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Effect of macrocycle stereoisomerism on extraction of Li$^+$ cations from chloride media by solutions of dicyclohexano-14-crown-4 in 1,1,7-trihydrododecafluoroheptanol

Olga A. Zakurdaeva,*[a] Andrey F. Asachenko,[b] Maxim A. Topchiy[b] and Sergey V. Nesterov[a]

[a] *N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation. E-mail: olzak@mail.ru*
[b] *A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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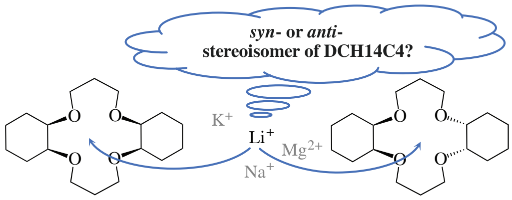
The new extractant based on dicyclohexano-14-crown-4 solution in 1,1,7-trihydrododecafluoroheptanol is proposed for the removal of lithium cations from the chloride media, such as reservoir waters. The stereoisomerism of the macrocyclic ligand is revealed to be a key factor determining the efficiency and selectivity of this system.



Selective solvent extraction of Li$^+$ from associated water of gas and oil production

Keywords: dicyclohexano-14-crown-4, 1,1,7-trihydrododecafluoroheptanol, stereoisomerism, lithium extraction, selectivity.

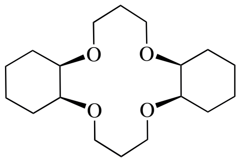
The lithium shortage predicted in the coming years is caused, among other things, by replacing internal combustion engines in personal and passenger vehicles with electric ones. This promotes the development of new technologies, which are an alternative to pyrometallurgical reprocessing of spodumene ores or basin evaporation from the concentrated brines of salt lakes.[1] In particular, the removal of lithium salts from highly mineralized lithium underground brines, reservoir and associated waters of oil and gas recovery by liquid–liquid extraction is considered very promising.[2,3] The relatively low content of Li$^+$ (0.01–3.0 g dm^{-3}) against the background of high concentrations of Na$^+$ (1–150 g dm^{-3}), K$^+$ (3–28 g dm^{-3}) and Ca^{2+} (0.3–74 g dm^{-3})[4,5] cations is challenging for efficient and selective separation of lithium from these brines. In this regard, compositions based on 14-membered aliphatic crown ethers (CEs) are presumed to be some of the best extractants.[6] It was previously shown that solutions of these ligands were able to remove lithium salts from model aqueous phases much better than their benzo-substituted analogues and 15-membered crown ethers.[6,7] For instance, dicyclohexano-14-crown-4 (DCH14C4) **1** turned out to be very efficient. A characteristic feature of this compound, which is a key to the successful design of a selective extractant, is the stereoisomerism of the macrocyclic molecule. Specifically, according to Sachleben and Moyer,[6] solutions of the *cis-syn-cis*-isomer of DCH14C4 **1a** in 1-octanol are characterized by both better extraction ability with respect to lithium chloride (30-fold excess) and higher selectivity of Li$^+$/Na$^+$ and Li$^+$/K$^+$ (3-fold excess) compared to those of the *cis-anti-cis*-isomer **1b**.

Generally, the effect of macrocycle stereoisomerism on complexing ability toward metal cation is pronounced in dicyclohexano-substituted CEs such as DCH14C4 and dicyclohexano-18-crown-6 (DCH18C6), a homologue with a higher molecular weight widely used in separation science. This feature previously described in ‘classical’ works on macrocyclic chemistry[8] and chemistry of extraction systems based on these CEs[9] implies the need for careful characterization of the stereoisomeric composition to obtain reproducible results in metal extraction tests. Nevertheless, the stereoisomerism of the molecules, as a rule, is ignored in modern studies on the extractability of DCH14C4.[3,10]

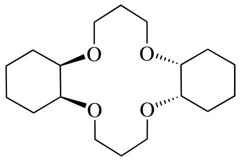
Despite the outstanding cation-binding characteristics of the DCH14C4 solutions in 1-octanol,[6] their use for the industrial design of lithium-selective extraction process is problematic. The dicyclohexano-substituted CEs are measurably soluble in water,[11] and their transfer from the organic phase to the aqueous one occurs in extraction processes.[12] Recently, as exemplified with DCH18C6, we have shown a successful route to overcome this disadvantage by replacing the ‘traditional’ solvents such as aliphatic alcohols and chloroform with 1,1,7-trihydrododecafluoroheptanol $C_7H_3F_{12}OH$.[13]

In this work, we synthesized DCH14C4 using the Pedersen’s method[8] and isolated its individual stereoisomers **1a** and **1b** in accordance with the Buchanan procedure,[14] estimated the resistance of the macrocyclic ligand dissolved in $C_7H_3F_{12}OH$ to transfer from organic to aqueous phase and studied the efficiency and selectivity of Li$^+$ extraction from aqueous LiCl solutions, including those containing potassium chloride. The last is one of the main interfering components commonly present in natural lithium brines.

