIL samples equilibrated with water.

Tetrahexylammonium dihexylsulphosuccinate ([THA][DHSS]) was synthesized according to [14] as a transparent viscous liquid (yield: 85%), analysed by NMR, and then used without further purification. The NMR spectra revealed: ^{1}H NMR (500 MHz, solvent $CDCl_3$, TMS) 0.88 (18 H), 1.33 (36 H), 1.55 (12 H), 3.2 (12 H), 4.1 (3 H) ppm; ^{13}C NMR (126 MHz, solvent DMSO-D_6, TMS) 13.64, 13.69, 13.71 (CH_3); 20.91, 21.76 ($C^*H_2CH_3$), 21.87, 24.82, 24.85, 25.34, 27,95, 27.99, 30.47, 30.75, 30.82 (CH_2CH_2 fragments); 34.01 (OOC^*CH_2CH-); 57.63 (CH_2N); 63.89 (CH_2O); 168.31, 170.97 COOR). Analyses, found: C, 66.67; H, 11.31; N: 1.97, S: 4.49; calc.: C, 66.71; H, 11.34; N: 1.94, S: 4.45. The absence of halogen ions was proved by $AgNO_3$ test. Water content in a RTIL, mass % - 4.4.

1-butyl-3-methylimidazolium hexafluorophosphate was purchased from Merck. The purity of RTIL was studied by ^{1}H NMR and then used without further purification. Water content in a RTIL, mass % - 1.9.

1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulphonyl]imide was purchased from Sigma-Aldrich. The quality of RTIL was controlled by ^{1}H NMR and then used without further purification. Water content in a RTIL, mass % - 0.5.

1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulphonyl]imide was provided by Solvent Innovation, puriss. 99%. The quality of RTIL was controlled by ^{1}H NMR and then used without further purification. Water content in a RTIL, mass % - 1.3.

2.2. Sample preparation

The exact mass of solid cesium nitrate was mixed with the calculated mass of 18C6, 15C5 or 12C4 and then 1 mL of RTIL was added. Within each series of 11 to 16 samples, the concentration of cesium was kept constant at a level of 0.005 or 0.004 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. Because the NMR chemical shifts of alkali cations are sensitive to both metal concentration and complex formation, the sample-by-sample measurement eliminated the sample dilution and is more accurate than the common titration procedure [15].

The dissolution process was performed within 3 to 5 min at 110 ^{o}C because a sufficient reduction of solvent viscosity was found to occur within this time. The establishment of equilibrium took 1 to 2 hr and it was controlled occasionally by the NMR measurement of some selected samples. Before NMR measurement, all samples were allowed to equilibrate in closed glass tubes at room temperature for 24 hr. According to the pH measurements, all RTILs were neutral solutions. The pH measurements were made by using METTLER Toledo 320 pH meter, calibrated by standard buffer solutions (Oy FF-Chemicals).

A complex stability in RTIL depends on the water content [16]. The water content of each sample was controlled with the Karl Fisher method and ^{1}H NMR by a comparison of signal intensities between water and RTIL.

2.3. NMR Measurements

^{133}Cs NMR measurements were recorded with Bruker AVANCE II 300 spectrometer, operating at 39.38 MHz, in a 5 mm diameter sample tubes at the steady temperatures between 27 and 50 ^{o}C**.** After each temperature change, the sample was kept in the probe head for 10 min before 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 D_2O (added for the lock), which provided a 0.04 $\mathrm{mol \cdot dm^{-3}}$ concentration of each cation. Downfield shifts were denoted by a positive sign. All the literature data on molecular solvents taken for comparison are converted into this scale.

2.4. NMR Data treatment, complex formation constants evaluation

Generally, the complex formation equilibrium can be described by simple reactions:

$$Cs^+ + L \leftrightarrows [CsL]^+ \qquad K_1 = [CsL][Cs]^{-1}[L]^{-1} \qquad (1)$$

$$CsL^+ + L \leftrightarrows [CsL_2]^+ \qquad K_2 = [CsL_2][CsL]^{-1}[L]^{-1} \qquad (2)$$

For [TOMA][Sal], [THA][DHSS], [BMIM][PF_6], only CsL for 18C6 was found at any Cs/L mole ratios. The same situation was observed for cesium complexes with 12C4 and 15C5 in [BMIM][$N(Tf)_2$]. An experimentally observed δ_{obs} single time-averaged ^{133}Cs chemical shift of “free” cation and a ligand-bonded cation can be given by an equation (2) [17]:

$$\delta_{obs} = (\delta_{Cs} + K_1[L]\delta_{CsL})/(1 + K_1[L]) \qquad (3)$$

where

$$[L] = C_L – C_{Cs}X_{CsL} \qquad (4)$$

$$X_{CsL} = (\delta_{obs} - \delta_{Cs})/(\delta_{CsL} - \delta_{Cs}) \qquad (5)$$

C_L is a total concentration of the ligand, [L] is a free concentration of the ligand, C_{Cs} is 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 equations (3), (4) and (5). The stability constant K_1 was calculated by the non-linear curve-fitting program HypNMR [18] operating with 11 to 16 experimental points for a curve. 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 δ_{CsL}calc, δ_{Cs}calc and experimental δ_{Cs}obs values have been obtained, providing additional fitting degree estimate, Tables 1, 2.

