

Stability of crown-ether complexes with alkali-metal ions in ionic liquid-water mixed solvents

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Abstract Stability constants of sodium and cesium ion complexes with 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) in N-butyl-4-methyl-pyridinium tetrafluoroborate [BMP][BF₄] aqueous solutions were measured using the ²³Na and ¹³³Cs NMR technique at 23 °C. To the best of our knowledge, the estimated values of stability constants reported in this study are the first such values given for ionic liquid solutions. The cationic exchange between the free and complexed species is rapid, and only formation of the 1:1 complexes [M(18C6)]⁺ and [M(DB18C6)]⁺ (M = Na⁺, Cs⁺) were observed. The complex formation constants demonstrated a strong dependence on the [BMP][BF₄] concentration. For [M(18C6)]⁺, in solutions with a 0.33–0.70 mole fraction

of water in [BMP][BF₄], lg *K* values are found to be more than one unit higher than the lg *K* values measured in pure aqueous solutions, although no information concerning the influence of [BMP][BF₄] on the complex formation selectivity could be observed. DB18C6 complexes revealed significantly lower stability under the same conditions. An extrapolation to zero water content gave the lg *K* = 2.42 for [Cs(18C6)]⁺ in [BMP][BF₄]. It was discovered that when added to water, [BMP][BF₄] increases the solubility of crown ethers and decreases the solubility of alkali metal nitrates. Complex formation with crown ethers enhances the solubility of alkali metal salts in [BMP][BF₄].

Keywords Ionic liquid · Crown-ether · Alkali metal ions · Stability constants · Complexes · ²³Na NMR, ¹³³Cs NMR

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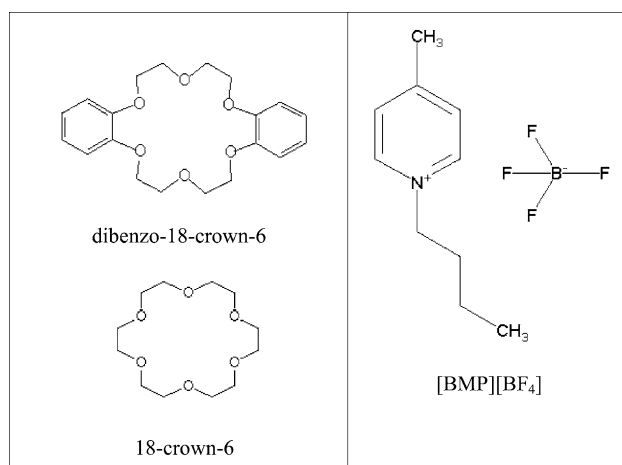
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Introduction

Room temperature ionic liquids (RTILs) are gaining wide recognition as successful solvents for a variety of reactions [1, 2] and separation processes [3–6]. Complex formation with either RTIL anions or with dissolved chelating agents is demonstrated to play an important role in cation extraction [4–7]. Meanwhile, almost nothing is known about the numerical values of complex formation constants in RTILs. A single publication [8] reports on a significant increase of stability in the case of Ag⁺ complexes with cryptand 222 in a series of RTILs relative to DMSO. The overall aim of this research is to study the complex formation of sodium and cesium ions with 18-crown-6 and dibenzo-18-crown-6 N-butyl-4-methyl-pyridinium tetrafluoroborate aqueous solutions using the ²³Na and ¹³³Cs NMR technique.



Experimental

Reagents

Sodium nitrate and cesium nitrate were used in the form that they were received from Merck and they were preliminary dried at 110 °C for one day. 18-crown-6 (Fluka) was dried at 35 °C for one day, while dibenzo-18-crown-6 (Parish Chemical) was dried at 110 °C for one day. The N-butyl-4-methyl-pyridinium tetrafluoroborate sample (Merck) was 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). The sample was thereafter used without any additional treatment. ¹H NMR revealed no water signals.

