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A correlation of caesium–18-crown-6 complex formation constants with the extraction capability for hydrophobic ionic liquids

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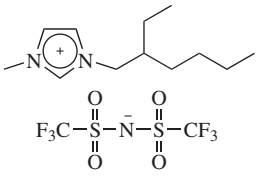
Thermodynamic data for caesium complexation with 18-crown-6 in various hydrophobic room-temperature ionic liquids were measured using ^{133}Cs NMR spectroscopy at 25 °C; the stability constants correlate well with crown ether assisted extraction degree of caesium from water into room temperature ionic liquids indicating an importance of complex stability for the extraction process.

Room-temperature ionic liquids (RTILs) are attracting increasing attention in solvent extraction processes due to important advantages over conventional organic diluents, such as negligible vapour pressure, low flammability, moisture stability, and possibility to eliminate aqueous phase acidification. For inorganic cations, the extraction process can be strongly enhanced by a chelating agent.[1–6] Besides the issues of cation, ligand and complex solubility in water and RTIL, the relative stabilities of complex formation in both phases are of significant importance for extraction selectivity. Unfortunately, the complex formation constants in RTIL are unknown. The aim of this work was to study the complexation of caesium ions with 18-crown-6 (L, 18C6) in the following hydrophobic RTILs: trioctylmethylammonium salicylate ([TOMA][Sal]), tetrahexylammonium dihexylsulfosuccinate ([THA][DHSS]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][$N(Tf)_2$]), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][$N(Tf)_2$]) and 1-(2-ethylhexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EtHMIM][$N(Tf)_2$]) by ^{133}Cs NMR spectroscopy with an emphasis on thermodynamic data and relevance to extraction process.[†]

The selected RTILs include both common and widely used solvents ([BMIM][PF_6], [BMIM][$N(Tf)_2$]), their derivatives ([HMIM][$N(Tf)_2$], [EtHMIM][$N(Tf)_2$]), as well as some task-specific ionic liquids with anions capable to form chelated complexes ([TOMA][Sal], [THA][DHSS]).

Like in water only CsL complexes have been found in [TOMA][Sal], [THA][DHSS] and [BMIM][PF_6], while in [BMIM][$N(Tf)_2$], [HMIM][$N(Tf)_2$] and [EtHMIM][$N(Tf)_2$] both species CsL and CsL_2 are registered. The latter case is typical of solvents such as DMF, acetonitrile, acetone and propylene carbonate.[7]

The stability constants of caesium complexes in hydrophobic RTILs (log K_1) for CsL in [HMIM][$N(Tf)_2$], [EtHMIM][$N(Tf)_2$], [BMIM][$N(Tf)_2$], [BMIM][PF_6], [TOMA][Sal] and [THA][DHSS] at 25 °C were evaluated to be 4.4, 3.4, 3.4, 2.4, 1.45 and 0.77, respectively. With the exception of [THA][DHSS], all of them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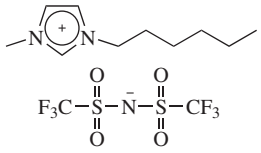
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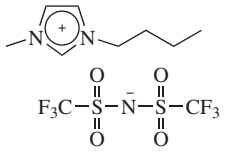
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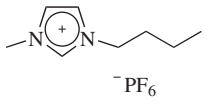
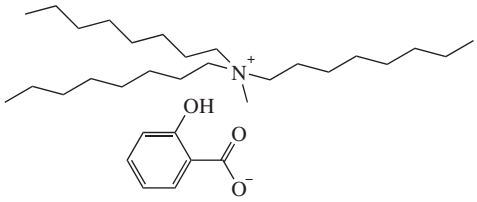
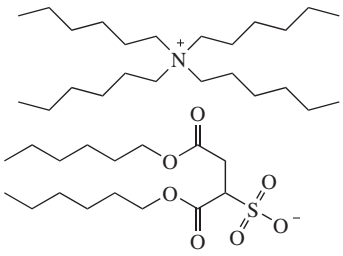

[BMIM][PF_6]


[TOMA][Sal]


[THA][DHSS]

[†] A full version of stability constants measurements is to be published in a book *Macrocyclic Chemistry: New Research Developments*, Nova Science Publishers Inc., 2010. For the extraction experiments, see ref. 13.