For [BMIM][N(Tf)$_2$] and [HMIM][N(Tf)$_2$] both CsL and CsL$_2$ complexes formed with 18C6. The titration curve was treated using equation (2) separately for L/Cs mole ratios from 0 to 0.8 and from 1.5 to 20. For the latter case an equation (5) was treated by HypNMR diminishing the [L]/[Li] mole ratio by one unit against the real one:

$$\delta_{obs} = (\delta_{LiL} + K_2[L]\delta_{LiL2})/(1 + K_2[L]) \qquad (6)$$

Such an approach gives a better fitting relative to the treatment by HypNMR of the whole curve at once. Additionally one can get two δ_{CsL}calc values obtained from two sets of data (L/Li<1 and L/Li>1). The corresponding values demonstrated a good agreement. The typical titration curves are presented at Figure 1. Values of calculated ln K_1 and ln K_2 were then plotted versus 1/T. A linear relationship was obtained in all cases, indicating the constancy of ΔH_1 and ΔH_2 within the temperature range 27 to 50 ^oC. Then the values ΔH^o_n, $T\Delta S^o_n$ (n=1, 2) were calculated, using the reaction isobar equation and the Aqua Solution Software [19]. The experimental results are presented in Tables 1 to 4. The log K_n, ΔH^o_n and δ_{calc} for 25 ^oC values are obtained by the data extrapolation.

The reliability of equilibrium complex formation data is a serious concern of the chemistry community. Thus in Tables 3 and 4, the experimental data are given along with values reported previously for hydrophilic RTILs: *N*-butyl-4-methyl-pyridinium tetrafluoroborate ([BMPy][BF$_4$]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]), and 1-butyl-3-methylimidazolium dicyanamide ([BMIM][N(CN)$_2$]) [13] and for molecular solvents [17,20,21], and are compared with IUPAC recommended (**R**) or provisional (**P**) [20] values where possible.

2. Results and Discussion

2.1. 12-crown-4 and 15-crown-5 complexes in [BMIM][N(Tf)$_2$]

Within the temperature range 27 to 50 ^oC all the ^{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. An increase of 12C4 and 15C5 concentration in [BMIM][N(Tf)$_2$] led at 27 ^oC to the monotonous increase of δ_{obs}, which corresponds to the formation of

$[Cs(12C4)(N(Tf)_2)_m]^{1-m}$ and $[Cs(15C5)(N(Tf)_2)_n]^{1-n}$ species, where m>n, Fig.1. Evidently, 12C4 occupies less space in the cesium coordination sphere than 15C5 and the corresponding chemical shift is less dependent on a ligand concentration. Therefore, $[Cs(12C4)]^+$ complex is less stable than $[Cs(15C5)]^+$ one, Table 1.

Indeed, an estimated value log K_1= 1.75 (0.04) for 15C5 at 25 °C is higher than that for 12C4, log K_1=1.4 (0.1), Table 2. These values are in a reasonable agreement with those found for molecular solvents. IUPAC evaluation gives log K_1 values for $[Cs(12C4)]^+$ complexes: 1.43 (propylene carbonate) and 1.62 (MeOH), while for $[Cs(5C5)]^+$ in acetonitrile, propylene carbonate, acetone, MeOH, DMFA and water these are: 3.0; 3.39, 3.68, 0.91 and 0.9 respectively [20].

The thermodynamic quantities of $[Cs(12C4)(N(Tf)_2)_m]^{1-m}$ and $[Cs(15C5)(N(Tf)_2)_n]^{1-n}$ species formation are very similar. In both cases an enthalpy change ΔH_1^o is around the zero, while ΔS_1^o values are both positive and are responsible for the complex stability. However, an entropy contribution to the complex stability for 15C5 is twice higher than that for 12C4. This corresponds well with the model where 15C5 substitutes more $N(Tf)_2$ anions than 12C4 (m>n).

At the same, time neither ^{133}Cs chemical shifts, nor HYP NMR data treatment indicate any evidence of a bis-complex CsL_2 formation for both 12C4 and 15C5 although cesium provides enough space for the second crown ether molecule coordination. Thus $N(Tf)_2$ anions are capable of competing for a space in the cesium environment with a second molecule of a low denticity neutral macrocyclic ligand.

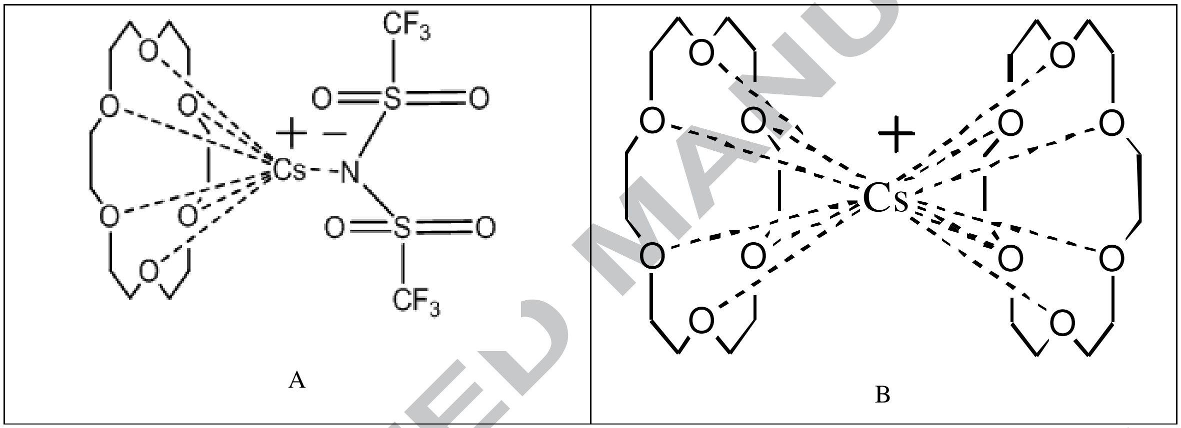
2.2. 18-crown-6 complexes in [BMIM][N(Tf)$_2$]and in[HMIM][NTf$_2$]

