Russian Chemical Bulletin, International Edition, Vol. 64, No. 4, pp. 905—908, April, 2015

4-*tert*-Butylcalix[4]arenes containing azacrown ether substituents at the narrow rim as membrane carriers

E. A. Ivanova,[a] P. E. Prokhorova,[a] Yu. Yu. Morzherin,[a★] A. P. Lukyanenko,[a,b] E. A. Alekseeva,[b] and S. S. Basok[b]

[a]*Ural Federal University,*
19 ul. Mira, 620002 Ekaterinburg, Russian Federation.
E-mail: yu.yu.morzherin@urfu.ru
[b]*A. V. Bogatskii Physicochemical Institute of the National Academy of Sciences of the Ukraine,*
86 ul. Lyustdorfskaya doroga, 65080 Odessa, Ukraine.
Fax: +38 (048) 765 9602

Calixarenes substituted at the narrow rim with one or four *N*-methoxycarbonylmonoaza-12-crown-4 moieties were used in liquid membranes to transport transition metal chlorides.

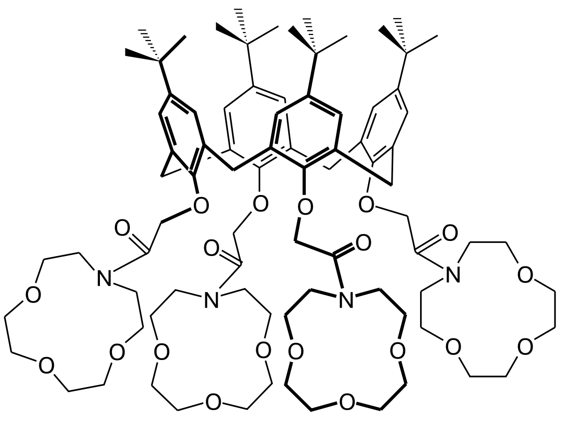
Key words: calixarenes, liquid membranes, metal ion transport.

Together with crown ethers,[1,2] cryptands,[2,3] and cyclodextrines,[4,5] calixarenes[6—8] are a large class of supramolecular hosts, which can recognize cations,[9—11] anions,[12—14] and neutral molecules,[15] as well as are used for the energetic transport.[16]

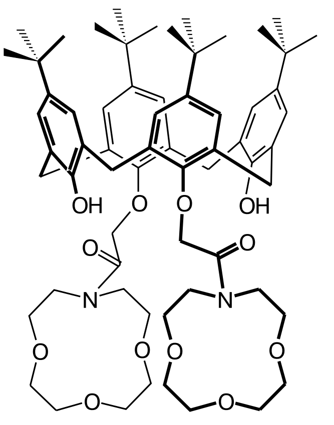
The transport of molecules or ions which uses liquid membranes is very promising as an approach to the selective separation, since in liquid membranes, in contrast to the solid, one can use carrier molecules, that considerably increases selectivity of the membranes. In particular, liquid membranes were used to extract heavy metals from industrial waste water.[17—19]

The selectivity can be significantly increased by the introduction in the liquid membrane of carrier molecules having an affinity to any component in the source phase. The carrier accelerates the transport of this specific component.[20] Usually, crown ether derivatives are used as carrier molecules. Calixarenes are also promising substrates for the use in liquid membranes.[21] We believe that the introduction of several aza-12-crown-4 moieties into a preorganized structure of calix[4]arene in the cone conformation will make it possible to design a selective receptor for transition metal ions. Since the calixarene core is a relatively rigid framework, and crown ethers are attached to it by a short linker, one should expect that the sandwich or pseudosandwich type of complexes will be formed with the metal cations with large ionic radius.

