

Crown Ethers Assisted Cesium Extraction from Aqueous Solutions into a Hydrophobic Room Temperature Ionic Liquid 1-Butyl-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]imide

Andrey G. Vendilo, Vyacheslav I. Chistov, Julia M. Dikareva, and Konstantin I. Popov[@]

RJSC R&D Fine Chemicals Centre, 107564 Moscow, Russia
[@]Corresponding author E-mail: ki-popov49@yandex.ru

Crown ethers (L) assisted extraction of Cs^I from aqueous neutral solutions (pH 5-6) into a hydrophobic ionic liquid 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide was studied at 22 °C operating with: 12-crown-4 (12C4), 15-crown-5 (15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7) and dibenzo-24-crown-8 (DB24C8). The distribution coefficients ($\log D_{Cs}^L$) are found to increase from 0.30 to 1.7 as the size of L is changing from 15C5 to DB21C7. A further increase of L size (DB24C8) leads to a sufficient decrease of $\log D_{Cs}^L$ up to 0.9. The maximal $\log D_{Cs}^L$ value corresponds to the better cation-crown ether fitting. Well expressed correlation between $\log D_{Cs}^L$ values and stability constants of CsL in ionic liquid ($\log K_{CsL}$) is obtained and is interpreted for the crown ether series.

Keywords: Cesium, extraction, crown ethers, room temperature ionic liquids.

Экстракция ионов цезия в присутствии краун-эфиров из нейтральных водных растворов в гидрофобную ионную жидкость бис[(трифторметил)сульфонил]имид 1-бутил-3-метилимидазолия

А. Г. Вендило, В. И. Чистов, Ю. М. Дикарева, К. И. Попов[@]

ПАО Научный центр «Малотоннажная химия», 107564 Москва, Россия
[@]E-mail: ki-popov49@yandex.ru

Изучена экстракция Cs^I из нейтральных водных растворов (pH 5-6) в гидрофобную ионную жидкость бис[(трифторметил)сульфонил]имид 1-бутил-3-метилимидазолия ([BMIM][N(Tf)₂]) в присутствии серии краун-эфиров (L): 12-краун-4 (12C4), 15-краун-5 (15C5), 18-краун-6 (18C6), дибензо-18-краун-6 (DB18C6), дибензо-21-краун-7 (DB21C7) и дибензо-24-краун-8 (DB24C8) при 22 °C. Показано, что коэффициенты распределения ($\log D_{Cs}^L$) монотонно возрастают при переходе от 15C5 к DB21C7 от 0.30 до 1.7, а затем снижаются до 0.9 (DB24C8). Максимальное значение $\log D_{Cs}^L$ наблюдается для краун-эфира с наилучшим соответствием размера полости ионному радиусу катиона. Для исследованных краун-эфиров выявлена и объяснена линейная корреляция между $\log D_{Cs}^L$ и константами устойчивости комплексных соединений CsL в ионной жидкости ($\log K_{CsL}$).

Ключевые слова: Цезий, экстракция, краун-эфиры, ионная жидкость.

Introduction

Hydrophobic crown ethers are widely used for a selective extraction of cations from aqueous solution into organic phase.^[1-5] Recently the hydrophobic room temperature liquids (RTILs) are intensively studied as an alternative to the volatile and flammable conventional organic solvents.^[6-11] An increasing interest is observed towards extraction of radionuclides,^[9,11] lanthanides,^[12] copper,^[13] lithium,^[14] and other metals. Intensive studies in this field were initiated since an outstanding dicyclohexyl-18-crown-6 assisted removal of strontium from aqueous solution into triflimide-based RTIL has been reported. The corresponding distribution coefficient $D_{Sr}^L = 1.1 \cdot 10^{4[6]}$ was incomparably higher than that for toluene (0.76) and chloroform (0.77).^[9]