An increase of 18C6 concentration in [BMIM][N(Tf)$_2$] led at 27 °C and at other temperatures to the intensive, monotonous increase of δ_{obs}, like it was observed for 12C4 and 15C5, Fig.1. At the same time, an excess of 18C6 over [L]/[Cs] 1:1 molar ratio showed a decrease of a chemical shift indicating the CsL_2 complex formation. The upfield shift followed by a sharp break and a downfield shift can be explained by the formation of a highly stable CsL complex followed by the addition of the second ligand molecule to form a “sandwich” CsL_2 complex

[17,22], Scheme 2.

It is interesting to note that chemical shifts of $[Cs(18C6)_2]^+$ are essentially independent of solvent's nature, Table 3, providing almost the same values for RTIL and for molecular solvents. This observation indicates that in a "sandwich"-type complex two crown ether molecules effectively shield the cesium ion from an interaction with a solvent, Scheme 2, B. This indicates the similarity of sandwich complexes structures.

By contrast, the chemical shifts of $[Cs(18C6)]^+$ are strongly solvent dependent both in RTIL and in molecular solvents. This fact supports the supposition that besides 18C6 some anions of a RTIL are also coordinated by Cesium in CsL species, Scheme 2A.



Scheme 2. Tentative structures of $[Cs(18C6)N(Tf_2)]^o$ (A) and $[Cs(18C6)_2]^+$ in $[BMIM][N(Tf)_2]$.

A comparison of cesium complexes stability with 12C4, 15C5 and 18C6 reveals an almost linear increase of log K_1 values as the ring size is increasing. This is similar to the trend found for methanol solutions, Fig.2: 12C4 < 15C5 < 18C6. Such a result is in a good agreement with the detection that cesium ion fits better into the 18C6 cavity than the 12C4 and 15C5 ones.

The ^{133}Cs chemical shift variation as a function of 18C6 concentration in $[HMIM][N(Tf)_2]$ is very similar to that in $[BMIM][N(Tf)_2]$, Fig.1. Moreover, even the chemical shift values estimated for 25 °C (δ_{Cs}calc, δ_{CsL}calc, δ_{CsL2}cal) are nearly the same, Table 3. Therefore, the cesium environment in $[HMIM][N(Tf)_2]$ and in $[BMIM][N(Tf)_2]$ is similar. However, the stability constant log K_1 in

[HMIM][N(Tf)$_2$] is one logarithmic unit higher than in [BMIM][N(Tf)$_2$], Table 2. Thus, not only the nature of the anion of the RTIL affects the complex stability, but the nature of the cation as well.

The thermodynamic quantities for the formation of [Cs(18C6])$^+$ in [HMIM][N(Tf)$_2$] or [BMIM][N(Tf)$_2$] are also very similar, Table 2. Alternatively to the molecular solvents and hydrophilic RTILs, the [Cs(18C6)]$^+$ complex in [HMIM][N(Tf)$_2$] or [BMIM][N(Tf)$_2$] is entropy stabilized, as well as [Cs(15C5)]$^+$ and [Cs(14C4)]$^+$.

The log K_2 values for [BMIM][N(Tf)$_2$] and [HMIM][N(Tf)$_2$] were very close to each other, and 2 to 3 log units lower than log K_1: 1.29 (0.07) and 1.13 (0.07) respectively, Table 2. These values correspond well to those found for molecular solvents [20].

2.3. 18-crown-6 complex in [BMIM][PF$_6$]

The ^{133}Cs NMR chemical shift of Cs$^+$ (δ_{Cs}calc) in [BMIM][PF$_6$] is about −90 ppm at ambient temperature. This value is the most negative shift among all RTILs studied, Table 3. The change of the chemical shift was uniform or the same within the whole range of [L]/[Cs] ratios studied, indicating the existence of only a single CsL complex and the absence of CsL$_2$ species. Meanwhile, δ_{CsL}calc was very close to those found for [Cs(18C6)]$^+$ species in [BMIM][N(Tf)$_2$] and [HMIM][N(Tf)$_2$].

The stability constant value log K_1=3.2 is also very close to that found for [BMIM][N(Tf)$_2$]. At the same time, the thermodynamic quantities for [Cs(18C6)]$^+$ formation were sufficiently different. This complex in [BMIM][PF$_6$], unlike [BMIM][N(Tf)$_2$] and [HMIM][N(Tf)$_2$], is enthalpy stabilized.

2.4. 18-crown-6 complex in [TOMA][Sal] and [THA][DHSS]

[TOMA][Sal] and [THA][DHSS] represent the task-specific ionic liquids. Indeed both anions [Sal] and [DHSS] are capable of forming the chelated complexes with cesium. By a contrast to [BMIM][N(Tf)$_2$], [HMIM][N(Tf)$_2$] and [BMIM][PF$_6$], at 25 °C the δ_{Cs}obs values in [TOMA][Sal] and [THA][DHSS] were positive. Meanwhile, the chemical sifts of ^{133}Cs decreased as 18C6 was added to the [TOMA][Sal] or [THA][DHSS] solution. Thus, the complex formation diminishes the differences in Cs^+ environment and brings chemical shifts δ_{CsL} closer together for all RTILs, relative to δ_{Cs}. This observation is consistent with the fact that in all solvents 18C6 occupies the major part of the cesium coordination sphere in a more or less similar way. However, the resonances of ^{133}Cs in $[CsL]^+$ have still different values and signs indicating different solvation and/or ligand conformation in $[Cs(18C6)]^+$, Table 3.