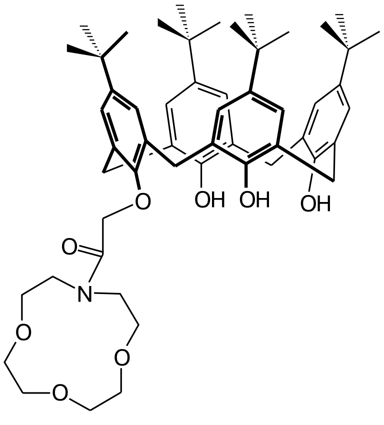
The purpose of the present work is to study the transport of transition metal cations through a liquid membrane, using calixarene derivatives **1**—**3** modified at the narrow rim with one, two, or four carbonylazacrown ether moieties as carrier molecules. Calixarene crown ethers **1** and **3** were obtained similarly to calixarene **2** (see Ref. 22 and 23) by the alkaline hydrolysis from tetra and mono esters of calix[4]arene derivatives **4** and **5** with subsequent



1



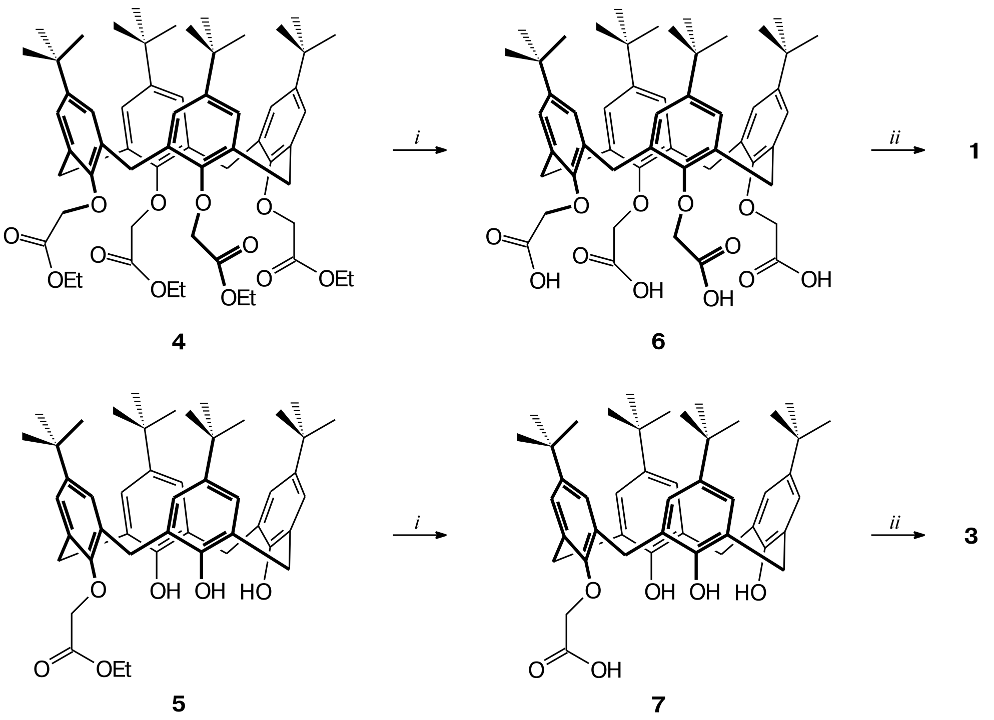
2



3

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 0905—0908, April, 2015.

Scheme 1



Reagents: *i*. 1) NaOH, 2) HCl; *ii*. 1-aza-12-crown-4, DCC.

amidation of the corresponding carboxylic acids **6** and **7** by carbodiimide method (Scheme 1).

We studied the transport of salts $CoCl_2$, $NiCl_2$, $CuCl_2$, and $MgCl_2$ through the liquid membrane impregnated with calixarenes **1**—**5**. A typical pattern of the increase in the concentration of the salt in the receiving phase is shown in Fig. 1. In control experiments, the substrates under study were transported through the membrane containing no carrier. Based on the data obtained, an increase in the flow through the membrane containing a carrier molecule in comparison with the control experiment was determined for each salt. The data are given in Table 1.