Our previous studies of cesium extraction into six hydrophobic RTILs in presence of 18-crown-6 (18C6, L) and dibenzo18-crown-6 (DB18C6, L) run in the wide pH range, reveal a rather complicated correlation between the stability constant of CsL complexes in RTIL ($\log K_{CsL}$) and cesium distribution coefficient ($\log D_{Cs}^L$).^[15,16] In present paper an extraction of Cs^I from neutral aqueous solutions into 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulphonylimide ([BMIM][N(Tf)₂]) (Figure 1) at 22 °C for a series of crown ethers with monotonously increasing cavity size, and known $\log K_{CsL}$ value is considered: 12-crown-4 (12C4, L), 15-crown-5 (15C5), 18C6, DB18C6, dibenzo-21-crown-7 (DB21C7, L) and dibenzo-24-crown-8 (DB24C8, L).

Experimental

1-Butyl-3-methylimidazolium bis(trifluoromethyl)sulphonylimide (Sigma-Aldrich) was used without additional treatment. Reagent grade crown ethers 12C4, 15C5, 18C6, DB18C6, DB21C7, and DB24C8 have been also supplied by Sigma-Aldrich, while CsNO₃ sample was purchased from Merck.

Cesium distribution coefficients D_{Cs}^L have been measured after 2 hours shaking of 10 ml of 0.001 M CsNO₃ neutral aqueous solution,

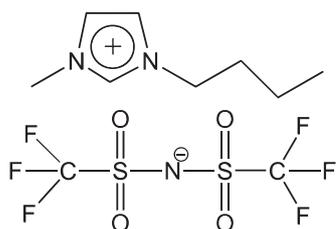


Figure 1. Chemical formula of [BMIM][N(Tf)₂].

and 1 ml of 0.1 M crown ether solution in RTIL at 22 °C. After organic and aqueous phases separation the residual concentration of cesium in an aqueous phase was measured operating ICP iCAP 6000 instrument (model iCAP 6300 Duo).

An extraction degree (R_{Cs}^L , %) and the distribution coefficient (D_{Cs}^L) have been calculated according to equations (1) and (2):

$$R_{Cs}^L, \% = \left(1 - \frac{C_w(Cs)}{C_0(Cs)} \right) \times 100\%, \quad (1)$$

$$D_{Cs}^L = \frac{C_o(Cs)}{C_w(Cs)} = \frac{V_w}{V_o} \cdot \frac{R_{Cs}^L \%}{100 - R_{Cs}^L \%}, \quad (2)$$

where $C_o(Cs)$ and $C_w(Cs)$ indicate the initial and equilibrium cesium concentrations in aqueous phase, while V_w and V_o correspond to the total volumes (ml) of aqueous and organic phases respectively. The standard errors of R_{Cs}^L and D_{Cs}^L measurement are estimated to be within 10 %.

The results are presented in Table 1 and Figures 2, 3. Where it is possible the extraction data are referred to the stability constants of cesium with crown ethers in aqueous ($\log K_{ML}^w$) and in RTIL phase ($\log K_{ML}^{RTIL}$).^[17-20] The priority was given to the IUPAC critically evaluated values.^[17]

Results and Discussion

When L is not present in [BMIM][N(Tf)₂], then cesium is poorly extracted. The corresponding $\log D_{Cs}$ value constitutes -0.67.^[16] An administration of L into a RTIL phase enhances cesium accumulation (Table 1). For 18C6 and DB18C6 the $\log D_{Cs}^L$ values agree well with those found by us earlier:^[16] 1.56 and 2.06 respectively. The higher values reported in^[16] in comparison with present data are due to the higher L/Cs mole ratio ($C(18C6)_0 = 1.5 \cdot 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$, $C(Cs^+)_0 = 5 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) relative to the present study. An increase of L/Cs leads to a higher $\log D_{Cs}^L$ values. It should be noted that relative to 1,2-dichloroethane (1,2DCE) in presence of 18C6 ($\log D_{Cs}$ 0.8)^[5] the RTIL medium appears to be much preferable ($\log D_{Cs}$ 1.3). The similar effect was also observed for dicyclohexane-18-crown-6 assisted cesium extraction into [BMIM][N(Tf)₂] and 1,2DCE: D_{Cs}^L for RTIL constituted 80, while for 1,2DCE 0.080.^[9] Actually the differences between [BMIM][N(Tf)₂] and 1,2DCE are even more drastic as far as L concentration was smaller for RTIL (0.01 mol·dm⁻³) than for 1,2DCE (0.43 mol·dm⁻³).^[9]

