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Unusual extraction behaviour of crown ether when intercalated in bentonite

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Dicyclohexano-18-crown-6 (DCH18C6) has been intercalated in bentonite and the product, Ben-Crown, characterized by microelemental analysis, TG-DTA analysis, X-ray diffraction and IR spectroscopy. The permanent negative charge present in the bentonite layer has been exploited for more efficient extraction of cesium and strontium by Ben-Crown at nitric acid concentrations (<1.0 M) that gave only a meagre extraction when either DCH18C6 or bentonite alone were employed. The extraction of cesium and strontium has been investigated as a function of time, temperature, and the concentrations of nitric acid, metal ion and sodium nitrate. An unusual extraction phenomenon was observed at low concentrations of nitric acid (<1.0 M) in the absence of any organophilic agents. Rapid extraction of the metal ion was followed by the establishment of an equilibrium, which occurred after 150 min. Distribution coefficients (K_d) of 599 and 1007 ml g^{-1} were obtained, respectively, for the extraction of cesium and strontium from 0.1 M nitric acid by Ben-Crown; K_d decreased with an increase in the temperature or in the concentrations of nitric acid and sodium nitrate. The extraction data were fitted by the Langmuir adsorption model and the apparent experimental exchange capacity obtained by linear regression analysis was in good agreement with the amount of crown ether (0.22 mmol g^{-1}) intercalated in bentonite. The enthalpy change (ΔH°) for the extraction of cesium and strontium was found to be exothermic.

Introduction

Crown ethers form very stable complexes with alkali and alkaline earth metal ions due to strong host–guest interactions.[1] The potential applications of crown ether and its derivatives in the nuclear industry, especially the selective separation of radioactive ^{137}Cs, ^{90}Sr from nuclear wastes,[2–4] are well-documented. Crown ether, being a neutral donor, extracts both cations and anions from the aqueous phase, leading to the formation of ion pairs in the organic phase. Therefore, the efficiency of extraction strongly depends not only upon the target metal ion but also on the anion with which it is associated; the lipophilicity of the anion; the physical properties of the diluent, *etc.*, employed during extraction.[2,5] Thus, cesium and strontium coexisting with hydrophobic or lipophilic anions, for example, picrates,[6] are more readily extracted into the organic phase than strongly solvated anions such as nitrate, which is likely to be present in radioactive wastes.

In addition, diluents with a high dielectric constant and having the ability to extract water improve the extraction of metal ion when compared to non-polar diluents.[5,6] The extracted water stabilizes the ion-pair present in the organic phase. Thus, Horwitz *et al.*[7] prepared an adsorbent impregnated with both the solvent di-*tert*-butylcyclohexano-18-crown-6 (DtBuCH18C6) for extracting the target ion pair and the diluent, 1-octanol, for extracting water and stabilizing the ion pair in the inert solid support (Amberlite XAD-7). Thus, studies reported[5–7] so far indicate that the transport of anions along with cations during extraction and the stabilization of the ion pair in the organic phase after extraction are imperative when crown ether was employed as the extractant. However, instead of organic non-ionic adsorbents as the support material, some inorganic layered materials that have a permanent negative layer charge can also be exploited for the impregnation of crown ethers.

The naturally occurring swelling clay, bentonite, is one such material[8] whose structure consists of an octahedral layer made up of aluminium oxide sandwiched between two tetrahedral silicon oxide sheets, resulting in a 2 : 1 arrangement. The octahedral and tetrahedral sheets are bonded together by sharing a common oxygen atom. These aluminosilicate layers are electrically neutral. However, isomorphous substitution of Si^{4+} by trivalent Al^{3+} in the tetrahedral sites or substitution of Al^{3+} in the octahedral position by Mg^{2+} cations results in the generation of a net negative charge in the layer, which is normally compensated by cations such as Na^+, Ca^{2+} or Mg^{2+}. These cations are situated between the layers and can be exchanged with any desired cations by simple ion exchange. A large number of ion exchange, retardation, and adsorption studies of various metal ions on bentonites[9,10] have indeed been reported, even though bentonites are not very selective. Nevertheless, the selectivity can be improved by impregnation or intercalation of any organic material[11] that is specific to hazardous and radioactive metal ions into the interlayer of bentonite.