Sample preparation

N-butyl-4-methyl-pyridinium tetrafluoroborate is a water soluble RTIL. However, the solid alkali metal nitrates, chlorides and perchlorates with an ionic crystal structure appeared to be almost insoluble in [BMP][BF₄], while the solubility of both crown ethers studied was sufficient in order to provide for 0.2 mol·dm⁻³ solutions. Hence, the direct NMR measurement of stability constants in [BMP][BF₄] turned out to be impossible. Meanwhile, the water portions added to RTIL increased the inorganic salts solubility causing no observable decrease of crown ether solubility in the mixed solvent up to a 0.98 mole fraction of water. It can therefore be stated that [BMP][BF₄] increases the solubility of crown ethers in water for several orders of magnitude, and produces an opposite effect concerning alkali metal salts.

Series of aqueous solutions of alkali metal nitrates were prepared. For each sample, the total metal ion concentra-

tion was kept constant at 0.0025, 0.0050, and 0.0083 (Cs), or 0.0420 (Na) mol·dm⁻³ for the particular RTIL/water vol/vol ratio. Concurrently, the concentration of a ligand varied in such a way that the metal-to-ligand mole ratio changed steadily from 0 to 10–20 for Cs, and from 0 to 2–5 for Na. To attain the objective of 1 ml of liquid, RTIL was added to the exact mass of solid crown ether, after which it was equilibrated until the complete dissolution took place. Excluding the high [BMP][BF₄] viscosity for 18C6, the dissolution passed within half an hour at room temperature. That did not happen in the case of DB18C6, the crystals of which do not dissolve completely within 24 hours of storage in a glass bottle. Therefore, the dissolution process for DB18C6 was performed within 3–5 min at 110 °C due to the sufficient decrease of solvent viscosity. After the solutions were cooled, no crystallisation of DB18C6 could be observed.

Subsequently, an aqueous solution of alkali cation nitrate was added to the solution of crown ether in [BMP][BF₄]. The process of equilibrium establishment was controlled by periodic NMR measurement of some selected samples. Despite of a high viscosity of low water content samples, the complex formation equilibrium was established in approximately 60 min. Nevertheless, all samples measured were allowed to equilibrate in closed glass tubes at room temperature for a period of 24 h before the NMR measurement.

The pH measurements of the samples indicated that their high acidity varied from pH 0.9 at highest water content to below zero in case of the samples with 0.33 mol parts of water. The pure [BMP][BF₄] also revealed a pH < 0. Thus the solvent acidity adds at least one unit to the total ionic strength provided by RTIL basic ions. As in the systems studied there is no ligand protonation or formation of metal hydrolysed species, no impact of pH on crown ether complex formation equilibrium with alkali metals can take place. We have therefore confined ourselves by a qualitative pH control, operating pH-meter readings maintained with the METTLER Toledo 320 pH meter, calibrated by standard aqueous buffer solutions (FF-Chemicals Ltd., Haukipudas, Finland).

The water content in each sample was initially calculated using the [BMP][BF₄] density, after which samples were finally controlled with ¹H NMR by a comparison of water and [BMP][BF₄] NMR bands integral intensities. Thus all the values are presented as mole fraction of water.

NMR measurements

²³Na and ¹³³Cs NMR spectra were recorded on the Bruker DPX400 spectrometer, operating at 105.84 MHz and 52.48 MHz respectively, and using a 5 mm diameter sample tube at 23 °C (thermostated room). The external

standard placed in a 1 mm coaxial inner tube represented a 1:1 vol/vol mixture of an 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 ionisation time-of-flight mass spectrometry

The electrospray ionisation time-of-flight mass spectrometry (ESI-ToF MS) was used as a supporting method for a qualitative RTIL solution characterisation. Electrospray ionisation mass spectrometry has become a very powerful tool in investigating complexation mechanisms due to the low energy, which is introduced into the system. It is especially suitable for ionic liquids dominated by charged species. In this study ESI-ToF mass spectra have been recorded with a Micromass LCT mass spectrometer equipped with a Z-spray electrospray interface. The liquid sample with cesium and sodium aqueous solutions in RTIL with a tenfold excess of either 18C6 or DB18C6 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 ion mode was applied using the MassLynx NT software.

