Improved extraction-spectrophotometric method for determination of dicyclohexano-substituted crown ethers in aqueous solutions

O. A. Zakurdaeva · S. V. Nesterov

Abstract A highly sensitive extraction-spectrophotometric method for determination of dicyclohexano-substituted crown ethers in aqueous solutions is described. It is based on the extraction of the macrocyclic complex, which comprises bromothymol blue as a colored organic anion, from aqueous solution into toluene. This method allows obtaining the limit of DCH18C6 detection in water of 2×10^{-7} M. It provides an efficient tool for monitoring the stability of crown-containing extractants and adsorbents upon contact with water and nitric acid solutions.

Introduction

Design of novel efficient and selective adsorbents for metal ion recovery from liquid radioactive wastes is a challenging task in modern separation science [1–5]. Macrocyclic compounds, in particular, dicyclohexano-substituted crown ethers (CE) are of special interest in the preparation of such adsorbents because of their excellent functionality [6, 7]. Typically, dicyclohexano-18-crown-6 (DCH18C6) and di-*tert*-butylcyclohexano-18-crown-6 (DtBuCH18C6) are used in radiochemical applications for binding the radioactive

O. A. Zakurdaeva (✉) · S. V. Nesterov
Enikolopov Institute of Synthetic Polymer Materials of RAS, ul. Profsoyuznaya, 70, 117393 Moscow, Russia
e-mail: olzak@mail.ru

S. V. Nesterov
Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia

strontium due to their ability to extract Sr^{2+} cations with high values of the distribution coefficient in solvent extraction [8, 9] and sorption processes [10, 11], as well as their adequate chemical [7] and radiation stability [12] in oxidative media. The problem to be solved in the preparation of the adsorbents is reliable incorporation and retention of dicyclohexano-substituted crown ethers in a bulk or on the surface of suitable supports. Up to now, a number of methods for covalent and "non-covalent" immobilization of CE have been proposed. Generally, most of them have been discussed in the reviews [12, 13]. Since the materials based on CE are designed for use in aqueous media, their stability to the washing-out of the crown ethers is one of the key issues. In spite of low solubility of DCH18C6 and, especially, DtBuCH18C6 in water, remarkable loss of crown ethers has been observed during a contact of crown-containing adsorbent materials with neutral and acidic aqueous solutions [14, 15]. In addition, solubility of DCH18C6 and DtBuCH18C6 in water increases in the presence of dissolved metal salts [6], and this tendency should be also taken into account. As a consequence, the losses of CE from prepared materials upon contact with water may be significant. It results in the decrease in capacity and selectivity of sorption, poor reproducibility of the results, limited lifetime of adsorbent, and deterioration of other functional characteristics. Taking into account all these issues, the losses of CE should be controlled, and an analytical procedure for the precise determination of CE concentration in the aqueous phase is vital. At the same time, only a few methods for the determination of CE content in aqueous media have been currently developed. For example, one study on DtBuCH18C6 losses from an adsorbent material has been published [14]. Analysis of total organic carbon (TOC) has been used as a monitoring tool. It should be noted that TOC analysis is not selective towards DtBuCH18C6, and water-soluble organic impurities in the CE and traces of

solvent (e.g., octanol [15]) may misrepresent the results significantly. In fact, the situation is the same in the case of DCH18C6. A method for DCH18C6 determination that comprised extraction of CE from aqueous solutions with a membrane disk followed by gas chromatographic analysis of extracts has been described [16]. The proposed procedure was multistage, sophisticated and time-consuming. Extraction of DCH18C6 from the aqueous solution to the organic solvent in combination with subsequent IR-FT analysis of the organic phase has been used for estimation of CE washing-out from polymer hydrogels [17, 18]. However, the sensitivity of that procedure was low and did not allow determining the concentration of CE below 10^{-4} M. In addition, several techniques for extraction-spectrophotometric detection of CE in water (including DCH18C6) have been suggested [19–21]. These procedures were selective and sensitive to CE. Nevertheless, they had a drawback discussed below. Briefly, the extraction-spectrophotometric method for CE determination is based on the ability of CE to form stable macrocyclic complexes with metal cations and dye anions in aqueous media, which can be quantitatively extracted into an organic solvent as ion pairs. The dye itself has low solubility in the organic solvent so its transfer to the organic phase is rather small in the absence of CE. Accordingly, the final concentration of dye anions in the organic phase after extraction is directly proportional to the initial concentration of CE in the aqueous solution. Due to the high molar absorption coefficient for the extracted macrocyclic complex with anion of organic dye, it is possible to measure even low amounts of CE by UV–Vis spectroscopy. Usually, picrate ion, bromothymol blue and metanil yellow as colored anions and chloroform as an organic solvent have been tested in the systems for determination of DCH18C6 in water solutions [19–21]. Bromothymol blue (BTB) proved to be more preferable because of higher extractability and UV–Vis absorbance of the macrocyclic complex with this dye anion [21] that resulted in better sensitivity of the method. However, some BTB transfer from the aqueous solution into chloroform has been observed even in the absence of crown ether, with UV–Vis absorbance of organic phase being measurable [21]. It is a critical drawback of chloroform that affects the reproducibility of measurements and the sensitivity of this method. Furthermore, chloroform is partially soluble in water, has a low boiling point and high vapor partial pressure at room temperature, which may be a source of experimental errors.