As compared to the control experiment, calixarene **3** increases the transport rate of nickel and magnesium chlorides three-fold, of cobalt chloride two-fold, but does not affect the transport of copper chloride. Compound **1** increases two-fold the flow rate of copper and magnesium chlorides through the membrane and considerably increases the flow of cobalt (72-fold) and nickel (17-fold) chlorides. It should be noted that the introduction of azacrown

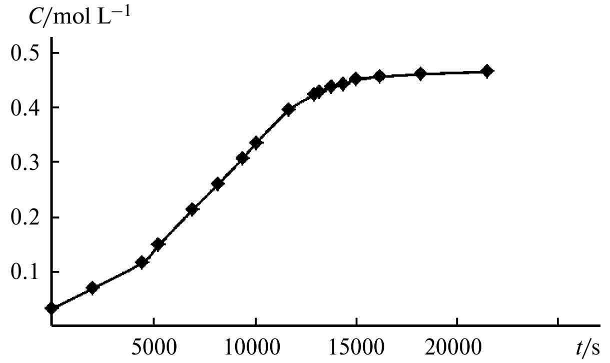


Fig. 1. Increases in the concentration of $CoCl_2$ (C) in the receiving phase with time (t).

Table 1. The values of initial flow (mol s^{-1} m^{-2}) of salts through the liquid membrane impregnated with calix[4]arenes **1**—**5** at 20 °C

Salt	1	2	3	4	5	Control
$CoCl_2$	$5.38 \cdot 10^{-4}$	$5.17 \cdot 10^{-4}$	$1.69 \cdot 10^{-5}$	$2.62 \cdot 10^{-5}$	$8.32 \cdot 10^{-6}$	$7.50 \cdot 10^{-6}$
$NiCl_2$	$6.87 \cdot 10^{-5}$	$6.45 \cdot 10^{-5}$	$1.29 \cdot 10^{-5}$	$2.15 \cdot 10^{-5}$	$5.30 \cdot 10^{-6}$	$4.14 \cdot 10^{-6}$
$CuCl_2$	$1.40 \cdot 10^{-5}$	$1.57 \cdot 10^{-5}$	$6.50 \cdot 10^{-6}$	$1.34 \cdot 10^{-5}$	$7.34 \cdot 10^{-6}$	$6.38 \cdot 10^{-6}$
$MgCl_2$	$1.58 \cdot 10^{-5}$	$1.55 \cdot 10^{-5}$	$2.24 \cdot 10^{-5}$	$1.50 \cdot 10^{-5}$	$1.36 \cdot 10^{-5}$	$7.20 \cdot 10^{-6}$

* The experimental error is less than 5% at a 95% confidence interval.

ether moieties into the structure of ligands **1—3** instead of tetra ester derivatives **4** also increases the flow of cobalt and nickel chlorides, however, only an insignificant increase in the flow is observed for copper and magnesium chlorides. The use of the disubstituted calix[4]arene **2** as a carrier gave the results similar to those obtained for tetrasubstituted calixarene **1**, hence, a possible formation of the sandwich complex can be suggested.

In conclusion, we showed that calixarenes substituted at the lower rim with the *N*-methoxycarbonylmonoaza-12-crown-4 ether fragments can be used for the membrane transport, with di- and tetrasubstituted calix[4]arenes being the most efficient for the transport of cobalt and nickel chlorides.

Experimental

Reaction progress and individuality of synthesized compounds were monitored by thin-layer chromatography on Silufol UV-254 plates in the systems chloroform, chloroform—ethanol (9 : 1), ethyl acetate—hexane (1 : 1), (1 : 2), (1 : 5). ^{1}H NMR spectra were recorded on a spectrophotometer Bruker DRX-400 (400 MHz) with Me_4Si as an internal standard. Elemental analysis was performed on a PE 2400 Series II CHNS-analyzer. Mass spectra were recorded on a Varian MAT 311A spectrometer (electron impact) at 70 eV of ionizing voltage with direct injection of samples into the source of ions. Conductivity of solutions was measured on a Radelkis OK-102 conductometer. Solvents were purified according to the standard procedures. Melting points were not corrected.

Compounds **2**,[22,23] **4**,[24,25] **5**,[26] **6**,[24] and **7**[27] were synthesized according to the described procedures.

