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

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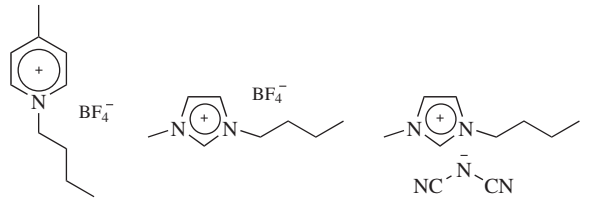
Thermodynamic data for the formation of cesium complexes with 18-crown-6 (18C6, L) $[Cs(18C6)]^+$ in *N*-butyl-4-methylpyridinium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium dicyanamide, measured using ^{133}Cs NMR spectroscopy at 23–50 °C, revealed that the stability of cesium complex in ionic liquids is affected by the nature of both cation and anion of room temperature ionic liquid and is in the range between the values found for water and DMF.

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, unusual extraction regularities and possibility to eliminate aqueous phase acidification.[1–4] It was demonstrated that extraction efficiency of RTIL can be modulated by chelating agent administration.[2,3] Unfortunately, almost nothing is known about the numerical values of complex formation constants in RTILs.[5,6] This work aims to diminish this gap by studying the complex formation of cesium ions by 18-crown-6 (L, 18C6) in three hydrophilic RTILs: *N*-butyl-4-methylpyridinium tetrafluoroborate ([BMPy][BF_4]) **1**, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) **2** and 1-butyl-3-methylimidazolium dicyanamide ([BMIM][$N(CN)_2$]) **3** using ^{133}Cs NMR spectroscopy with an emphasis on thermodynamic data. The experimental details and data treatment procedure are described elsewhere.[6]



1 **2** **3**

Only $[Cs(18C6)]^+$ complexes have been found in all three RTILs. ^{133}Cs chemical shifts demonstrated different features depending on particular RTIL (Table 1). It has been shown that δ_{CsL} depends on the anion of RTIL rather than on the cation. This can be expected reasonably, as the coordination 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.

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 **1**, **2** and **3** were evaluated to be 2.5, 2.8 and 2.94, respectively, and were found to be rather close to each other. 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 DMF and water.

An increase in the temperature leads to a decrease in the stability constants of CsL in all three RTILs. However, the degree of such a decrease is different. The thermodynamic quantities for the formation of $[Cs(18C6)]^+$ in RTIL are summarized in Table 1 together with those in molecular solvents.[7] It became evident that complex formation is more exothermic in RTILs than in water.

Generally, it can be seen that enthalpy change promotes complex formation in RTIL, whereas the corresponding change of entropy is negative and results in the decomposition of $[Cs(18C6)]^+$. However, the thermodynamic quantities indicate clearly that the contributions to the overall stability of CsL complex may differ 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 **2**. 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 in Table 1 obviously indicate that both cation

Table 1 Chemical shifts, stability constants and thermodynamic quantities ΔG_1, ΔH_1, ΔS_1 of cesium complex formation with 18-crown-6 at 25 °C.[a,b]

Solvent	δ_{Cs}(calc)/ppm	δ_{CsL}(calc)/ppm	log K_1	ΔG_1/kJ mol^{-1}	ΔH_1/kJ mol^{-1}	$T\Delta S_1$/kJ mol^{-1}	Ref.
Acetonitrile	24.1	14.8	4.8	–27.3	–17(1)	10.3	7, 8
Propylene carbonate	–36.5	–8.1	4.50	–25.7	–43.3	–17.6	7, 8
Acetone	–35.8	–6.4	4.51	–25.6	–52.8(0.4)	–27.2	7, 8
DMF	–0.8	3.37	3.64	–20.8	–49.2(0.8)	–28.4	7, 8
RTIL **3**	91(1)	34(1)	2.94 (0.05)	–16.9 (0.3)	–47 (2)	–30 (2)	This work
RTIL **2**	–68(4)	–22(4)	2.8 (0.2)	–16 (1)	–80 (3)	–64 (2)	This work
RTIL **1**	–70(7)	–17(5)	2.5 (0.2)	–14.8(0.8)	–47 (1)	–32 (1)	This work
Water	~0	—	0.96	–5	–17(1)	–12	7

[a]Thermodynamic data for molecular solvents are taken from ref. 7 and refer to 25 °C, I = 0–0.1 mol dm^{-3}, IUPAC selection, while the chemical shift data are taken from ref. 8. [b]All chemical shifts are given relative to $CsNO_3$ solution in water, downfield shifts are denoted as positive.

and anion of RTIL affect the complex formation stability and thermodynamic functions change.[†]

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.

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[†] ^{133}Cs NMR was recorded with a 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. 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 lock), which provided a 0.04 mol dm^{-3} concentration of each cation. Chemical shifts were measured with an accuracy of no less than 0.05 ppm. Downfield shifts are denoted as positive. Stability constant calculations have been performed operating with 10–12 points at each temperature.

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