In spite of the drawback discussed above, the extraction-spectrophotometric method for CE determination in aqueous media seems to be very attractable for laboratory and pilot tests because of detection limits, simplicity of the analytical procedure and method implementation. Furthermore, this method apparently possesses a potential for the analysis of DtBuCH18C6 content in aqueous solutions.

Thus, the aim of the present study was to improve the extraction-spectrophotometric method for the determination of DCH18C6 in aqueous solutions, to adopt this method for the detection of DtBuCH18C6, and to examine the applicability of this method for the estimation of DCH18C6 and DtBuCH18C6 retention on adsorbent materials upon contact with water and nitric acid solutions.

Experimental

Reagent and materials

DCH18C6 (mixture of isomers, 99 % assay) and DtBuCH18C6 (mixture of isomers, 96 % assay) were purchased from Ecolan, Russia. Sodium salt of bromothymol blue (Merck, Germany), KCl, NaOH, $Sr(NO_3)_2$, HNO_3, diethyl ether, methanol, chloroform and toluene (Reakhim, Russia) had analytical reagent grades and were used as received. Three different types of supports were used for preparation of crown-loaded adsorbent materials: silica gel Silochrom S-120 (specific surface area (SSA) of 100–140 $m^2\ g^{-1}$, from Khimtekhmash, Russia), cross-linked styrene–divinylbenzene (St-DVB_{cross}) copolymer (SSA = 700 $m^2\ g^{-1}$) and styrene–divinylbenzene (St-DVB_{hydr}) copolymer modified with tertiary amine groups (SSA = 1,200 $m^2\ g^{-1}$).

Determination of DCH18C6 in water

Calibration solutions with CE concentrations in the range of $(1 \times 10^{-6}$–$1 \times 10^{-4})$ M were prepared by dissolution of the precise weight of DCH18C6 in the deionized water followed by dilution to the predetermined values. Aliquots of the calibration solutions or of the analyzed solutions having volume (V_{al}) of 3 or 20 ml were mixed with 0.5 ml of 1 M solution of KCl and 1.5 ml of 1×10^{-3} M solution of sodium salt of bromothymol blue (Na-BTB), and the resulting mixture was extracted with an organic solvent (5 ml).

The extraction procedures were carried out in the separation funnel during 3 and 5 min for V_{al} = 3 and 20 ml, respectively. After the phase separation (15–25 min) the organic phase was isolated and its UV–Vis spectra were measured with a Perkin-Elmer Lambda 9 spectrophotometer in the wave length range of 300–600 nm, with absorbance maximum of analyzed CE complex being at 394 nm. Calibration curves were plotted as UV–Vis absorbance of organic phase at 394 nm versus CE concentration in the aqueous solution. CE content in the analyzed solutions was determined using the calibration curves.

Determination of DCH18C6 in nitric acid solutions of strontium nitrate

The method for extraction-spectrophotometric determination of CE in water was adapted to the experimental conditions which actually occurred during radioanalytical applications of adsorbent materials containing CE. For this purpose, the solutions containing 2.3×10^{-3} M of $Sr(NO_3)_2$ and 3 M of HNO_3 were prepared and tested as a medium contacting with the adsorbents. After the predetermined contact time with the adsorbent, an aliquot (3 or 20 ml) of the acidic aqueous phase was taken for CE determination. Since bromothymol blue has a water-insoluble, protonated form at the acidic medium (at pH < 3), the preliminary stage of neutralization of the aqueous phase was included in the method prior to extraction with the organic solvent. Neutralization was accomplished with the NaOH solution in two stages. First, a part of alkaline solution was added to the analyzed aliquots under stirring to provide solubility of Na-BTB, then anion dye (1.5 ml of 1×10^{-3} M solution) was added followed by pouring the remaining portion of NaOH solution to complete the neutralization. At this point, a slight orange coloration of analyzed solution was changed to the green one (pH 6.8). Strontium nitrate (0.5 ml of 1 M solution) was used instead of KCl on the final stage of preparing the aqueous solutions for extraction. Then 5 ml of an organic solvent was added, and the extraction-spectrophotometric procedure was carried out as described above for neutral aqueous solutions.