Table 1 Chemical shifts and stability constants of caesium complex with 18C6 in RTILs and molecular solvents at 25 °C.[a,b]

Solvent	ΔH_1[c]/kJ mol^{-1}	ΔS_1/J mol^{-1} K^{-1}	δ_{Cs}^{calc}/ppm	δ_{CsL}^{calc}/ppm	$\delta_{CsL_2}^{calc}$/ppm	log K_1	log K_2	Reference
1,2-Dichloroethane	—	—	—	—	—	7.98	2.58	9
[HMIM][NTf$_2$]	–9.5 (0.4)	53 (15)	–30.7(0.6)	–5 (1.0)	–50 (4)	4.4 (0.1)	1.13 (0.07)	This work
[EtHMIM][NTf$_2$]	9 (18)	100 (60)	–30.6 (0.2)	–3.9 (0.2)	–51 (4)	3.4 (0.4)	1.16 (0.08)	This work
[BMIM][NTf$_2$]	–7 (2)	42 (6)	–29.6 (0.5)	–6.5 (0.7)	–47 (1)	3.4 (0.5)	1.29 (0.07)	8, This work
[BMIM][PF$_6$]	–21 (1)	–25 (5)	–91 (2)	–7 (14)		2.4 (0.2)		This work
[TOMA][Sal]	3.9 (0.3)	40.3 (0.7)	31 (0.7)	–29 (1)		1.45 (0.05)		This work
Water	–17 (1)	–39	~0	—		0.96 (0.03)		7[b]
[THA][DHSS]	2.1 (0.3)	22(6)	22.5 (0.3)	–47 (2)		0.77 (0.06)		This work

[a] δ_{Cs}^{calc}, δ_{CsL}^{calc} and $\delta_{CsL_2}^{calc}$ denote the calculated chemical shifts of ^{133}Cs NMR in RTIL phase for Cs$^+$, CsL$^+$ and CsL$_2^+$, respectively. [b] log K_1 values for 25 °C, I = 0–0.1 mol dm^{-3}, IUPAC selection; [c] ΔH_2: –17.5 (0.3) ([EtHMIM][NTf$_2$]) and –17.8 (0.3) ([HMIM][NTf$_2$]) kJ mol^{-1}.

are higher than the stability constant of CsL in water (0.98). The log K_2 values for [EtHMIM][N(Tf)$_2$] and [HMIM][N(Tf)$_2$] appeared to be 2 to 3 log units lower than log K_1: 1.16 and 1.13, respectively (Table 1). These values correspond to those found for polar molecular solvents[7] and for [BMIM][N(Tf)$_2$] determined earlier.[8]

An increase in temperature decreases the stability constants of CsL for [HMIM][N(Tf)$_2$], [BMIM][N(Tf)$_2$] and [BMIM][PF$_6$], but increases them for [TOMA][Sal], [THA][DHSS]. The linear plots of ln K_1 and ln K_2 *versus* 1/T gave the possibility to estimate both ΔH_1 and ΔH_2 values (Table 1).

With the exception of [THA][DHSS] and [TOMA][Sal], the solubility of caesium nitrate 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.

Generally, the enthalpy change promotes complex formation in molecular solvents and hydrophilic RTILs, whereas the corresponding change of entropy is negative and provides the decomposition of [Cs(18C6)]$^+$.[7] 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 [BMIM][N(Tf)$_2$], [TOMA][Sal] and [THA][DHSS]. Only one hydrophobic RTIL ([BMIM][PF$_6$]) demonstrates the same behaviour as hydrophilic RTILs and polar molecular solvents.

Formation of crown ether complexes promotes caesium extraction into hydrophobic RTIL from water if the complex stability in RTIL is higher than in water (Table 2). Indeed, for [BMIM][N(Tf)$_2$], [HMIM][N(Tf)$_2$], [EtHMIM][N(Tf)$_2$], [BMIM][PF$_6$] and [TOMA][Sal] log K_1^{RTIL} > log K_1^{water} and caesium content in RTIL increases due to 18C6 administration. For [THA][DHSS] log K_1^{RTIL} < log K_1^{water} and crown ether decreases caesium content in RTIL. As far as we know, this is the first example of a negative contribution of a crown ether to the extraction process of an alkali cation. The log D_{Cs}^{18C6} values have the same order of magnitude for RTILs, 1,2-dichloroethane and other volatile organic diluents,[9] while the hazardous properties of the latter are much higher.

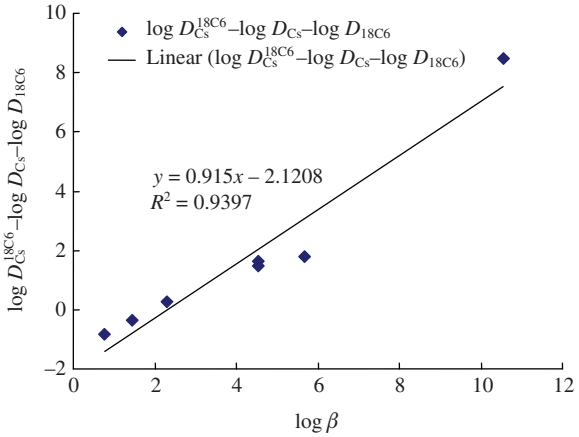


Figure 1 Plot of [log D_{Cs}^{18C6} – log D_{Cs} – log D_{18C6}] *vs.* log $\beta_{1,2}$ for [TOMA][Sal], [THA][DHSS], [BMIM][PF$_6$], [BMIM][N(Tf)$_2$], [HMIM][N(Tf)$_2$], [EtHMIM][N(Tf)$_2$] and 1,2-dichloroethane at 22–25 °C.