In our case within the set of crowns 12C4, 15C5, 18C6, DB18C6, DB21C7 and DB24C8 the D_{Cs}^L are changing in a non monotonous way as the cavity size^[22,23] is increasing, indicating a maximal value for DB21C7 (Table 1, Figure 2).

Table 1. The D_{Cs}^L values for a crown ether assisted cesium extraction from aqueous solution into [BMIM][N(Tf)₂] at 22 °C.

L	R_{Cs}^L , %	D_{Cs}^L	$\log D_{Cs}^L$	$\log K_{CsL}^{RTIL}$	$\log K_{CsL}^w$	Crown cavity size R_L , nm ^[22,23]
12C4	Extraction is not detected			1.42 ^[19]	No data	0.06
15C5	17	2.0	0.30	1.75 ^[19]	0.80 ^[17]	0.086-0.092
18C6	50	19	1.3	3.40 ^[19]	0.96 ^[17]	0.134-0.143
DB18C6	26	14	1.3	3.47 ^[20]	0.74 ^[21]	0.134-0.143
DB21C7	82	47	1.7	3.52 ^[20]	No data	0.17
DB24C8	46	8.6	0.9	2.91 ^[20]	1.41 ^[21]	0.20

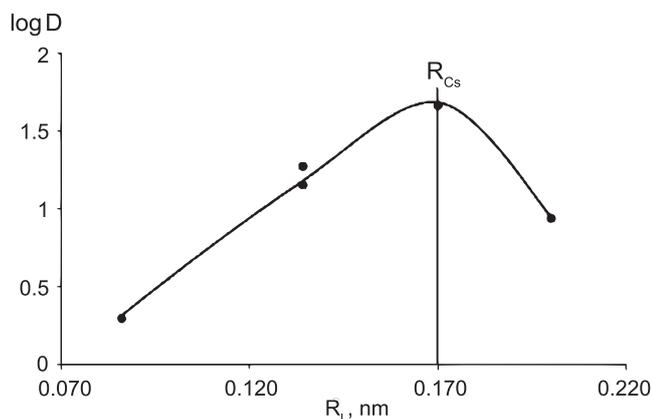


Figure 2. $\log D_{\text{Cs}}^{\text{L}}$ ($\log D$) dependence on the crown cavity size R_{L} for 15C5, 18C6, DB18C6, DB21C7 and DB24C8.

Indeed, for 12C4, 15C5, 18C6 and DB18C6 the cavity size is smaller than cesium ion diameter (0.17 nm^[22]), while for DB24C8 it is remarkably bigger. According to the crystallographic data and the structural data for the aqueous phase^[24,25] the cesium cation in its complexes with 18C6 is placed slightly above the plane, constituted by the oxygen atoms of the ligand, being a bit bigger than the cave size. The best cation-cave fitting should take place for DB21C7. Then a change of DB21C7 for DB24C8 should lead to some decrease of CsL thermodynamic stability ($\log K_{\text{CsL}}^{\text{RTIL}}$), and therefore, to a corresponding decrease in the extraction efficiency.

As could be seen from the Table 1, the $\log K_{\text{CsL}}^{\text{RTIL}}$ values are sufficiently higher than those for the aqueous phase ($\log K_{\text{CsL}}^{\text{w}}$). At the same time both $\log K_{\text{CsL}}^{\text{RTIL}}$ and $\log D_{\text{Cs}}^{\text{L}}$ values change in a similar way as the crown cavity size is increasing. In turn it gives a linear correlation between $\log D_{\text{Cs}}^{\text{L}}$ and $\log K_{\text{CsL}}^{\text{RTIL}}$ (Figure 3) with the slope ~ 1.4 and $R^2 = 0.88$.