Preparation of crown-loaded adsorbent materials

The samples of crown-loaded adsorbents were prepared by stepwise impregnation of the supports with solutions of the crown-ethers in diethyl ether or diethyl ether/methanol mixture. The silica gel was preliminary dried by increasing the temperature in accordance with the following protocol: 30 min at 100 °C, 30 min at 150 °C, 30 min at 200 °C and 60 min at 250 °C. Porous styrene–divinylbenzene copolymers were triply washed with acetone, a residual amount of the solvent was evaporated at 50 °C to a virtually constant weight of support, and then the solution of CE ($c_{DCH18C6} = 1.5 \times 10^{-2}$ M or $c_{DtBCH18C6} = 1.15 \times 10^{-2}$ M) was gradually added to the prepared material. The total volume of the added CE solution was about 20 ml per 1 g of support. The solvent was evaporated at room temperature under moderate stirring. After the evaporation of most part of the solvent, the adsorbents were dried at 50 °C up to constant weight. Final CE loading in the samples was about 10 wt%.

Resistance of the prepared materials to CE washing-out was estimated by contact with water or nitric acid solution of strontium nitrate in batch method under stirring. The
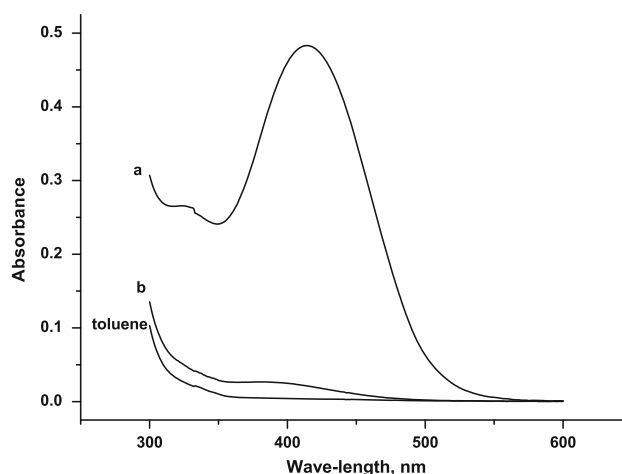

Fig. 1 UV–Vis spectra of toluene and organic phase after contact of chloroform (*a*) and toluene (*b*) with crown-free aqueous solution. $V_{al} = 3$ ml, $V_{KCl} = 0.5$ ml, $V_{NaBTB} = 1.5$ ml, $V_{toluene} = 5$ ml

ratio of the adsorbent weight to the volume of the aqueous phase was equal to 100 mg/20 ml. Solid and liquid phases were separated, and the aqueous solution was analyzed by the extraction-spectrophotometric method. The value of CE washing-out was determined from the equation:

$$CE_{losses} = n/n_0 \cdot 100 \%,$$

where n is a quantity of CE washed-out into the aqueous phase (mol), and n_0 is an initial loading of CE in the sample (mol).

Results and discussion

Modification of extraction-spectrophotometric procedure for CE determination in aqueous solution

To overcome the problems related to chloroform usage, careful selection of organic solvents was carried out and chloroform was substituted with toluene. Toluene is transparent in the visible range (Fig. 1, lower curve) and, in contrast to chloroform, has lower solubility in water, a higher boiling point and dielectric constant. In addition, it dissolves DCH18C6 and DtBuCH18C6 at adequate levels (>0.5 mol L^{-1} and >0.2 mol L^{-1}, respectively) [22]. The result of the substitution of chloroform for toluene is shown in Fig. 1 (cf. UV–Vis absorbance values of spectra (a) and (b)). One can see from the figure that absorbance caused by transfer of the BTB salt from the crown-free solution into the organic solvent was negligible, if toluene was used instead of chloroform. It gives the opportunity to considerably improve the sensitivity of CE determination.

Figure 2 presents the calibration curves of UV–Vis absorbance of the organic phase versus DCH18C6 concentration in aqueous solutions for this new system. The

$A_a = (0.020 \pm 0.005) + (12400 \pm 200) \cdot c$
$R = 0.9993$

$A_c = (0.04 \pm 0.02) + (113000 \pm 3000) \cdot c$
$R = 0.9986$

$A_b = (0.0180 \pm 0.0045) + (59900 \pm 1100) \cdot c$
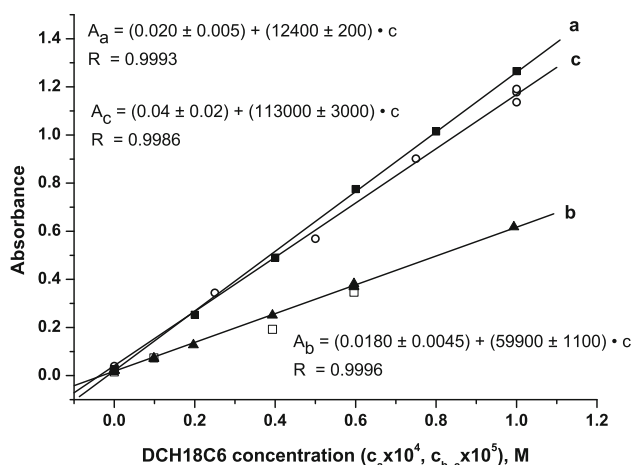$R = 0.9996$