For [TOMA][Sal] and [THA][DHSS] no formation of $[Cs(18C6)_2]^+$ was detected. This might be linked to the rather stable mixed ligand complexes $[Cs(18C6)(Sal)]^o$ and $[Cs(18C6)(DHSS)]^o$. A strong competition of [Sal] and [DHSS] anions with 18C6 for cesium ion did not prevent only the $[Cs(18C6)_2]^+$ formation, but led also to the rather low log K_1 values, Table 2. Indeed, the corresponding stability constant values were the lowest among the hydrophobic RTILs studied. Moreover, the log K_1 for [THA][DHSS] was even smaller than for water, Table 4. The thermodynamic quantities for the $[Cs(18C6]^+$ formation in [TOMA][Sal] and [THA][DHSS] were very close to those for $[HMIM][N(Tf)_2]$ and $[BMIM][N(Tf)_2]$, Table 2.

2.5. Chemical shifts of cesium in RTILs

^{133}Cs NMR chemical shifts of Cs^+ cation in RTILs span a very broad range from – 90 ppm ($[BMIM][PF_6]$) to 90 ppm ($[BMIM][N(CN)_2]$) clearly indicating their dependence on the RTIL's anion nature, but not on the cation's one, Table 3. Indeed, for both $[N(Tf)_2]$-based RTIL the chemical shifts of Cs^+ are the same within the experimental error. At the same time the highly negative shift for $[BMIM][PF_6]$ is rather close to those observed for RTILs with fluorinated anions $[BMPy][BF_4]$ and $[BMIM][BF_4]$ (~ – 70 ppm).

For $[Cs(18C6)]^+$ species the chemical shifts reveal a much less diversity ranging from –47 ppm ([THA][DHSS]) to 30 ppm ($[BMIM][N(CN)_2]$). Thus, a complex formation diminishes the differences in Cs^+ environment and brings 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 a more or less similar way. However, the resonances of ^{133}Cs in $[CsL]^+$ still remain different in values and signs indicating different solvation and/or different ligand conformation of a complex, Table 3.

Generally, chemical shift of ^{133}Cs 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 $[Cs(18C6)]^+$ are almost the same in [BMIM][BF_4] and [BMPy][BF_4] as well as in [BMIM][$N(Tf)_2$] and [HMIM][$N(Tf)_2$].

This is consistent with formation of similar species $[Cs{\cdot}(BF_4)_n]^{1-n}$ and $[Cs(18C6){\cdot}(BF_4)_{n-x}]^{1-n+x}$ in both [BF_4]-based RTILs, as well as $\{Cs{\cdot}[N(Tf)_2]_m\}^{1-m}$ and $\{Cs(18C6){\cdot}[N(Tf)_2]_{m-x}\}^{1-m+x}$ in those [$N(Tf)_2$]-based. Meanwhile, for [BMIM][$N(CN)_2$] and [THA][DHSS] the chemical shifts of δ_{Cs} and δ_{CsL} are definitely different, demonstrating different environment of cesium in both species relative to those mentioned above.

It is interesting to note that chemical shifts of $[Cs(18C6)_2]^+$ are essentially independent of solvent's nature, Table 3, 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, Scheme 2, B. By contrast, the chemical shifts of $[Cs(18C6)]^+$ are strongly solvent dependent both in RTIL and in molecular solvents. This fact supports the supposition that besides 18C6 some anions of a RTIL are also coordinated by Cesium in CsL species, Scheme 2,A .

2.6. Stability constants of cesium complexes in RTILs

The log K_1 values for $[Cs(18C6)]^+$ complexes in hydrophobic RTILs [HMIM][$N(Tf)_2$], [BMIM][$N(Tf)_2$], [BMIM][PF_6], [TOMA][Sal] and [THA][DHSS] at 25 °C span the range over 3 logarithmic units from 4.4 ([HMIM][$N(Tf)_2$]) to 0.76 ([THA][DHSS]). With an exception of [THA][DHSS], all of them are higher, then the stability constant of $[Cs(18C6)]^+$ in water (0.98 [20]). This makes most of them rather attractive for the cesium extraction applications. It is reasonable to note, that an ability to form $[Cs(18C6)]^+$ complexes in hydrophobic RTILs reveals a reversed linear correlation with cesium distribution coefficients ($\log D_{Cs}$) between water and RTIL without crown-ether, e.g., if the ionic liquid better dissolves ”free” cesium ions, then the stability of $[Cs(18C6)]^+$ in it would be lower.