Data treatment, complex formation constants evaluation

The complex formation study by NMR and ESI-ToF MS revealed only ML complexes in all of the systems.

An equilibrium can therefore be described by a simple reaction:



The δ_{obs} single time-averaged ¹³³Cs or ²³Na chemical shift of a «free» cation and a ligand bonded cation, as observed experimentally, can be indicated by a simple equation:

$$\delta_{\text{obs}} = (\delta_M + K[L]\delta_{\text{ML}})/(1 + K[L]) \quad (2)$$

where

$$[L] = C_L - C_M X_{\text{ML}} \quad (3)$$

$$X_{\text{ML}} = (\delta_{\text{obs}} - \delta_M)/(\delta_{\text{ML}} - \delta_M) \quad (4)$$

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

The free-ligand concentration $[L]$ was found by an iteration method using equations (2), (3) and (4). The stability constant K was calculated by a non-linear curve-fitting programme SigmaPlot [9], operating with 9–11 experimental points for a curve. All iterations have been performed without fixation of either δ_{ML} or δ_M values, treating them equally just as in the case of any δ_{obs} experimental points. Therefore, in Tables 1 and 2, both calculated and experimental chemical shifts for δ_{ML} and δ_M

Table 1 Chemical shifts and lg K values of sodium and cesium complexes with 18C6 and DB18C6 for 0.7 mole fraction of water in [BMP][BF₄] mixed solvent at 23 °C

Cation	L	L/M	δ_M , ppm exp	δ_M , ppm calc	δ_{ML} , ppm exp	δ_{ML} , ppm calc	lg K
Cs ⁺ , 0.0083 mol/L	18C6 0–0.18 mol/L	0–20	-50.7	-52.3 (1.8)	-18.9	-16.2 (1.0)	2.20 (0.08)
Cs ⁺ , 0.0083 mol/L	DB18C6 0–0.1 mol/L	0–12	-51.9	-51.7 (0.2)	–	-38.8 (1.3)	1.10 (0.08)
Na ⁺ , 0.0420 mol/L	18C6 0–0.20 mol/L	0–4.8	-5.0	-4.8 (0.2)	-11.9	-12.3 (0.1)	2.18 (0.04)
Na ⁺ , 0.0420 mol/L	DB18C6 0–0.09 mol/L	0–2.1	-5.4	-5.5 (0.4)	–	-20.1 (2.5)	1.39 (0.15)

Table 2 Chemical shifts and lg K values of cesium complexes with 18C6 in water/[BMP][BF₄] mixed solvents at 23 °C

Water content, mole fraction	L	L/M	δ_M , ppm exp	δ_M , ppm calc	δ_{ML} , ppm exp	δ_{ML} , ppm calc	lg K	Ref.
1.00							0.96 (0.03)	[12]
0.96	0–0.03 mol/L	0–6.2	-25.2	-25.3 (0.1)	–	-7.0 (1.4)	1.48 (0.06)	Present work
0.70	0–0.18 mol/L	0–20	-50.7	-52.3 (1.8)	-18.9	-16.2 (1.0)	2.20 (0.08)	Present work
0.48	0–0.019 mol/L	0–15	-58.4	-58.5 (1.5)	-20.5	-15.8 (1.5)	2.33 (0.08)	Present work
0.33	0–0.08 mol/L	0–32	-62.2	-62.3 (1.4)	-21.7	-18.1 (1.2)	2.37 (0.08)	Present work
→ 0 *							2.4 (0.1)	Present work