Fig. 2 Calibration curves for determination of DCH18C6 concentration in aqueous solutions at different organic solution/aqueous solution ratios: (a) DCH18C6—water, $V_{al} = 3$ ml; $V_{KCl} = 0.5$ ml. (b) DCH18C6—water, $V_{al} = 20$ ml, $V_{KCl} = 0.5$ ml. (c) DCH18C6—3 M HNO$_3$, $V_{al} = 20$ ml; $V_{Sr(NO3)2} = 0.5$ ml

$A = (113.4 \pm 2.3) \cdot c$
$R = 0.99786$

Fig. 3 Distribution of DCH18C6 between water and toluene at equilibrium state

experimental data were reasonably approximated by linear regressions, and equations of the regression and correlation coefficients are given in the figure. Based on the data of blank tests, the limit of DCH18C6 detection in water was calculated according to the formula: $c_{min} = 3s_0/b$ [23, 24], wherein s_0 is a standard deviation of blank measurements and b is a slope of calibration curve. For the aqueous phase to toluene ratio of 1:1 (Fig. 2a), c_{min} was equal to 8×10^{-7} M (eight blank tests). This value can be still improved by increasing the aqueous phase/organic phase ratio. For example, the calibration curve was obtained for solutions with CE concentrations less than 1×10^{-5} M at the ratio of the analyzed aqueous phase to toluene of 4:1 (Fig. 2b). In this case, CE detection limit was 2×10^{-7} M (ten blank tests) and the relative standard deviation for three measurements at DCH18C6 concentration of 6×10^{-6} M was calculated as 1.8 %. In such a way, the method for extraction-spectrophotometric determination of CE in aqueous solutions is significantly improved as compared with the previous systems based on chloroform [21].

Some aspects of using the modified extraction-spectrophotometric procedure for DCH18C6 determination in various aqueous media and a possibility of its adaptation for the analysis of DtBuCH18C6 will be discussed below.

DCH18C6 distribution in H$_2$O/toluene system

In spite of wide applications of the crown ethers in extraction processes for radioactive waste reprocessing [1, 8, 9, 12], the data on distribution of DCH18C6 between aqueous and organic phases are limited. Moreover, to the best of our knowledge, there are only few studies dealing
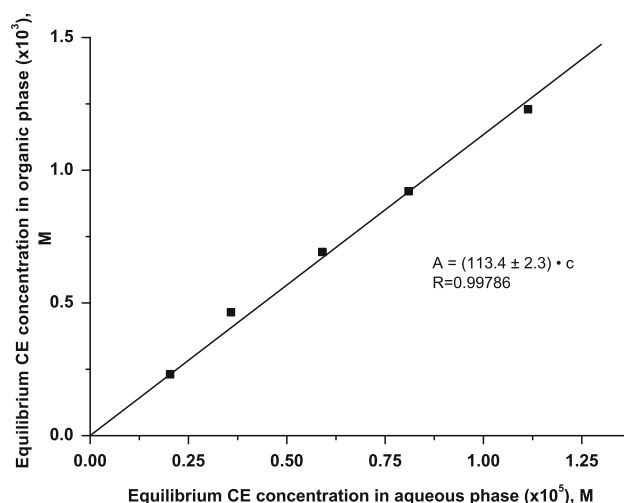
with DCH18C6 and DtBCH18C6 distribution between water and toluene [22, 25]. McDowel and coauthors have reported data on "reverse" distribution of the crown ethers from toluene to water, which was 7 % for DCH18C6 and <0.1 % for DtBuCH18C6 [22]. Lakkis and coauthors have given the value of DCH18C6 distribution coefficient ($\log K_D = 2.30$) between aqueous solutions of lithium salts and toluene [25]. Furthermore, mathematical modelling, which allow the prediction of distribution constant in case of unsubstituted and benzosubstituted CE, have a number of restrictions for DCH18C6 and DtBCH18C6 [26]. Taking this into account, we tested the above-described extraction-spectrophotometric procedure to measure the distribution of DCH18C6 in H$_2$O/toluene system.

For this purpose, five DCH18C6 aqueous solutions with CE concentrations in the range of $(6.0 \times 10^{-5}$–$3.2 \times 10^{-4})$ M were prepared. Aliquot (20 ml) of each solution was extracted with 5 ml of toluene during 5 min. After the phase separation, the aqueous phase was isolated and analyzed for CE content by the extraction-spectrophotometric procedure described above. As a result, equilibrium concentrations of DCH18C6 in the aqueous phase were found. Subsequently, the equilibrium concentrations of DCH18C6 in the organic phase were calculated as follows:

$$c_{org}^{eq} = \left(c_{aq}^0 - c_{aq}^{eq} \right) \cdot \frac{V_{aq}}{V_{org}}$$

where c_{org}^{eq} and c_{aq}^{eq} are the equilibrium concentration of DCH18C6 in organic and aqueous phases, c_{aq}^0 is the initial concentration of DCH18C6 in the aqueous solution (all concentration in mol L^{-1}), V_{aq} and V_{org} are the volumes of the aqueous solution and the organic phase (ml).