Although a number of data on cesium stability constants in RTIL is still rather poor, one can preliminary make some solvent gradation taking $[Cs(18C6)]^+$ complex as a probe. In this respect the hydrophobic non-specific RTILs ([HMIM][$N(Tf)_2$], [BMIM][$N(Tf)_2$], [BMIM][PF_6]) provide more stable $[Cs(18C6)]^+$ complexes than hydrophilic non-specific RTILs ([BMIM][$N(CN)_2$], [BMPy][BF_4], [BMIM][BF_4], [BPy][$MeSO_4$]), which in turn demonstrate the higher stability over hydrophobic task-specific RTILs ([TOMA][Sal], [THA][DHSS]). A comparative study of $[Cs(18C6)]^+$ stability in RTILs is estimated to be in the range between water and acetonitrile with constants increasing in the order [THA][DHSS] < [TOMA][Sal] < [BMIM][PF_6] < [BMIM][$N(Tf)_2$] < [HMIM][$N(Tf)_2$].

As it was noted for hydrophilic RTIL, the magnitude of $\log K_1$ for hydrophobic RTILs falls inside, but not outside the range of those for molecular solvents, with location between acetone and water, Table 4. The $\log K_1$ value for an alkali metal cation with crown ether in molecular solvents is correlated [22] with donor number (DN) of the solvent [23], Table 4, although some exceptions for $[Cs(18C6)]^+$ are known (pyridine: DN 33.1; $\log K_1 = 5.7$ [22]). In this sense, the $\log K_1$ values obtained in the present study suggest that hydrophobic RTILs [HMIM][$N(Tf)_2$], [BMIM][$N(Tf)_2$], [BMIM][PF_6], [TOMA][Sal] have DN between 33 (water) and 14 (acetone), 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, $\log K_1 = 7.98$ [24]). This observation is in a reasonable agreement with data of Nishi *et al.* [25] 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 demonstrated to have DN between 4.4 (nitrobenzene) and 0 (1,2-dichloroethane).

2.7. The thermodynamic quantities of [Cs(18C6]$^+$ formation

The thermodynamic quantities for the formation of [Cs(18C6)]$^+$ in RTILs are summarized in Tables 2 and 4 together with those for molecular solvents. An increase of temperature does not affect the stability constants of CsL for [BMIM][N(Tf)$_2$], [TOMA][Sal] and [THA][DHSS] within the experimental errors. However, the data treatment with Aqua Solution Software [19] reveals ΔH^o_1 to be varied from –5.0 to 3.6 kJ/mol. Compared with the molecular solvents and hydrophilic RTILs the [Cs(18C6)]$^+$ complex in these RTILs is entropy stabilized, Table 4. For [HMIM][N(Tf)$_2$] and [BMIM][PF$_6$] log K_1 values are decreasing as the temperature increases. The linear plots of ln K_1 versus 1/T gave the possibility to estimate both ΔH^o_1 as –13.1 and –18.8 kJ/mol respectively, Fig.2.

With an exception of [THA][DHSS] and [TOMA][Sal], the cesium nitrate solubility in RTIL is much less then 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 interactions are expected to make complex formation more exothermic in RTIL than in water. Indeed, for CsL formation ΔH^o_1 is negative for all hydrophilic RTILs, [HMIM][N(Tf)$_2$], [BMIM][PF$_6$], [BMIM][N(Tf)$_2$], and almost for all polar molecular solvents. A nearly zero ΔH^o_1 value for [TOMA][Sal] and [THA][DHSS] could be explained by a capability of anions of these RTIL's to form complexes with Cs$^+$.

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], [THA][DHSS], that reveal a positive entropy change like acetonitrile. Moreover, the entropy change gives the dominating contribution to CsL stability in [HMIM][N(Tf)$_2$], [BMIM][N(Tf)$_2$], [TOMA][Sal] and [THA][DHSS]. Only one hydrophobic RTIL ([BMIM][PF_6]) demonstrates the same behavior as hydrophilic RTILs and polar molecular solvents.

Thus, 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 diversity, than log K_1 depending on RTIL composition. The complexation of Cs^+ is the most exothermic in [BMIM][BF_4]. 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 4 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 (6) is more complicated than that one in molecular solvents [26,27]. In general, both the ionic liquid forming ions (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:

$$CsX_n^{1-n} + Z_mL^{m+} \leftrightarrows CsLX_{n-p}^{1-n+p} + mZ^+ + pX^- \quad (6)$$

The NMR chemical shift data indicate that crown ether does not substitute all RTIL anions X^- in coordination sphere of cesium in CsL complexes. This observation agrees well with X-ray structural data for cesium complexes with 18-crown-6 in a solid state [28,29] and in an aqueous solution [30], as well as with classical molecular dynamics simulations [31]. 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 [20]). 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_1 and ΔS_1 values of complex formation is observed when RTILs [BMIM][BF_4] and [BMPy][BF_4] are compared, indicating Z^+-crown ether interactions of various intensity. Such an interaction has also analogues among molecular solvents. For example, for acetonitrile (AN), nitromethane (NM) and even for dichlormethane the solvates 18-crown-6·2AN, 18-crown-6·2NM and 18-crown-6·2CH_2Cl_2 have been isolated and their structures have been determined by X-ray crystallography [32-35]. 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 then ΔH_1, at the same time ΔS_2 is negative, while ΔS_1 is positive. For the second crown ether molecule coordination in [BMIM][$N(Tf)_2$] and [HMIM][$N(Tf)_2$], (7):

$$CsLX_n^{1-n} + Z_mL^{m-} \leftrightarrows CsL_2^+ + mZ^+ + nX^- \qquad (7)$$

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 $N(Tf)_2^-$ anion towards alkali and alkaline earth cations [36]. Alternatively, in [BMIM][PF_6], [BMIM][BF_4], [BMPy][BF_4] and [BMIM][$N(CN)_2$], the solvent's anion X^- is bound to cesium more tightly and prevents CsL_2^+ complex formation. Such an interpretation is supported by a much better extraction of $CsNO_3$ from water into RTIL for [TOMA][Sal], [THA][DHSS] and [BMIM][PF_6] relative to [BMIM][$N(Tf)_2$] and [HMIM][$N(Tf)_2$] in an absence of 18C6 [12].