Pioneering work on the intercalation of crown ethers and other organic molecules into phyllosilicate clays was carried out by Ruiz-Hitzky and co-workers.[12,13] The process of intercalation of crown ethers and cryptands into 2 : 1 phyllosilicates

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was reported to be exothermic and the magnitude of heat energy liberated depends strongly upon the nature of the crown ether and interlayer cations.[13] Intercalation of crown ether into phyllosilicates results in a propping apart of the interlayers by 0.4 to 0.8 nm, depending whether a 1 : 1 or 2 : 1 complex of the crown ether-metal ion is employed. Most of the organic intercalated clay materials and metal oxide pillared clays find their applications in the field of catalysis[14] and only a few reports are available on the adsorption or separation of radioactive metal ions.[11,15] To the best of our knowledge, crown ether intercalated bentonite has not been evaluated for the separation of fission products and other metal ions from waste solutions.

Thus, the objective of the present work was to intercalate dicyclohexano-18-crown-6 (DCH18C6) and exploit the advantage of the permanent charge present in the host clay layer for the favourable extraction of fission products. DCH18C6 has been chosen for intercalation in the present study because it exhibits a very high selectivity for strontium[16] over other crown ethers and as well as 18-crown-6. Extraction of these Sr, as well as Cs, by the intercalated material has been studied as a function of various parameters and the results are reported in this paper.

Experimental

Materials

All the reagents used were of analytical AR grade. Commercial bentonite was procured from M/s Sigma Enterprises, Chennai, India. The chemical composition of bentonite was found to be: 58.5% SiO_2, 10.4% Al_2O_3, 2.1% TiO_2, 1.3% FeO, 2.9% Fe_2O_3, 1.25% Na_2O, 0.6% K_2O, 3.7% CaO, 6.1% MgO. Loss on ignition was 14%. The cation-exchange capacity of bentonite was measured by the procedure reported earlier[17] and it was found to be 0.3 mequiv. g^{-1}. Radioactive isotopes $^{85+89}$Sr and ^{134}Cs were obtained from the Board of Radiation and Isotope Technology (BRIT), Mumbai, India. Dicyclohexano-18-crown-6 (DCH18C6) was procured from Aldrich, USA.

Intercalation procedure

The procedure for intercalation of DCH18C6 in bentonite was described elsewhere.[13] It involves converting bentonite into its homo-ionic sodium form by repeatedly equilibrating bentonite with 1.0 M NaCl. The product [bentonite(Na)] was washed thoroughly with water and dried at 333 K. Intercalation of DCH18C6 was performed by contacting 1 g of bentonite in this sodium form with a solution containing 1.96 g of DCH18C6 dissolved in 25 ml of acetonitrile and 10 ml of 1 M NaCl. The mole ratio of the sodium capacity of bentonite to the amount of crown ether taken for equilibration was about 1 : 20. After 7 days of equilibration, the mixture was filtered and washed with acetonitrile and water. The final product (Ben-Crown) was dried at 323 K under vacuum.

Characterization

Small-angle X-ray powder diffraction patterns of bentonite before and after intercalation was taken using a Phillips 1011 X-ray diffractometer with Cu Kα radiation at 40 mV voltage and 45 mA current. TG-DTA curves for Ben-crown and bentonite(Na) were recorded using a Mettler TGA/SDTA 851^e in the temperature range 25–600 °C at a heating rate of 10 °C min^{-1} in air. Microelemental CHNS analysis of the sorbent was determined using an Elementer Vario-EL. IR spectra was taken using a Bomem FTIR spectrometer, model 103.