A linear correlation between ($\log D_{\text{Cs}}^{\text{L}} - \log D_{\text{Cs}} - \log D_{\text{L}}$) and $\log K_{\text{CsL}}^{\text{RTIL}}$ has been observed by us earlier for $[\text{Cs}(\text{18C6})]^+$ and $[\text{Cs}(\text{DB18C6})]^+$ complexes in six hydrophobic RTILs,^[15,20] where $\log D_{\text{Cs}}$ corresponds to a cesium distribution without crown ether, while $\log D_{\text{L}}$ – to the distribution of L between aqueous and RTIL phases. Meanwhile, a direct correlation between $\log D_{\text{Cs}}^{\text{L}}$ and $\log K_{\text{CsL}}^{\text{RTIL}}$ was not detected for these systems.

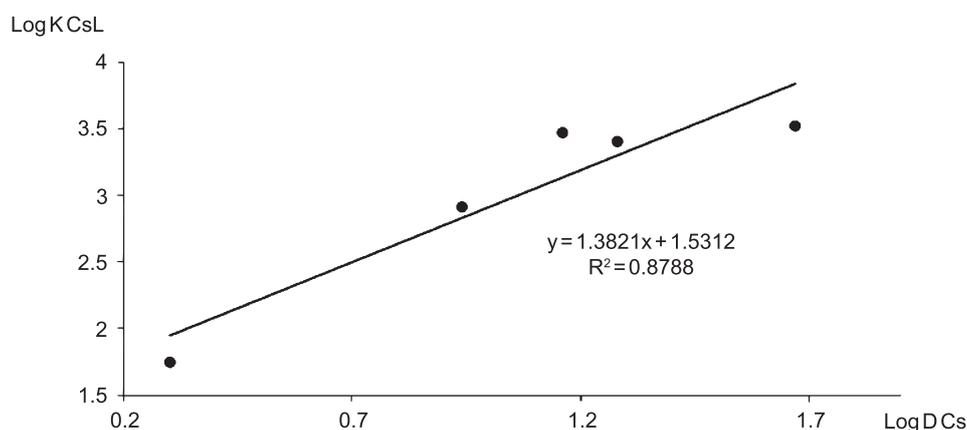
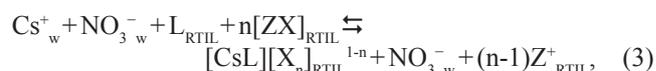


Figure 3. A correlation between $\log D_{\text{Cs}}^{\text{L}}$ and $\log K_{\text{CsL}}^{\text{RTIL}}$ values for 15C5, 18C6, DB18C6, DB21C7 and DB24C8 at 22-25 °C.

Such a correlation indicates a dominating role of complex formation in a RTIL phase in the crown ether assisted extraction processes. For cesium transfer from neutral aqueous solution into RTIL phase an ion exchange mechanism prevails^[29] (3):



where indexes “RTIL” and “w” denote organic and aqueous phase respectively, while Z^+ and X^- correspond to the RTIL’s cation and anion, and L indicates a crown ether molecule.