* → 0 Indicates the value obtained by an extrapolation to the zero water content

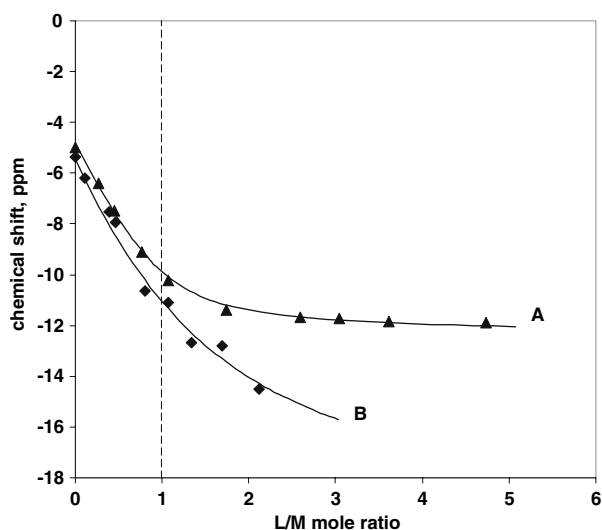


Fig. 1 The variation of ^{23}Na NMR chemical shift as a function of crown ether/ Na^+ mole ratio: (A) in Sodium 18C6 system; and (B) in Sodium DB18C6 system for solutions containing 0.7 mole fraction of water in $[\text{BMP}][\text{BF}_4]$. Solid line represents the least square fit using Eq. (2)

are given. This provides an additional verification of the quality of the fitting procedure. As can be seen in Figs. 1–2, the values used in this study are within the standard value range usually applied. The SD for the measured $\lg K$ values also meets the requirements for crown ether complexes with alkali cations [10]. The experimental results are presented in Tables 1 and 2, as well as in Figs. 1–3.

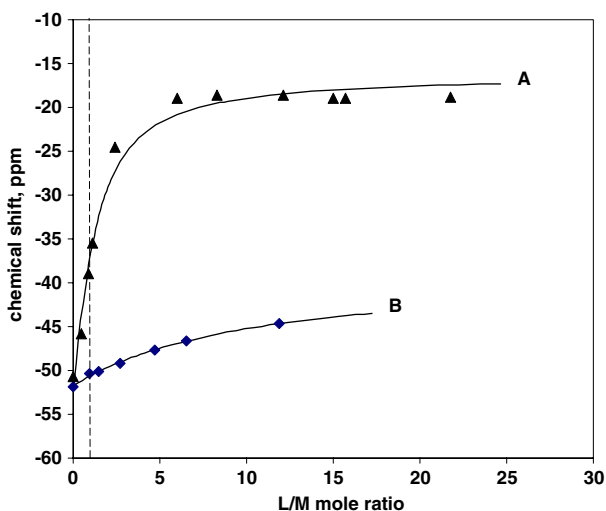


Fig. 2 The variation of ^{133}Cs NMR chemical shift as a function of crown ether/ Cs^+ mole ratio: (A) in Cesium-18C6 system; and (B) in Cesium-DB18C6 system for solutions containing 0.7 mole fraction of water in $[\text{BMP}][\text{BF}_4]$. Solid line represents the least square fit using Eq. (2)

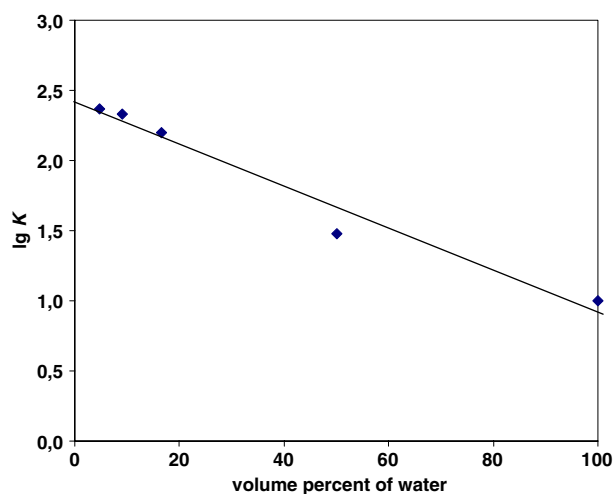


Fig. 3 A plot of $\lg K$ versus volume percent of water in Cesium 18-crown-6 system. Solid line represents the least square fit of linear function

Results and discussion

At room temperature, both ^{23}Na and ^{133}Cs resonances reveal a single time averaged signal, indicating the fast exchange of “free” and coordinated metal species even for highly viscous solutions. The negative chemical shifts for all solutions have been observed, Tables 1 and 2, being strongly dependent on both the total water and ligand concentrations.