Extraction studies

All the equilibration experiments are conducted at 300 K with a batch factor (V/m) of 200 ml g^{-1} unless otherwise noted. All the extraction experiments were performed in duplicate and the error in the measurements was found to be within ±5%. Extraction of cesium and strontium as a function of the concentration of nitric acid was studied by equilibrating 0.05 g of the sorbent with 10 ml of the solution containing the desired concentration of nitric acid spiked with either the ^{134}Cs or $^{(85+89)}$Sr tracer. After 24 h, the equilibration tube was centrifuged and an aliquot was taken from the supernatant. The radioactivity of the tracer present in the aqueous phase before and after equilibration was measured using a NaI(Tl) scintillation detector. The distribution coefficient and the amount of cesium or strontium extracted can be calculated using eqn. (1):

$$K_d(\mathrm{ml/g}) = \frac{A_i - A_f}{A_f}\left(\frac{V}{m}\right) \text{ or } \%\mathrm{Sorb} = \left(\frac{A_i - A_f}{A_i}\right)100 \quad (1)$$

where A_i and A_f are the initial and final radioactivity of ^{134}Cs or $^{(85+89)}$Sr. V (in ml) and m (in g) are the volume of the solution and the mass of the sorbent used for equilibration.

The rate of extraction of cesium and strontium as a function of its concentration was studied by the batch equilibration method. The experiment involved shaking 0.05 g of the sorbent with 10 ml of the solution containing the desired concentration of the metal ion spiked with the corresponding tracer. At various intervals of time the equilibration was stopped and the radioactivity of the supernatant was measured as described above.

The effect of the sodium ion concentration on the distribution coefficient of strontium was studied by equilibrating 0.05 g of the sorbent with 10 ml of the solution containing 0.1 M nitric acid, 1.14 × 10^{-5} M strontium ion spiked with $^{(85+89)}$Sr and the desired concentration of sodium nitrate. After 24 h the radioactivity of the supernatant was measured as described above.

The effect of metal ion concentration on the extraction equilibrium was studied by equilibrating 0.05 g of the sorbent with 10 ml of the solution containing the desired concentration of the metal ion, varied from 10^{-5} M to 10^{-2} M, spiked with the corresponding tracer present in 0.1 M nitric acid. The quantity of metal ion extracted was calculated from the radioactivity measurements.

The influence of temperature on the distribution coefficient was studied by equilibrating 0.05 g of the sorbent with 10 ml of the solution containing 0.1 M nitric acid and 1.14 × 10^{-3} M of either Cs^+ or Sr^{2+} spiked with the corresponding tracer at 300 K. The distribution coefficient was calculated using eqn. (1) and similar experiments were performed at various temperatures.

Results and discussion

Microelemental analysis of carbon and hydrogen present in Ben-Crown indicated the presence of 0.22 mmol of DCH18C6 in 1 g of bentonite. TG, DTG and DTA curves for Ben-Crown and bentonite(Na) are shown in Fig. 1. The weight loss occurring below 100 °C is attributed to the loss of water molecules present in the interlayer. The amount of water molecules present in Ben-Crown (3.6%) was found to be lower than in its precursor, bentonite (Na) (8.7%), which is in good agreement with the results reported by Ruiz-Hitzky *et al.*[12] This suggests that some water molecules originally present as part of the hydration sphere of cations in bentonite(Na) are displaced by crown ether molecules during intercalation. There is no weight loss in the temperature range 240–370 °C for bentonite(Na), whereas Ben-Crown shows an 8.3% weight loss, which could correspond to the loss of DCH18C6. This is also shown by the endothermic peak at 334 °C in the DTG pattern of Ben-Crown. An exothermic peak is obtained in the