Table 1 Washing-out of the CE from the adsorbents (CE$_{losses}$) upon contact with water and aqueous nitric acid solution (2.3×10^{-3} M of Sr(NO$_3$)$_2$ in 3 M of HNO$_3$)

Sample	Crown-ether loading (mol/g)	Time of contact with water and acidic solution (h)	Concentration of CE in water and acidic solution after contact with sample[a] (M)	Washing-out of the CE (mol%)	
				H$_2$O	Acidic solution
S-120-DCH	2.7×10^{-4}	2	1×10^{-3}	80 ± 1[b]	–
S-120-DtB	2.9×10^{-4}	2	8.7×10^{-5} (3.2×10^{-4})	5.9 ± 0.4[b]	22
St-DVB$_{hydr}$-DCH	3.0×10^{-4}	144	9.4×10^{-5} (1.5×10^{-4})	6	9
St-DVB$_{hydr}$-DtB	2.3×10^{-4}	144	4.3×10^{-6} (6.5×10^{-6})	<1	<1
St-DVB$_{cross}$-DCH	2.9×10^{-4}	480	3.7×10^{-7} (1.8×10^{-6})	≪1	<1
St-DVB$_{cross}$-DtB	2.2×10^{-4}	480	2×10^{-7} (1×10^{-6})	≪1	<1

[a] Average value of two parallel tests (concentrations of CE in acidic solution are given into parentheses)

[b] Average value of three parallel tests

The equilibrium concentrations of DCH18C6 in the organic phase were plotted as a function of the equilibrium concentrations of DCH18C6 in the aqueous phase (Fig. 3) and the distribution coefficient K_D was determined as a slope of that curve.

The obtained $K_D = 113 \pm 2$ (log$K_D = 2.05$) is in reasonably good agreement with the value (log$K_D = 2.30$) reported by Lakkis et al. [25]. On the base of K_D, the percentage of DCH18C6 extraction (E) was estimated:

$$E = \frac{K_D}{K_D + V_{aq}/V_{org}}$$

The percentage of DCH18C6 extraction from water into toluene at a phase ratio of 4:1, calculated by this equation, was approximately 97 %. This value is indicative of sufficiently complete extraction of CE.

Testing the procedure for the analysis of DCH18C6 and DtBuCH18C6 washing-out from CE-loaded adsorbent materials exposed to water and nitric acid solutions

The above data on limits of detection testifies that the modified extraction-spectrophotometric method is a very precise tool for determination of low CE concentrations in water and aqueous solutions. We examined its applicability to analyze DCH18C6 and DtBuCH18C6 washing-out from crown-loaded adsorbent materials in different conditions. Six samples with compositions given in Table 1 were prepared and tested.

Tests in water

The DCH18C6- and DtBuCH18C6-loaded samples were in contact with water (pH 7) for a predetermined time, following which the aqueous phases were separated and analyzed by the procedure described above. In the presence
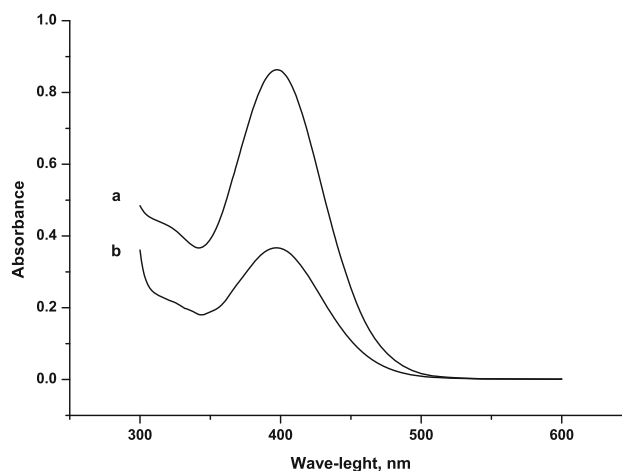
Fig. 4 UV-Vis spectra of organic phase after extraction of macrocyclic complex from aqueous solutions obtained from the contact of S-120-DCH (*a*) and S-120-DtBu (*b*) adsorbents with water (100 mg of adsorbent/20 ml H$_2$O, time of contact 2 h). The aqueous solutions were diluted tenfold (*a*) and threefold (*b*) with water before the analysis. $V_{al} = 3$ ml, $V_{KCl} = 0.5$ ml, $V_{NaBTB} = 1.5$ ml, $V_{toluene} = 5$ ml

of KCl, the formation of the macrocyclic complex and its extraction follows the reaction:

$$K_{aq}^+ + CE_{aq} + BTB_{aq}^- \leftrightarrow [K(CE)BTB]_{org}$$

wherein subscripts aq and org relate to water and organic phase, respectively. Representative UV–VIS spectra of the organic phase obtained after the extraction stage are given in Fig. 4. These spectra demonstrate that both DCH18C6 and DtBCH18C6 were washed-out from the adsorbents into water.