Formation of crown ether complexes promotes cesium extraction [12] into hydrophobic RTIL from water if the complex stability in RTIL is higher than in water, Table 4. Indeed for [BMIM][$N(Tf)_2$], [HMIM][$N(Tf)_2$], [BMIM][PF_6] and [TOMA][Sal] $\log K_1^{\mathrm{RTIL}} > \log K_1^{\mathrm{water}}$ and cesium content in RTIL increases due to 18C6 administration. For [THA][DHSS] $\log K_1^{\mathrm{RTIL}} < \log K_1^{\mathrm{water}}$ and crown ether decreases cesium content in RTIL. It should be noted that the complex stability in RTIL increases linearly as the RTIL ability to extract cesium without 18C6 (D_{Cs}) decreases.

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Table 1. Chemical shifts and stability constants of $[CsL]^+$ complexes with 12C4, 15C5 and 18C6 in RTILs at 27 to 57 ^{o} C

T, °C	δ_{Cs}calc, ppm	δ_{Cs}obs, ppm	δ_{CsL}calc, ppm	log K_1	T, °C	δ_{Cs}calc, ppm	δ_{Cs}obs, ppm	δ_{CsL}calc, ppm	log K_1
12C4 in **[BMIM][N(Tf)$_2$]**					**15C5** in **[BMIM][N(Tf)$_2$]**				
25	−35.1(0.2)	−35.14	−30(3)	1.4(0.1)	27	−32.5(0.6)	−31.82	−1(4)	1.6 (0.1)
35	−35.1(0.2)	−35.05	−31(2)	1.5(0.2)	37	−32.4(0.6)	−31.79	−4 (4)	1.6 (0.2)
45	−34.9(0.2)	−34.97	−30(4)	1.3(0.2)	47	−32.5(0.6)	−31.84	−6 (4)	1.6 (0.2)
55	−34.8(0.2)	−34.88	−32(1)	1.6(0.3)	57	−32.4(0.5)	−31.83	−9 (4)	1.6 (0.2)
18C6									
[HMIM][N(Tf)$_2$]					**[BMIM][PF$_6$]**				
27	−31 (6)	−31.24	−4.4(0.9)	4.4(0.5)	27	−91(2)	−90.04	−6(14)	2.3(0.2)
35	−30.3 (0.7)	−31.20	−4.0(0.9)	4.4(0.5)	32	−90(2)	−89.61	1(16)	2.2(0.2)
43	−30.3(0.7)	−31.18	−3.8(0.9)	4.3(0.5)	37	−90(1)	−89.51	3(16)	2.2(0.2)
50	−30.1(0.6)	−30.89	−3.7(0.9)	4.3(0.4)	42	−90(1)	−89.35	5(17)	2.2(0.2)
[BMIM][N(Tf)$_2$]					**[THA][DHSS]**				
27	−29.6(0.5)	−39.31	−5(4)	3.4(0.9)	27	22.9(0.3)	22.53	−43(2)	0.77(0.04)
35	−29.6(0.5)	−29.31	−4(5)	3.3(0.9)	35	23.4(0.2)	23.38	−33(2)	0.77(0.04)
43	−29.6(0.4)	−29.27	−3(5)	3.3(0.8)	43	23.8(0.2)	23.85	−26(2)	0.79(0.04)
50	−29.5(0.5)	−29.23	−3(5)	3.3(0.9)	50	24.1(0.4)	24.89	−21(3)	0.79(0.08)
[TOMA][Sal]									
35	31.8(0.7)	32.97	−24(2)	1.45(0.07)	50	33.2(0.8)	34.48	−15(2)	1.48(0.07)
43	32.5(0.8)	33.79	−19(2)	1.47(0.06)					
* Standard deviations are indicated in parentheses									

Table 2. Stability constants and thermodynamic quantities of $[CsL]^+$ and $[CsL_2]^+$ complexes formation in RTILs at 25 ^{o} C

RTIL	log $K_{1(2)}$	$\Delta G^o_{1(2)}$, kJ/mol	$\Delta H^o_{1(2)}$, kJ/mol	$\Delta S^o_{1(2)}$, J/(mol·K)	$T\Delta S^o_{1(2)}$, kJ/mol	Ref.
$[Cs(18C6)]^+$						
[HMIM][N(Tf)$_2$]	4.4 (0.3)	– 25	– 9 (1)	53 (3)	16	Present work
[BMIM][N(Tf)$_2$]	3.4 (0.2)	– 19	– 8 (2)	40 (5)	12	Present work
[BMIM][PF$_6$]	3.2 (0.1)	– 18	– 18.8 (0.5)	– 7	–2	Present work
[TOMA][Sal]	1.43 (0.06)	– 8	3.9 (0.2)	40.0 (0.7)	12	Present work
[THA][DHSS]	0.76 (0.05)	– 4	3.2 (0.5)	25 (2)	8	Present work
[BMIM][N(CN)$_2$]	2.9 (0.3)	– 17	– 52 (1)	–119 (3)	–36	[13]
[BMIM][BF$_4$]	2.8 (0.2)	– 16	–65 (6)	–160 (20)	–48	[13]
[BMPy][BF$_4$]	2.6 (0.2)	– 15	–48 (1)	–113 (4)	–34	[13]
$[Cs(18C6)_2]^+$						
[HMIM][N(Tf)$_2$]	1.13 (0.07)	–6.4	–17.8 (0.3)	–38.3 (0.9)	–11.4	Present work
[BMIM][N(Tf)$_2$]	1.29 (0.07)	–7.3	– 41.3 (0.7)	–114 (1)	–34	Present work
$[Cs(15C5)]^+$						
[BMIM][N(Tf)$_2$]	1.75 (0.04)	– 10.0	2.9 (0.2)	43.3 (0.5)	12.9	Present work
$[Cs(12C4)]^+$						
[BMIM][N(Tf)$_2$]	1.4 (0.1)	–8.0	2 (4)	21 (15)	6	Present work