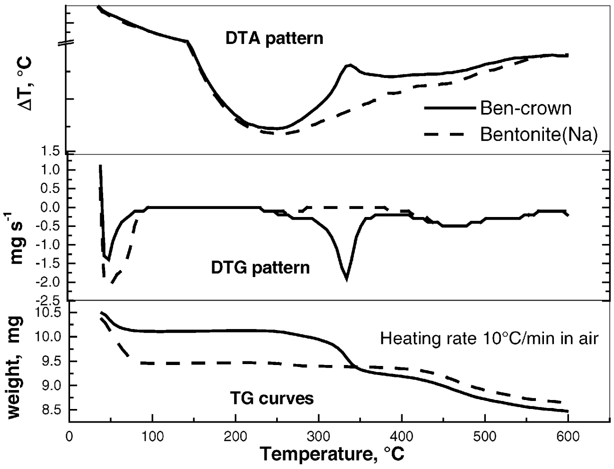


Fig. 1 TG, DTG and DTA curves for Ben-Crown and bentonite(Na).

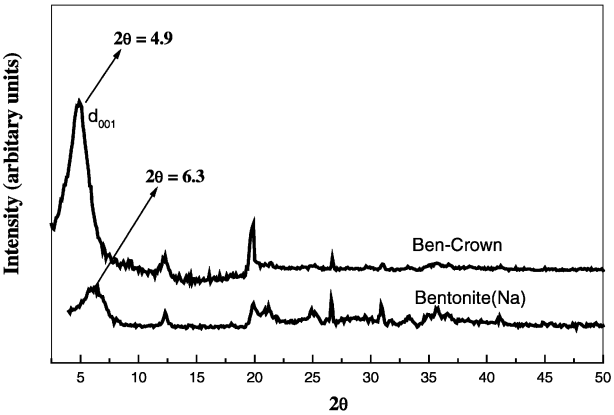


Fig. 2 X-Ray powder diffraction patterns of Ben-Crown and bentonite(Na).

DTA curve of Ben-crown (Fig. 1), which is due to the combustion of DCH18C6. Thus, 83 mg of DCH18C6 was found to be lost from one gram of Ben-Crown, indicating the presence of 0.22 mmol of crown ether per gram of the Ben-Crown, which agrees well with the C and H elemental analysis of the material. The weight loss above 450 °C is due to the dehydroxylation of the host lattice.[18]

It is interesting to note that only 70% of the sodium ions present in bentonite(Na) (capacity = 0.3 mmol g^{-1}) are thus complexed by the crown ether during intercalation. Due to steric hindrance, complete complexation of the sodium ions was not possible. The X-ray diffraction patterns of the intercalated bentonite and bentonite(Na) are shown in Fig. 2. A shift of the d_{001} peak from $2\theta = 6.3°$ in bentonite(Na) to $2\theta = 4.9°$ in Ben-Crown indicates that an increase in the basal *d* spacing from 1.42 nm to 1.81 nm occurs during intercalation, as illustrated in Scheme 1. The result obtained in the present study is in good agreement with the results of Ruiz-Hitzky *et al.*[12]

The IR spectrum of bentonite(Na) and Ben-Crown are shown in Fig. 3. It is seen that most of the IR absorption bands due to crown ether are obscured by the presence of O–H (arising from surface hydroxyl groups and water) and Si–O (matrix) stretching frequencies. However, a band at 2922 cm^{-1} due to the C–H stretching of crown ether is present only in Ben-Crown.

Table 1 shows the distribution coefficients (K_d) for cesium and strontium as a function of nitric acid concentration. It is seen that the K_d of both metal ions are higher when Ben-Crown is used as the sorbent in place of bentonite(Na). In contrast to crown ether,[5,7] an unusual extraction behaviour is observed at low nitric acid concentrations with Ben-Crown. The K_d values for both cesium and strontium were found to decrease with increase in the concentration of nitric acid. In comparison, extraction of strontium by DtBuCH18C6 impregnated[7] in XAD-7 gave a very low distribution coefficient of ~0.1 in 0.01 M nitric acid, which increased to ~100 in 3 M nitric acid. The present study shows the opposite trend (as compared to Horwitz *et al.*[7]) in which the K_d value for strontium decreases from 19 472 to 50 ml g^{-1} when the concentration of nitric acid is increased from 0.001 M to 1 M. Above 1 M the K_d value is further lowered. Similarly, the distribution coefficient of cesium decreases from 7382 to 44 ml g^{-1} as the concentration of nitric acid is increased from 0.001 M to 1.0 M. The extraction of metal ion by crown ether is generally governed by the following equilibrium:

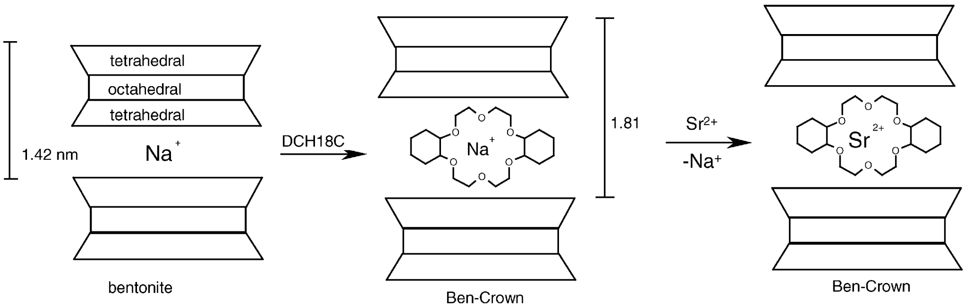
$$M^{n+}_{(aq)} + Crown_{(org)} + nNO_{3(aq)} \Leftrightarrow M(Crown)(NO_3)_{n(org)} \quad (2)$$

which gives

$$\log K_d = \log K + \log[Crown_{(org)}] + n\log[NO_3] \quad (3)$$

where *K* is the equilibrium constant for the extraction. Thus, the plot of logK_d *versus* log[NO_3] is expected to give a positive slope of 2 for strontium extraction and 1 for cesium extraction. Log–log plots for the extraction of cesium and strontium by Ben-Crown are shown in Fig. 4. A negative slope of −0.8 is obtained for the extraction of both cesium and strontium in the present study. Since bentonite(Na) exhibits an appreciable distribution coefficient at 0.001 M nitric acid, when this data point is omitted in the regression analysis, a slope of −1.0 is obtained for the extraction of the metal ions by Ben-Crown. These results indicate that unlike solvent extraction of cesium and strontium by crown ether, the co-ion (*i.e.*, nitrate in this case) plays a negligible role in governing the stoichiometry of the extraction. Ben-Crown is behaving more like a cation exchanger, in which the host bentonite contains the negative charge with the exchangeable sodium ion. The decrease in distribution coefficient with increase in nitric acid concentration can be attributed[19] to the competition of H^+ with cesium or strontium.

If an ion-exchange mechanism is believed to be operative for the extraction of strontium, then an increase in the



Scheme 1 Intercalation of crown ether in bentonite, leading to propping of the layers and the ion exchange behaviour of Ben-Crown.

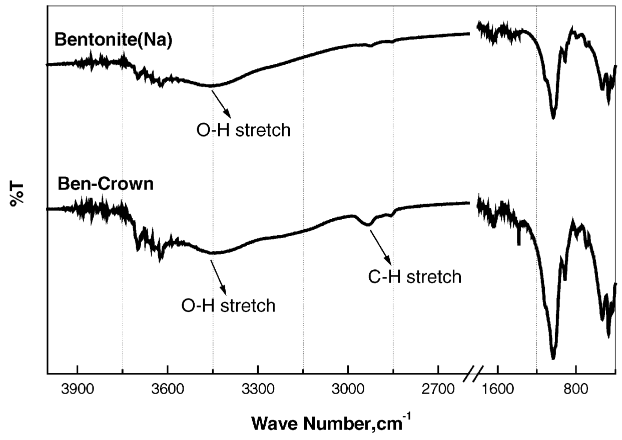


Fig. 3 IR spectra of Ben-Crown and bentonite(Na).