5,11,17,23-Tetra-*tert*-butyl-25,26,2728-tetra((1,4,7-trioxa-10-azacyclodec-10-yl)carbonylmethoxy)calix[4]arene (1) was obtained similarly to calixarene **2**. The yield was 95%. B.p. 278—280 °C. ^{1}H NMR ($CDCl_3$), δ: 6.97 (s, 8 H, 8 ArH); 5.02, 3.39 (both d, 8 H, 4 $ArCH_2Ar$, J = 13.8 Hz); 4.81 (s, 8 H, 4 $OCH_2C{=}O$); 4.00 (br.t, 8 H, OCH_2, J = 4.8 Hz); 3.80 (br.t, 8 H, OCH_2, J = 4.5 Hz); 3.66 (br.t, 8 H, OCH_2, J = 4.8 Hz); 3.55—3.64 (m, 40 H, OCH_2, NCH_2); 1.21 (s, 36 H, 4 $(CH_3)_3C$). MS (EI, 70 eV), m/z (I_{rel} (%)): 1511 (12), 1510 (27), 1509 (30) $[M]^+$. Found (%): C, 66.47; H, 8.32; N, 3.65. $C_{84}H_{124}N_4O_{20}$. Calculated (%): C, 66.82; H, 8.28; N, 3.71.

5,11,17,23-Tetra-*tert*-butyl-25-(1,4,7-trioxa-10-azacyclodec-10-yl)carbonylmethoxy-26,27,28-trihydroxycalix[4]arene (3) was obtained similarly to calixarene **2**. The yield was 92%. B.p. 295—297 °C. ^{1}H NMR ($CDCl_3$), δ: 10.25 (s, 1 H, OH); 9.33 (s, 2 H, OH); 7.11 (s, 2 H, ArH); 7.08 (s, 4 H, ArH); 7.00 (s, 2 H, ArH); 4.90 (s, 2 H, $OCH_2C{=}O$); 4.50 (d, 2 H, $ArCH_2Ar$, J = 13.8 Hz); 4.31 (d, 2 H, $ArCH_2Ar$, J = 13.8 Hz); 4.02 (br.t, 2 H, OCH_2, J = 4.8 Hz); 3.80 (br.t, 2 H, OCH_2, J = 4.8 Hz); 3.67 (br.t, 2 H, OCH_2, J = 4.7 Hz); 3.55—3.64 (m, 10 H, OCH_2, NCH_2); 1.25 (s, 9 H, $(CH_3)_3C$); 1.22 (s, 18 H, $(CH_3)_3C$); 1.05 (s, 9 H, $(CH_3)_3C$). MS (EI, 70 eV), m/z (I_{rel} (%)): 865 (50), 864 (85) $[M]^+$. Found (%): C, 74.77; H, 8.75; N, 1.65. $C_{54}H_{73}NO_8$. Calculated (%): C, 75.05; H, 8.51; N, 1.62.

Studies of transport through a liquid membrane. The flow through the liquid impregnated membranes was measured in a glass vessel, using a platinum electrode. The liquid membrane was a solution of the carrier (0.02 mmol) in *o*-nitrophenyl octyl ether (0.02 mL) impregnated into the pores of polytetrafluoroethylene membranes (Sigma-Aldrich, diameter 25 mm, pore sizes 0.2 μm). The appliance was similar to that described in the work.[28] The source phase was a 1 *M* solution of the salt. The concentration of the substrate in the receiving phase (distilled water, V = 400 mL) was determined measuring the conductivity of the solution.

This work was financially supported by the Ministry of Education and Science of the Russian Federation (State Assignment No. 4.560.2014-K).