It should be noted that DtBuCH18C6 is rather hydrophobic and has low solubility in water that does not allow preparing its aqueous solutions for the calibration. However, one can use the calibration curves obtained for DCH18C6 to estimate DtBuCH18C6 washing-out in accord with the following. Both crown ethers form inclusion complexes [K(CE)$^+$] with 1:1 stoichiometry, and

stabilities of these complexes in water are similar [27]. Taking into account a correlation between the stability of the complex in the aqueous solution and its extractability [21], it is reasonable to suppose approximately the same extractabilities of the macrocyclic complexes with BTB anion dye and, hence, the molarity of anion dye in the organic phase for DCH18C6 and DtBuCH18C6. If one assumes that CE does not have a detectable influence on the molar extinction coefficient of BTB, the calibration curves for DCH18C6 and DtBuCH18C6 should be identical. Based on the above, DCH18C6 and DtBuCH18C6 concentrations accumulated in the aqueous phase were determined using calibration curves from Fig. 2 and, expectedly, washing-out of DtBuCH18C6 was much less in comparison with that of DCH18C6 (Table 1) for both inorganic (SiO$_2$) and polymer supports tested here. Moreover, the value of CE losses was most pronounced for the adsorbents based on silica gel and decreased by increasing the hydrophobicity of the supports.

Tests in nitric acid solutions

From an analysis of the literature data [26, 28], one can expect some increase in CE losses upon contact of adsorbents with aqueous nitric acid solutions in comparison with exposure to neutral water. The extraction-spectrophotometric method was tested to study the stability of the samples upon their contact with strontium nitrate solutions ($c_{Sr} = 2.3 \times 10^{-3}$ M) in 3 M HNO$_3$. In this case, CE forms a stable complex with Sr^{2+} ions in an aqueous solution, and extraction of this complex cation [Sr(CE)$^{2+}$] with toluene may be described as follows:

$$Sr^{2+}_{aq} + CE_{aq} + 2BTB^-_{aq} \leftrightarrow [Sr(CE)BTB_2]_{org} \qquad (1)$$
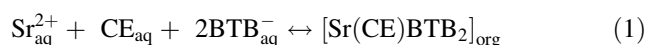
It has been demonstrated that the optimal range of pH for the extraction of the complex [Me(CE)]$^{n+}$BTB^-_n is 4–8 [21]. Accordingly, preliminary neutralization of the analyzed solutions with NaOH was carried out before the extraction-spectrophotometric procedure. As a result, the analyzed aqueous solutions contained significant quantities of nitrate-anions (~3 M) and Na$^+$ cations (~3 M) on the stage of extraction with toluene. It should be emphasized that both ion species can change the composition of the extracted macrocyclic complex and the concentration of BTB$^-$ in the organic phase. NO$_3^-$ anions can compete with BTB$^-$ for crown ether (reaction 2) that would eventually result in a decrease in UV–VIS absorbance of the organic phase.

$$Me^{n+}_{aq} + CE_{aq} + nNO^-_{3\,aq} \leftrightarrow \left[Me^{n+}(CE)(NO^-_3)_n\right]_{org} \qquad (2)$$
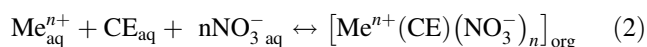
The presence of Na$^+$ cations is an important factor too. Despite an essential difference in constants of complex

formation of DCH18C6 with cations of sodium and strontium (log$K$ are equal to 1.21 and 3.24, respectively, for *cis-syn-cis* isomer) [27], the concentration of Na$^+$ after the stage of neutralization may be in large excess over Sr^{2+}, and a part of sodium cations will be able to form the macrocyclic complex:

$$Na^+_{aq} + CE_{aq} + BTB^-_{aq} \leftrightarrow [Na(CE)BTB]_{org} \qquad (3)$$
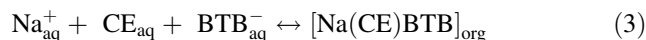
The participation of sodium cations in complexation with CE will reduce UV–VIS absorbance of the organic phase due to including only one BTB anion (instead of two species in case of Sr^{2+}) in the structure of the extracted macrocyclic complexes. In addition, higher concentration of metal cations in the aqueous solution can lead to increasing the extraction of crown-free salt Me^{n+}BTB^-_n (reaction 4) and the absorbance of the organic phase in blank tests.