concentration of sodium ion present in the aqueous phase should decrease the K_d value and a plot of log[K_d] with log[Na^+] should give a slope of −2. Fig. 5 presents such a plot. It is observed that the variation of distribution coefficient is negligible, since the slope is only −0.02 when the concentration of sodium is increased from 0.001 M to 0.01 M. A rapid decrease in the distribution coefficient of strontium is observed above a sodium ion concentration of 0.01 M, but the slope is still only −0.5. Various explanations[20,21] offered for deviations from the expected slope have been given elsewhere. However, the results obtained from Fig. 5 indicate that the influence of sodium ion on the extraction of strontium is less than anticipated and the mechanism of extraction is still ambiguous. However, our study indicates that the extraction behaviour of DCH18C6, when it is intercalated in bentonite, is very different from those reported so far.[5–7]

Bentonites were reported to leach out Al^{3+}, Fe^{3+} and Mg^{2+} ions and also to undergo exchange with the interlayer cations when contacted with acid[22] over a period of time. To test the stability of Ben-Crown, about 1 g of the sorbent was contacted with 50 ml of 1.0 M nitric acid for about 70 h and the distribution coefficient of strontium was measured. A K_d of 1195 ml g^{-1} (equal to the original value) is obtained for the extraction of strontium in 0.1 M nitric acid, indicating that Ben-Crown is sufficiently stable when contacted with nitric acid during the experimental study and the extraction of metal is only by the crown ether present in bentonite.

The rate of extraction of cesium and strontium by Ben-Crown is shown in Fig. 6. Rapid extraction of both metal ions occurs in the initial stages of equilibration, followed by the establishment of an equilibrium after 150 min. It is important to note that DCH18C6 is more selective for strontium: the rate and amount of strontium extraction being higher than those observed for cesium. The Langmuir plot for the extraction of cesium and strontium[23] by Ben-Crown from 0.1 M nitric acid is shown in Fig. 7. A classical Langmuir equation governing the adsorption of metal ions on the sorbent phase as a function of metal ion concentration in solution phase is given by eqn. (4):

$$\frac{C_f}{C_s} = \frac{1}{K_L b} + \frac{C_f}{b} \quad (4)$$

where C_f is the equilibrium metal ion concentration (mmol l^{-1}), C_s is the amount of metal ion extracted (mmol g^{-1}), K_L is the Langmuir adsorption constant (l $mmol^{-1}$), which is a measure of the affinity of the sorbent for the metal ion, and b (in mmol g^{-1}) is the experimental capacity. Thus, the plot of C_f/C_s against C_f should result in a straight line (as is effectively observed in Fig. 7) and the magnitudes of b and K_L can be obtained from the slope and intercept of the plot.

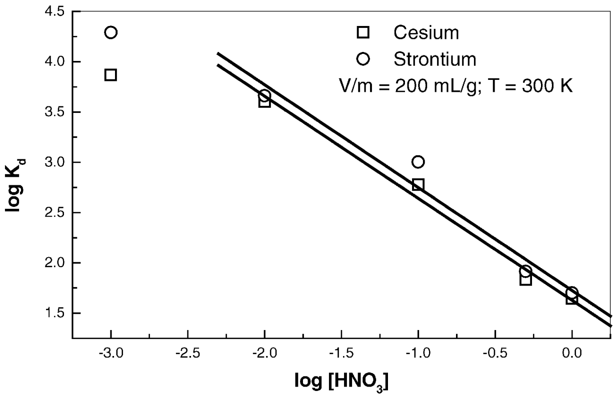


Fig. 4 Variation of logK_d with log[HNO_3] for the extraction of cesium and strontium on Ben-Crown.