Note that the complex stability in RTIL increases as the RTIL ability to extract caesium without 18C6 (D_{Cs}) decreases. Meanwhile, there are no simple relationships between log K_1 (log $\beta_{1,2}$) and crown ether-assisted extraction efficiency (D_{Cs}^{18C6}), Table 2. 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 extraction (D_L) and D_{Cs} are taken into account, a perfect linear relationship between [log D_{Cs}^{18C6}–log D_{Cs}–log D_L] and log $\beta_{1,2}$, is observed (Figure 1).

This linearity has a certain background. When an aqueous phase of caesium nitrate is in equilibrium with a RTIL organic phase containing crown ether L, the distribution ratio (D_{Cs}^{18C6}) for RTILs such as [TOMA][Sal], [THA][DHSS] and [BMIM][PF$_6$], where only CsL species are formed, is represented by the equation

$$D_{Cs}^{18C6} = ([Cs]^{RTIL} + [CsL]^{RTIL})/([Cs]^{water} + [CsL]^{water}), \quad (1)$$

where the superscripts 'RTIL' and 'water' denote organic and aqueous phases, respectively. When the total concentration $[L]^{total} \gg [Cs]^{total}$ and the stabilities of complexes in both phases

Table 2 Stability constants of caesium complex formation with 18C6 in RTILs and extraction efficacy from water.[a]

Solvent	log $\beta_{1,2}$	log D_{Cs}	log D_{Cs}^{18C6}	log D_{18C6}	log [D_{Cs}^{18C6}/($D_{Cs}D_{18C6}$)]
[HMIM][NTf$_2$]	5.57	–1.24	0.82	0.25	1.81
[EtHMIM][NTf$_2$]	4.56	–0.81	0.56	–0.27	1.64
[BMIM][NTf$_2$]	4.69	–0.67	1.56	0.77	1.46
[BMIM][PF$_6$]	2.4	–0.59	–0.20	0.13	0.26
[TOMA][Sal]	1.45	0.69	0.83	0.49	–0.38
[THA][DHSS]	0.77	1.21	0.25	–0.12	–0.84
1,2-Dichloroethane	10.56[b]	–7.7[c]	0.8[d]	0.03[e]	6.93

[a] Extraction data for 22 °C, pH$_{water}$ 5–7; [Cs]$_0$ = 0.0015 mol dm^{-3}, [18C6]$_0$ = 0.15 mol dm^{-3} and phases volume ratio V_{water}/V_{RTIL} = 10; D_{Cs} = [Cs]$_{RTIL}$/[Cs]$_{water}$; D_{Cs}^{18C6} = [Cs]$_{RTIL}$/[Cs]$_{water}$ in the presence of 0.15 mol dm^{-3} 18C6 in RTIL; D_{18C6} = [18C6]$_{RTIL}$/[18C6]$_{water}$ in the presence of 0.0015 mol dm^{-3} Cs$^+$; $\beta_{1,2} = K_1$ if no CsL$_2$ complexes are formed, and $\beta_{1,2} = K_1K_2$ if CsL$_2$ complex exists in a particular RTIL; all $\beta_{1,2}$ values correspond to 25 °C; [b] Ref. 9. [c] Ref. 10, picrate salt. [d] Ref. 11, picrate salt. [e] Ref. 12.

are high ($\log K_1^{RTIL} \geq 1$; $\log K_1^{water} \geq 1$), then $[Cs]^{RTIL} \ll [CsL]^{RTIL}$ and $[Cs]^{water} \ll [CsL]^{water}$. In this case, the equilibrium concentrations of $[Cs]^{RTIL}$ and $[Cs]^{water}$ in equation (1) can be neglected. Equation (1) is transformed into:

$$D_{Cs}^{18C6} = [CsL]^{RTIL}/[CsL]^{water} \quad (2)$$

or

$$D_{Cs}^{18C6} = (K_1^{RTIL}[Cs]^{RTIL}[L]^{RTIL})/(K_1^{water}[Cs]^{water}[L]^{water}) \quad (3)$$