$$Me^{n+}_{aq} + BTB^-_{n\,aq} \leftrightarrow Me^{n+}BTB^-_{n\,org} \qquad (4)$$

To study these effects, the aqueous solutions containing different HNO$_3$ concentrations were analyzed by means of the extraction-spectrophotometric procedure including the stage of neutralization. The plot of UV–Vis absorbance of the organic phases versus Na$^+$/Sr^{2+} mole ratio in the disacidified aqueous solutions is given in Fig. 5. It appeared that an increase in NO$_3^-$ and Na$^+$ concentration did not have a noticeable effect on the absorbance of the organic phase in case of crown-free solutions (Fig. 5a). This result testifies to relatively low solvation energy of both metal cations and nitrate anions by toluene. At the same time, some decrease in the absorbance of extracts was observed in the presence of CE (Fig. 5b). It seems reasonable to suppose that the decrease in absorbance of the organic phase in this case resulted from the competition between Na$^+$ and Sr^{2+} cations for the complexation with CE (reaction 3 and reaction 1) rather than NO$_3^-$ influence (reaction 2). To take into account this reduction in UV–Vis absorbance and provide an opportunity for quantitative measurements, a corresponding calibration curve was obtained (Fig. 2c) and used for determination of CE losses (CE$_{losses}$) in the tests with the acidic solution (Na$^+$/Sr^{2+} mole ratio at the stage of extraction was 120). The results of these tests are presented in Table 1.

The data given in Table 1 demonstrates that washing-out of the CE from the adsorbents was measurably increased in the presence of nitric acid. In addition, this value was surprisingly high (>20 %) for hydrophobic DtBuCH18C6 in case of silica gel support. As a whole, the tendency was the same as in the test with neutral water, namely the higher hydrophobicity of support and CE resulted in lower washing-out of CE.
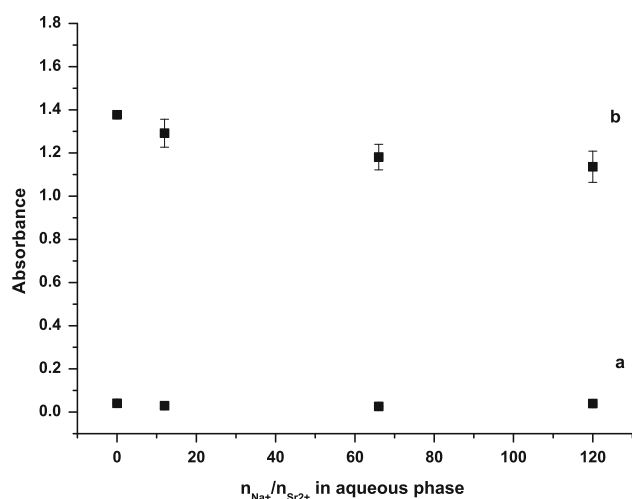
Fig. 5 Effect of Na^+ (or NO_3^-)/Sr^{2+} mole ratio on the absorbance of organic phase: (a) blank tests, (b) $c_{DCH18C6} = 1 \times 10^{-5}$ M. $V_{al} = 20$ ml, $V_{Sr(NO3)2} = 0.5$ ml, $V_{NaBTB} = 1.5$ ml, $V_{toluene} = 5$ ml

Conclusions

The improved extraction-spectrophotometric method provides an efficient tool for determination of low concentrations of DCH18C6 and DtBCH18C6 in water and nitric acid solutions. It is characterized by simplicity of implementation, high sensitivity, reproducibility of results and possibility of adaptation to the variations in experimental conditions. It was used to study the distribution of DCH18C6 between water and toluene, and the distribution coefficient K_D of 113 ± 2 was obtained. The efficiency of the method for determination of DCH18C6 and DtBuCH18C6 washing-out from the adsorbents into aqueous solutions was demonstrated. The method can be used in analytical and applied radiochemistry for estimating the stability of extractants and adsorbents to washing-out of the CE upon contact with aqueous solutions.