Neglecting a small contribution of $[\text{Cs}(\text{18C6})_2]^+$ and $[\text{Cs}(\text{DB18C6})_2]^+$ species in $[\text{BMIM}][\text{N}(\text{Tf})_2]$ to the total thermodynamic stability, one can express the distribution coefficient of cesium between aqueous and $[\text{BMIM}][\text{N}(\text{Tf})_2]$ phases in presence of crown ethers D_{Cs}^{L} by a rather simple equation (4):

$$D_{\text{Cs}}^{\text{L}} = ([\text{Cs}]^{\text{RTIL}} + [\text{CsL}]^{\text{RTIL}}) / ([\text{Cs}]^{\text{w}} + [\text{CsL}]^{\text{w}}) \quad (4)$$

As far as the total concentration of L $[\text{L}]^{\circ} \gg [\text{Cs}]^{\circ}$ (total cesium concentration); the stability constants of CsL complexes in a RTIL phase are high enough ($\log K_{\text{CsL}}^{\text{RTIL}} \geq 2$), and $[\text{L}]^{\text{RTIL}} \gg [\text{Cs}]^{\text{RTIL}}$, then $[\text{Cs}]^{\text{RTIL}} \ll [\text{CsL}]^{\text{RTIL}}$ and equilibrium concentrations $[\text{Cs}]^{\text{RTIL}}$ could be neglected. At the same time for an aqueous phase the $\log K_{\text{CsL}}^{\text{w}}$ are comparatively small, and $[\text{CsL}]^{\text{w}} \ll [\text{Cs}]^{\text{w}}$. Thus, $[\text{CsL}]^{\text{w}}$ values can be neglected. Therefore (4) can be transmitted into (5):

$$D_{\text{Cs}}^{\text{L}} = [\text{CsL}]^{\text{RTIL}} / [\text{Cs}]^{\text{w}} \quad (5)$$

or

$$D_{\text{Cs}}^{\text{L}} = (K_{\text{CsL}}^{\text{RTIL}} [\text{Cs}]^{\text{RTIL}} [\text{L}]^{\text{RTIL}}) / [\text{Cs}]^{\text{w}} \quad (6)$$

Taking into account that $[\text{Cs}]^{\text{RTIL}} / [\text{Cs}]^{\text{w}} = D_{\text{Cs}}$ the following expression is valid:

$$D_{\text{Cs}}^{\text{L}} = K_{\text{CsL}}^{\text{RTIL}} D_{\text{Cs}} [\text{L}]^{\text{RTIL}} \quad (7)$$

or

$$\log D_{\text{Cs}}^{\text{L}} = \log K_{\text{CsL}}^{\text{RTIL}} + \log D_{\text{Cs}} + \log ([\text{L}]^{\text{RTIL}}) \quad (8)$$

In contrast to the reports,^[15,20] in our case we have a single RTIL. Therefore $\log D_{Cs}$ is a constant for all the L series. At the same time $[L]^o \gg [Cs]^o$, and most of crowns used are poorly soluble in water, then an equilibrium concentration $[L]^{RTIL}$ should not change significantly for different crowns and would be close to $[L]^o$.

Therefore, a dependence of $\log D_{Cs}^L$ on $\log K_{CsL}^{RTIL}$ should be linear with the slope 1. Some deviation from this slope, presented in Figure 3 is probably due to some change of crowns solubility in an aqueous phase relative to each other. This relative solubility should also correlate with CsL complex stability: the less water soluble crowns form more stable complexes CsL in a RTIL phase. This statement is valid only for hydrophobic crowns. For example, 12C4 is water soluble. Then it reveals no extraction enhancement although the corresponding $[Cs(12C4)]^+$ complex is rather stable in the $[BMIM][N(Tf)_2]$ phase.

Conclusions

The thermodynamic stability of complexes in RTIL is of key importance for cesium extraction from aqueous phase into RTIL. The $\log D_{Cs}^L$ values increase steadily from 0.30 to 1.7 when 15C5 is changed for 18C6, DB18C6 and DB21C7, but then they decrease up to 0.94 (DB24C8). The maximal value for $\log D_{Cs}^L$ is observed for DB21C7 with the best fitting cesium ion radius and cavity size. For a set of crowns 12C4, 15C5, 18C6, DB18C6, DB21C7, and DB24C8 in $[BMIM][N(Tf)_2]$ a linear relationship between $\log D_{Cs}^L$ and $\log K_{CsL}$ is found and is interpreted.

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