References

1. X. Ji, J. Li, J. Chen, X. Chi, K. Zhu, X. Yan, M. Zhang, F. Huang, *Macromolecules*, 2012, **45**, 6457.
2. M. Zhang, K. Zhu, F. Huang, *Chem. Commun.*, 2010, **46**, 8131.
3. S. Ok Kang, J. M. Llinares, V. W. Dayc, K. Bowman-James, *Chem. Soc. Rev.*, 2010, **39**, 3980.
4. B. V. K. J. Schmidt, M. Hetzer, H. Ritter, C. Barner-Kowollik, *Prog. Polym. Sci.*, 2014, **39**, 235.
5. N. Zafar, H. Fessi, A. Elaissari, *Int. J. Pharmaceut.*, 2014, **461**, 351.
6. T. Nabeshima, S. Akine, *Chem. Rec.*, 2008, **8**, 240.
7. M. A. Qazi, I. Qureshi, S. Memon, *J. Fluoresc.*, 2011, **21**, 1231.
8. N. Basílio, Á. Piñeiro, J. P. Da Silva, L. García-Río, *J. Org. Chem.*, 2013, **78**, 9113.
9. B. Tabakci, O. Alici, I. Karatas, *Talanta*, 2013, **106**, 92.
10. A. A. Abramov, A. N. Vasiliev, O. V. Dubovaya, V. V. Kovalev, I. M. Vatsouro, *Mendeleev Commun.*, 2012, **22**, 260.
11. Y. Yang, X. Cao, D. W. Purkiss, J. F. Cannon, R. A. Bartsch, *Tetrahedron*, 2012, **68**, 2233.
12. N. Y. Edwards, A. L. Possanza, *Supramol. Chem.*, 2013, **25**, 446.
13. N. Y. Edwards, F. Liub, G. Chen, *Supramol. Chem.*, 2013, **25**, 631.
14. S. Licen, V. Bagnacani, L. Baldini, A. Casnati, F. Sansone, M. Giannetto, P. Pengo, P. Tecilla, *Supramol. Chem.*, 2013, **25**, 481.
15. P. Curínová, M. Pojarová, J. Budka, K. Lang, I. Stibor, P. Lhoták, *Tetrahedron*, 2010, **66**, 8047.
16. B. S. Creaven, D. F. Donlon, J. McGinley, *Coord. Chem. Rev.*, 2009, **253**, 893.
17. R. Ludwig, K. Kunogi, N. Dung, S. Tachimori, *Chem. Commun.*, 1997, 1985.
18. J. S. Kim, S. K. Kim, J. W. Ko, E. T. Kim, S. H. Yu, M. H. Cho, S. G. Kwon, E. H. Lee, *Talanta*, 2000, **52**, 1143.
19. M. Sugiura, *Sep. Sci. Techol.*, 1990, **25**, 1189.
20. M. Mulder, *Basic Prinsiples of Membrane Technology*, 2nd ed., Kluwer Acad. Publ., Derdrecht—Boston—London, 1996, 564 pp.
21. B. Mokhtari, K. Pourabdollah, *J. Chin. Chem. Soc.*, 2012, **59**, 1058.
22. E. A. Alekseeva, S. S. Basok, I. M. Rakipov, A. V. Mazepa, A. I. Gren´, *Russ. J. Org. Chem.* (*Engl. Transl.*), 2013, **49**, 1035 [*Zh. Org. Khim.*, 2013, **49**, 1050].
23. E. A. Alekseeva, S. S. Basok, A. V. Mazepa, A. P. Luk´yanenko, O. V. Snurnikova, A. I. Gren´, *Russ. J. Gen. Chem.*

(*Engl. Transl.*), 2013, **83**, 1738 [*Zh. Obshch. Khim.*, 2013, **83**, 1519].
24. S.-K. Chang, I. Cho, *J. Chem. Soc., Perkin Trans. 1*, 1986, 211.
25. J. A. J. Brunink, W. Verboom, J. F. J. Engbersen, S. Harkema, D. N. Reinhoudt, *Rec. Trav. Chim. Pays-Bas*, 1992, **111**, 511.
26. L. C. Groenen, B. H. M. Ruël, A. Casnati, W. Verboom, A. Pochini, R. Ungaro, D. N. Reinhoudt, *Tetrahedron*, 1991, **47**, 8379.
27. C. Gaeta, M. De Rosa, M. Fruilo, A. Soriente, P. Neri, *Tetrahedron: Asymmetry*, 2005, **16**, 2333.
28. I. S. Antipin, I. I. Stoikov, A. A. Khrustalev, A. I. Konovalov, *Russ. Chem. Bull.* (*Int. Ed.*), 2001, **50**, 2134 [*Izv. Akad. Nauk, Ser. Khim.*, 2001, 2038].

Received April 30, 2014;
in revised form September 30, 2014