Table 3. Chemical shifts of $[CsL]^+$ and $[CsL_2]^+$ complexes in RTILs and in molecular solvents at 25 ^{o} C

Solvent	δ_{Cs}calc, ppm	δ_{CsL}calc, ppm	δ_{CsL2}calc, ppm	Ref.
18C6				
Acetonitrile	24.1	14.8	-53	[17]
Propylene carbonate	-36.5	-8.1	-45	[17]
Acetone	-35.8	-6.4	-47	[17]
$[HMIM][NTf_2]$	−30.7 (0.6)	−5 (1.0)	−50 (4)	Present work
DMFA	-0.8	3.37	-48	[17]
$[BMIM][NTf_2]$	−29.6 (0.5)	−6.5 (0.7)	−47 (1)	Present work
DMSO	68	23.6	-49	[17]
$[BMIM][N(CN)_2]$	91 (1)	34 (1)		[13]
$[BMIM][BF_4]$	−68 (4)	−22 (4)		[13]
$[BMPy][BF_4]$	−70 (7)	−16 (5)		[13]
$[BMIM][PF_6]$	−91 (2)	−7 (14)		Present work
[TOMA][Sal]	31 (0.7)	−29 (1)		Present work
[THA][DHSS]	22.5 (0.3)	−47 (2)		Present work
15C5				
DMFA	−0.8	3.5		[21]
$[BMIM][NTf_2]$	−32.5(0.6)	−1		Present work

Table 4. Stability constants and thermodynamic quantities of $[Cs(14C4)]^+$, $[Cs(15C5)]^+$ and $[Cs(18C6)]^+$ at 25 ^{o} C in RTILs and in molecular solvents

Solvent	DN [23]	log K_1	ΔH_1^o , kJ/mol	$T\Delta S_1^o$, kJ/(mol·K)	Ref.
14C4					
Propylene carbonate	15,1	1.43			[20]
MeOH	19	1.62			[20]
[BMIM][N(Tf)$_2$]					Present Work
15C5					
Acetone	17,0	3.68(0.04)R	−19.4(0.4)R	1.6	[20]
Propylene carbonate	15,1	3.39 (0.05)	−17 (1)P		[20]
Acetonitrile	14,1	3.0 (0.1) P	−28 (1)R	– 11	[20]
MeOH	19	2.69 (0.08) P	−31.9 (0.1)		[20]
[BMIM][N(Tf)$_2$]		1.75 (0.04)	2.9 (0.2)	12.9 (0.5)	Present Work
DMFA	26,6	0.91 (0.04)			[20]
Water	33	0.8 (0.2)	−5.4(0.8)R	– 2.5	[20]
18C6					
Acetone	17,0	4.51 (0.04)R	−52.8(0.4)R	−27.2	[20]
[HMIM][N(Tf)$_2$]		4.5 (0.1)	– 13.1 (0.5)	43 (2)	Present Work
Propylene Carbonate	15,1	4.50 (0.02)R	−43.3(0.4)R	−17.6	[20]
Acetonitrile	14,1	4.36(0.08)	−17.4(0.4)P		[20]
DMFA	26,6	3.64 (0.02)R	−49.2(0.8)R	−28.4	[20]
[BMIM][N(Tf)$_2$]		3.4 (0.3)	– 5 (1)	48 (3)	Present work
[BMIM][PF$_6$]		3.2 (0.1)	– 18.8 (0.5)	– 2 (2)	Present work
DMSO	29,8	3.04 (0.02)R			[20]
[TOMA][Sal]		1.4 (0.1)	3.6 (0.5)	39 (2)	Present work
Water	33	0.96 (0.04)R	– 17 (1) P	12	[20]
[THA][DHSS]		0.79 (0.04)	– 3 (2)	5 (6)	Present work
[BMIM][N(CN)$_2$]		3.03 (0.08)	– 47 (2)	– 30 (2)	[13]
[BMIM][BF$_4$]		2.8 (0.3)	– 80 (3)	– 65 (3)	[13]
[BMPy][BF$_4$]		2.6 (0.3)	– 47 (1)	– 32 (1)	[13]

* For molecular solvents the log K_1 values correspond to $I = 0 – 0.1$ mol/dm^3 [20], followed by provisional (P) or recommended (R) IUPAC evaluation