However, the complex formation of cesium causes a chemical shift increase, while that of sodium demonstrates an opposite trend. For 18C6 complexes with cesium such a behaviour was observed in DMSO solutions [11] and for sodium in solvents such as propylenecarbonate, acetonitrile, tetrahydrofuran and nitromethane [12]. For both cations studied in all the systems, the change of chemical shift was monotonic, indicating the existence of only a single 1:1 ML complex, as well as the absence of ML_2 species. Otherwise, the change in chemical shift direction to an opposite one should be expected [12]. Qualitatively, this conclusion was supported by, ESI-ToF MS, which revealed ML species, but not the ML_2 . The ESI spectra showed that the most intense peak was typically at m/z 150, arising from BMP, and corresponding to the $[\text{BMP}][\text{BF}_4]$ content of the solution. The ML peak was detected at relatively high intensity in all compounds (1–30% of the highest peak): m/z 287 (Na, 18C6), m/z 383 (Na, DB18C6), m/z 397 (Cs, 18C6), and m/z 493 (Cs, DB18C6). In some of the spectra also the peak, at m/z 387, was intense. This was expected to arise possibly from $[\text{2-BMP}][\text{BF}_4]$. Our observations show $[\text{BMP}][\text{BF}_4]$ to be similar to such solvents as water, DMSO and DMF where, unlike acetone and pyridine, no formation of CsL_2 complex was found [11].

The formation of complexes concerning Na^+ with 18C6 and DB18C6 in [BMP][BF_4] solution broadened the ^{23}Na resonance from 34 to over 800 Hz, making the precise measurement of chemical shifts impossible. Thus the general accuracy of constants for sodium in this study is lower than that for cesium.

Generally, the fit of the experimental and calculated curves was good enough to provide a reasonable accuracy for stability constants (Figs. 1, 2).

The data, as presented in Table 1, permit a comparison of relatively complex stabilities for Cs^+ and Na^+ , as well as for 18C6 and DB18C6 for the constant water content: 0.70 mole fraction of water in [BMP][BF_4], which corresponds to a 5:1 vol/vol [BMP][BF_4]/water ratio, the ionic strength being around $4\text{--}5\text{ mol dm}^{-3}$. Evidently, the stabilities of 18C6 complexes with sodium and cesium are more than one order of a magnitude higher than those of DB18C6. Meanwhile, both crown ethers reveal no selectivity towards the cations studied. Within the experimental errors, the stability constants of cesium and sodium complexes with 18C6 are the same. The similar situation is observed when Cs^+ and Na^+ complexes of DB18C6 are compared. In this respect, [BMP][BF_4] unlike DMF and DMSO, demonstrates no selectivity enhancement in comparison with pure water, ethanol, acetone or acetonitrile [10].

However, the ionic liquid reveals a drastic increase of alkali metal stability for 18C6 relative to aqueous solutions (Table 1). We studied the variation of $\lg K$ for the samples with a different water content, for a cesium complex with 18C6 (Table 2). The stability of the complex increases evidently as the water content decreases. A similar behaviour was observed for $[\text{Cs}18\text{C6}]^+$ in methanol/water mixtures when the methanol content was increased [10]. A set of experimental $\lg K$ values with various water content combined with an IUPAC recommended value of 0.96 ± 0.2 (ionic strength $0\text{--}0.1\text{ mol dm}^{-3}$, $25\text{ }^\circ\text{C}$) [10], permitted a linear extrapolation to zero water content, through which an approximate value for $[\text{Cs}18\text{C6}]^+$ in [BMP][BF_4] ($\rightarrow 0$): $\lg K = 2.4 \pm 0.1$, could be obtained (Fig. 3 and Table 2). The estimation found by us seems to be reasonable: the stability constant of $[\text{Cs}18\text{C6}]^+$ in [BMP][BF_4] appears to be between the IUPAC recommended values for this complex dissolved in water ($\lg K = 0.96$ [10]), as well as in DMSO ($\lg K = 3.04$ [10]). To the best of our knowledge, the stability constants found are one of the first measured for RTILs and RTIL/water mixed solvents.

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