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

$$D_{Cs}^{18C6} = K_1^{RTIL} D_{Cs} D_L / K_1^{water} \quad (4)$$

or

$$\log D_{Cs}^{18C6} = \log K_1^{RTIL} + \log D_{Cs} + \log D_L - \log K_1^{water}. \quad (5)$$

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 of 1. Indeed, a plot of ($\log D_{Cs}^{18C6}$–$\log D_{Cs}$–$\log D_{18C6}^{Cs}$) *versus* $\log K_1^{RTIL}$ for [TOMA][Sal], [THA][DHSS] and [BMIM][PF_6] represents a perfectly strait line with a slope of 0.73 and $R^2 = 0.999$. For [BMIM][$N(Tf)_2$], [HMIM][$N(Tf)_2$], [EtHMIM][$N(Tf)_2$], equations (1)–(4) become more complicated due to formation of CsL_2 complexes and the lack of such complexes in water. For the molecular solvent 1,2-dichloroethane, equation (1) and its derivatives have to involve additionally the formation equilibrium for neutral complexes $CsL(NO_3)$ in both RTIL and aqueous phases. Nevertheless, the plot of ($\log D_{Cs}^{18C6}$–$\log D_{Cs}$–$\log D_L$) *versus* $\log K_1^{RTIL}$ for all six RTILs demonstrates a good linearity with a slope of 0.89 and the correlation coefficient $R^2 = 0.98$. Moreover, surprisingly all six solvents and 1,2-dichloroethane fit a linear relationship of ($\log D_{Cs}^{18C6}$–$\log D_{Cs}$–$\log D_L$) *versus* $\log \beta_{1,2}^{RTIL}$ with a slope of 0.92 and the correlation coefficient $R^2 = 0.94$ (Figure 1).

This indicates clearly the importance of complex stability contribution for hydrophobic RTILs in caesium extraction processes. At the same time, this trend is strongly modulated by a relative solubility of 18-crown-6 and alkali metal nitrate in water and in a RTIL phase.

The experiment was carried out as follows. The exact mass of solid caesium nitrate was mixed with the calculated mass of solid 18C6, and then 1 ml of RTIL was added. Within each series of 9 to 11 samples, the concentration of caesium was kept constant at a level of 0.005 mol dm^{-3}, whereas the concentration of the ligand varied as the ligand-to-metal molar ratio changed steadily from 0 to 10 or 20. The dissolution process was performed within 3 to 5 min at 110 °C because a sufficient reduction of solvent viscosity was found to occur in this time. The establishment of equilibrium controlled by periodic NMR measurements of some selected samples took 1 to 2 h.

^{133}Cs NMR spectra were recorded on a Bruker AVANCE II 300 spectrometer, operating at 39.38 MHz, in a 5 mm diameter sample tube with temperature steadily adjusted between 27 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 (v/v) mixture of aqueous solutions of NaCl and CsCl with D_2O (added for lock), which provided a 0.04 mol dm^{-3} concentration of each cation. Downfield shifts are denoted as positive.

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

$$Cs^+ + L \rightleftarrows [CsL]^+ \qquad K_1 = [CsL][Cs]^{-1}[L]^{-1} \quad (6)$$

$$CsL^+ + L \rightleftarrows [CsL_2]^+ \qquad K_2 = [CsL_2][CsL]^{-1}[L]^{-1} \quad (6a)$$

For [TOMA][Sal], [THA][DHSS], [BMIM][PF_6], only CsL was found at any Cs/L molar ratios. An experimentally observed δ_{obs} single time-averaged ^{133}Cs chemical shift of 'free' cation and a ligand-bonded cation can be given by the equation[8]

$$\delta_{obs} = (\delta_{Cs} + K_1[L]\delta_{CsL})/(1 + K_1[L]), \quad (7)$$

where $[L] = C_L - C_{Cs}X_{CsL}$, $X_{CsL} = (\delta_{obs} - \delta_{Cs})/(\delta_{CsL} - \delta_{Cs})$, 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 equation (7). The stability constant K_1 was calculated by the SigmaPlot non-linear curve-fitting program operating with 9 to 11 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 and experimental δ_{Cs} values have been obtained, providing additional fitting degree estimate.

For [BMIM][$N(Tf)_2$], [HMIM][$N(Tf)_2$] and [EtHMIM][$N(Tf)_2$] both CsL and CsL_2 complexes are formed. Thus, the two-step formation scheme was treated by the HypNMR and SigmaPlot software. 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 of 27 to 50 °C. Then, the values of ΔH_n ($n = 1, 2$) were calculated using a reaction isobar equation. The same isobar was used to calculate $\log K_1$ and $\log K_2$ for 25 °C.

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