References

1. Nash KL, Barrans RE, Chiarizia R, Dietz ML, Jensen MP, Rickera PG, Moyer BA, Bonnesen PV, Bryan JC, Sachleben RA (2000) Fundamental investigations of separations science for radioactive materials. Solv Extr Ion Exch 18:605–631
2. Sivanatham M, Rao Tata BV, Babu CA (2012) Synthesis of crown ether functionalized polyacrylamide gel beads and their extraction behaviour for strontium ions. Desalin Water Treat 38:8–14
3. Attallah MF, Borai EH, Hilal MA, Shehata FA, Abo-Aly MM (2011) Utilization of different crown ethers impregnated polymeric resin for treatment of low level liquid radioactive waste by column chromatography. J Hazard Mater 195:73–81
4. Bai F, Ye G, Chen G, Wei J, Wang J, Chen J (2013) New macrocyclic ligand incorporated organosilicas: co-condensation synthesis, characterization and separation of strontium in simulated high level liquid waste. React Funct Polym 73:228–236
5. Yakshin VV, Vilkova OM, Tsarenko NA, Tsivadze AYu (2010) Metal extraction from nitric acid solutions by the macrocyclic endoreceptor dicyclohexyl-18-crown-6 immobilized in a polymer matrix. Dokl Chem 430:54–57
6. Pedersen CJ (1967) Cyclic polyethers and their complexes with metal salts. J Am Chem Soc 89:7017–7036
7. Hiraoka M (1982) Crown Compounds: Their Characteristics and Applications (Studies in Organic Chemistry). Elsevier Science Ltd., Amsterdam
8. Blasius E, Klein W, Schön U (1985) Separation of strontium from nuclear waste solutions by solvent extraction with crown ethers. J Radioanal Nucl Chem 89:389–398
9. Horwitz EP, Dietz ML, Fisher DE (1991) SREX: a new process for the extraction and recovery of strontium from acidic nuclear waste streams. Solv Extr Ion Exch 9:1–25
10. Horwitz EP, Chiarizia R, Dietz ML (1992) A novel strontium-selective extraction chromatographic resin. Solv Extr Ion Exch 10:313–336
11. Horwitz EP, Dietz ML, Chiarizia R (1992) The application of novel extraction chromatographic materials to the characterization of radioactive waste solutions. J Radioanal Nucl Chem 161:575–583
12. Nesterov SV (2011) Dicyclohexanocrown ethers: from synthesis to radiochemical applications. Nova Science Publishers, New York
13. Nesterov SV (2000) Crown ethers in radiochemistry. Advances and prospects. Russ Chem Rev 69:769–782
14. Zhang A, Wei Y, Kumagai M (2005) Bleeding evaluation of the stationary phase from a few novel macroporous silica-substrate polymeric materials used for radionuclide partitioning from HLLW in MAREC process. J Radioanal Nucl Chem 265:409–417
15. Dietz ML, Yaeger J, Sajdak LR Jr, Jensen MP (2005) Characterization of an improved extraction chromatographic material for the separation and preconcentration of strontium from acidic media. Sep Sci Tech 40:349–366
16. Yamini Y, Shamsipur M (1996) Extraction and determination of crown ethers from water samples using a membrane disk and gas chromatography. Talanta 43:2117–2122
17. Zakurdaeva OA, Nesterov SV, Shmakova NA, Semenova GK, Sozontova EO, Feldman VI (2007) Radiation-chemical synthesis of poly(vinyl alcohol) hydrogel containing dicyclohexano-18-crown-6. Nucl Instrum Meth B 265:356–361
18. Zakurdaeva OA, Nesterov SV, Shmakova NA, Feldman VI (2008) Radiation-chemical synthesis of crown-containing poly(ethylene oxide) hydrogels. Swelling behavior and crown ether retention. Radiat Phys Chem 77:23–28
19. Frensdorff HK (1971) Salt complexes of cyclic polyethers. Distribution equilibriums. J Am Chem Soc 93:4684–4688
20. Lipkovskaya NA, Sukhan VV, Nazarenko AYu, Chuiko AA (1992) Preconcentration of polyethers by extraction and adsorption prior to their determination by solid-phase photometry. J Anal Chem 47:1033–1037
21. Vilkova OM, Yakshin VV (2003) Extraction-photometric determination of the composition of multicomponent crown ether–podand mixtures. J Anal Chem 58:27–30
22. McDowell WJ, Case GN, Aldrup DW (1983) Investigation of ion-size-selective synergism in solvent extraction. Sep Sci Tech 18:1483–1507
23. Long GL, Winefordner JD (1983) Limit of detection. A closer look at the IUPAC definition. Anal Chem 55:712A–724A
24. Eksperiandova LP, Belikov KN, Khimchenko SV, Blank TA (2010) Once again about determination and detection limits. J Anal Chem 65:223–228
25. Lakkis M, Brunette JP, Leroy MJF, Alstad J (1986) 18C6 and DC18C6 crown-ethers as synergic agents in the extraction of

Co(II) and Ni(I) from chloride media with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one in toluene. Solv Extr Ion Exch 4:287–299

26. Robak W, Apostoluk W, Maciejewski P (2006) Analysis of liquid–liquid distribution constants of nonionizable crown ethers and their derivatives. Anal Chem Acta 569:119–131

27. Izatt RM, Bradshow JS, Nielsen SA, Lamb J, Christensen J (1985) Thermodynamic and kinetic data for cation-macrocycle interaction. Chem Rev 85:271–339

28. Horwitz EP, Dietz ML, Fisher DE (1990) Extraction of strontium from nitric acid solutions using dicyclohexano-18-crown-6 and its derivatives. Solvent Extr Ion Exch 8:557–572