The new extraction systems based on **1a** and **1b** dissolved in $C_7H_3F_{12}OH$ proved to be extremely resistant to the leaching of the macrocycle into the aqueous phase. Thus, the distribution



1a



1b

coefficient (K_d) of **1a** between its solution in $C_7H_3F_{12}OH$ and aqueous LiCl solution was ~2×10^5. This value is orders of magnitude higher than the known K_d obtained for other systems based on dicyclohexano-substituted CEs.[11,12,15] In other words, the fluorinated alcohol suppresses the transfer of the macrocyclic ligand to the aqueous phase.

To estimate the efficiency of lithium extraction from single-component (LiCl) and two-component (LiCl + KCl) aqueous solutions, the equilibrium concentration of Li^+ in the organic phase ($[Li^+_{org}]^{eq}$) was measured and distribution ratios (D_{Li}) were calculated:

$$D_{Li} = [Li^+_{org}]^{eq}/[Li^+_{aq}]^{eq},$$

wherein $[Li^+_{aq}]^{eq}$ is the equilibrium concentration of Li^+ in the aqueous phase.

In parallel, the extractability of the system with respect to K^+ cations was analyzed. To determine the selectivity of extraction (Li^+/K^+) from two-component solutions, the parameter $\alpha_{Li/K} = D_{Li}/D_K$ was used.

We found that the extraction ability of the crown-free fluorinated alcohol with respect to Li^+ and K^+ was minimal (Table 1). Consequently, the solvent did not hinder selective binding of the lithium cations by the macrocycle. Further, the stereoisomers **1a** and **1b** extracted Li^+ efficiently from both single-component and two-component aqueous chloride solutions (Table 1, Figure 1). For both stereoisomers, a macrocycle conversion (based on $[Li^+]$ in organic phase) was more than 90%, when Li^+ was extracted from 3 M LiCl solutions (see Online Supplementary Materials, Table S1). From this point of view, $C_7H_3F_{12}OH$ is competitive, if not superior, to 1-octanol.[6] More intriguingly, **1b** dissolved in fluorinated alcohol proved to be much more selective to Li^+ than **1a**, since its D_K was almost two orders of magnitude lower than that of **1a** (see Table 1, Figure 1 and Online Supplementary Materials, Figures S1 and S2). For example, at the extraction from a two-component solution containing 0.1 M LiCl and 3 M KCl, the $\alpha_{Li/K}$ coefficients obtained for **1a** and **1b** significantly exceeded those of other macrocyclic extractants[3,6] and attained the values of 440 ± 40 and 740 ± 70, respectively. Basically, this is not typical for *cis-anti-cis*-isomers of 14- and 18-membered dicyclohexano-substituted macrocycles. It is accepted that they have lower extraction ability and selectivity compared to *cis-syn-cis*-isomeres.[6,16]

Table 1 Distribution ratios of Li^+ and K^+ during the extraction from single-component solutions.

Organic phase	D_{Li}	D_K
1a/$C_7H_3F_{12}OH^a$	0.2	5×10^{-2}
1b/$C_7H_3F_{12}OH^a$	0.1	7×10^{-4}
$C_7H_3F_{12}OH^b$	$<3.5\times10^{-4}$	8×10^{-4}

[a] $[M^+_{aq}]^{init} = 0.5$ M ($M^+ = Li^+$ or K^+) and $[DCH14C4_{org}]^{init} = 0.1$ M in the initial aqueous and organic phases, respectively. [b] $[M^+_{aq}]^{init} = 1$ M, ligand-free solvent; the volume ratio of aqueous phase to organic solution (a/o ratio) in all extraction tests was 1 : 1.

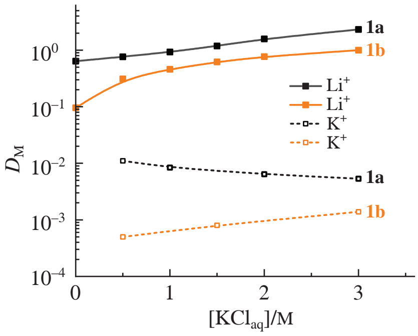


Figure 1 The distribution of Li^+ and K^+ between two-component aqueous phase containing LiCl ($[Li^+_{aq}]^{init} = 0.1$ M) and KCl ($[K^+_{aq}]^{init} = 0$–3 M) and the solutions of **1a** (*cis-syn-cis*-DCH14C4) and **1b** (*cis-anti-cis*-DCH14C4) in $C_7H_3F_{12}OH$ ($[DCH14C4_{org}]^{init} = 0.1$ M). Volume a/o ratio was 1 : 1.

Two general conclusions follow from these results. First, the stereoisomerism of the macrocycle is one of the key parameters that can specify the efficiency and selectivity of the extractant. Second, the combination of functional characteristics of DCH14C4, especially isomer **1b**, dissolved in $C_7H_3F_{12}OH$ creates background for the development of a promising extraction process for the selective removal of lithium chloride from multicomponent highly mineralized solutions such as reservoir waters.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7622.

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