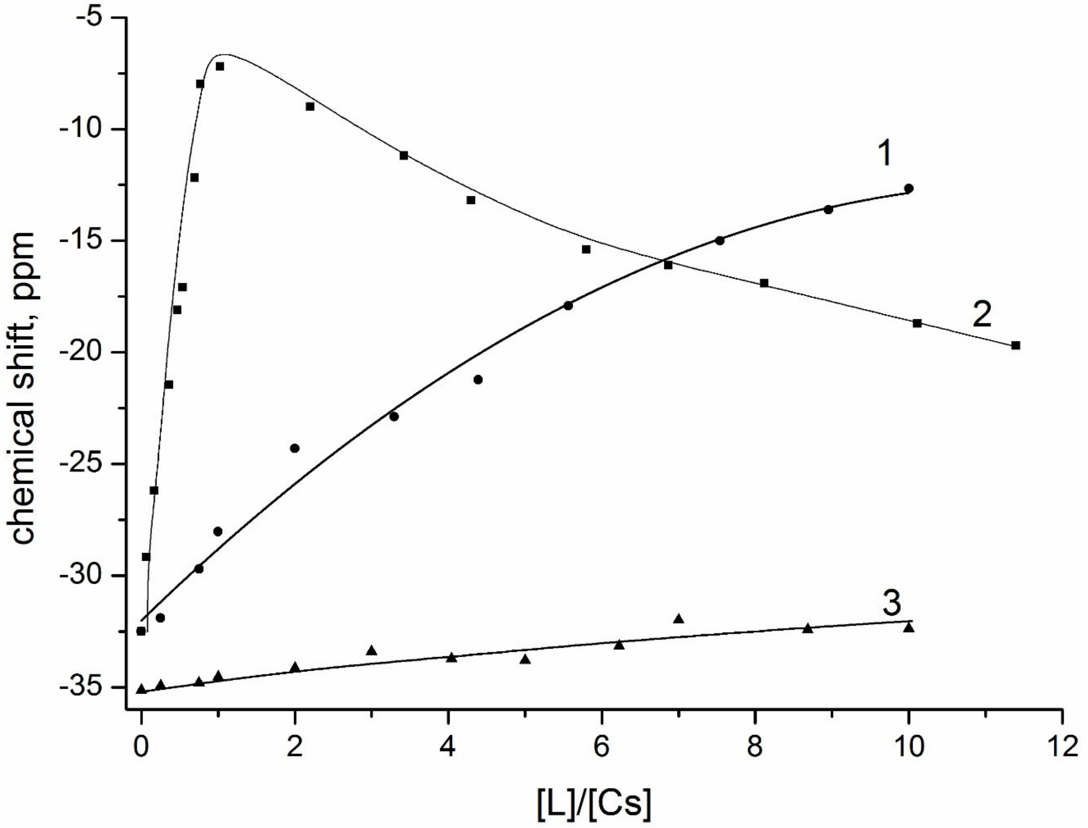


Fig. 1. Variation of ^{133}Cs NMR chemical shift versus ligand-to-cesium mole ratio [L]/[M] in [BMIM][N(Tf)$_2$] at 27 °C for 15C5 (1), 18C6 (2) and12C4 (3).

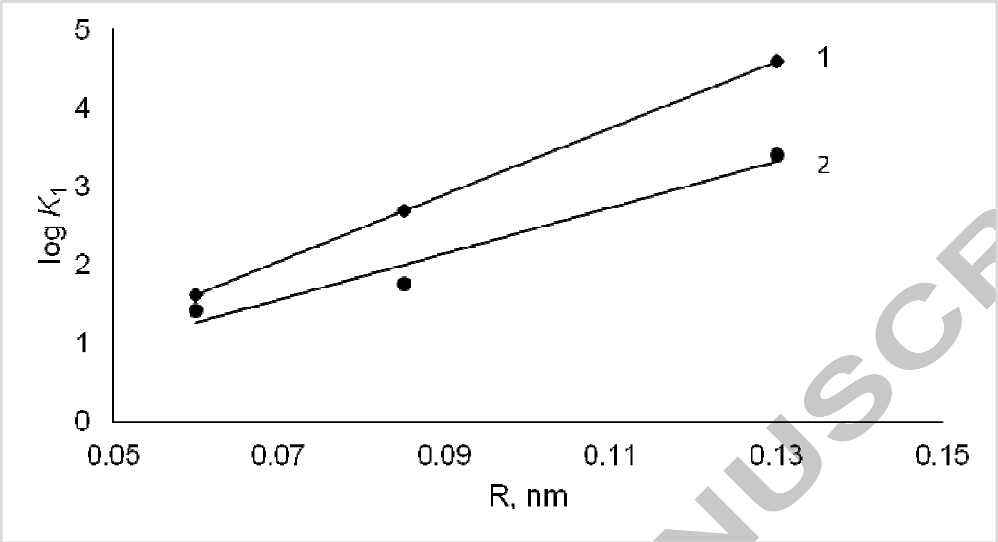
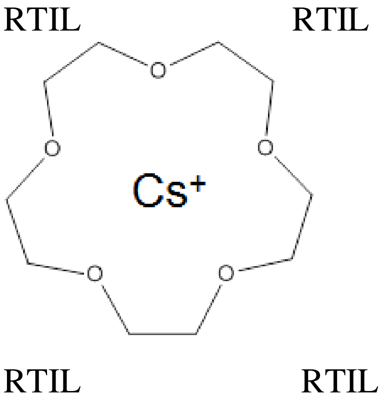


Fig. 2. Variation of log K_1 versus crown ether ring size R [20] at 25 °C for $[CsL]^+$ in MeOH (1) and in $[BMIM][N(Tf)_2]$ (2).


RTIL
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Cs+
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