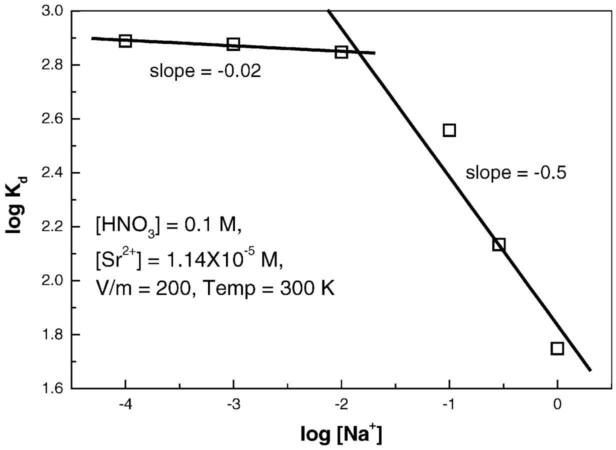


Fig. 5 Variation of logK_d with log[Na^+] for the extraction of strontium from 0.1 M nitric acid by Ben-Crown.

Table 1 Distribution coefficients of cesium and strontium on bentonite (Na) and Ben-Crown[a]

	K_d[b]/ml g^{-1}			
	Cs^+		Sr^{2+}	
[HNO_3]/ M	Bentonite (Na)	Ben-Crown	Bentonite (Na)	Ben-Crown
0.001	712	7382 (97.4)	920	19 472 (99.0)
0.01	20	4018 (95.1)	52	4580 (95.7)
0.1	2	599 (75)	7	1007 (84.5)
0.5	—	68 (25.3)	3	82 (29.1)
1	—	44 (17.9)	2	50 (20.1)

[a] ^{134}Cs, $^{(85+89)}Sr$ used as tracer, V/m = 200 ml g^{-1}, T = 300 K. [b] Values in parentheses indicates the percentage of extraction.

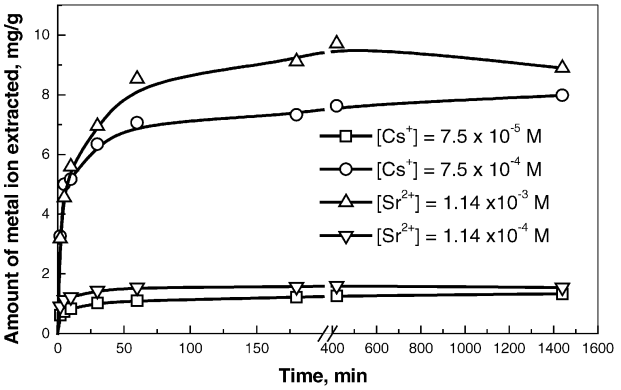


Fig. 6 Kinetics of the extraction of cesium and strontium by Ben-Crown.

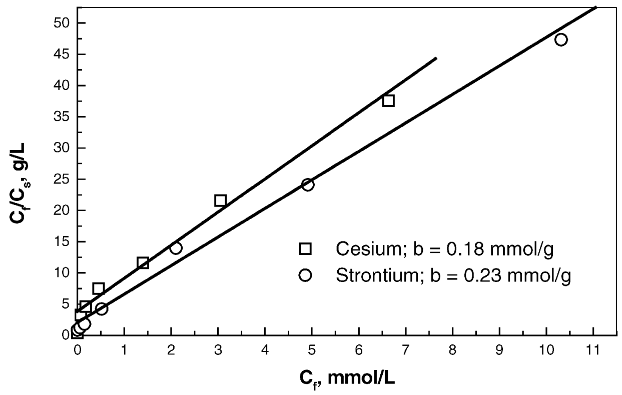


Fig. 7 Langmuir plot for the extraction of cesium and strontium by Ben-Crown from 0.1 M nitric acid.

A linear regression of the experimental data for the extraction of cesium and strontium by Ben-Crown yielded an experimental capacity of 0.18 mmol g^{-1} for cesium extraction and 0.23 mmol g^{-1} for strontium extraction. It is worthwhile to note that these capacity values are in close agreement with the theoretical capacity (0.22 mmol g^{-1}) obtained by CHNS analysis and TG-DTA curves. This close agreement is only possible when extraction is uniquely due to the crown ether present in bentonite. This conclusion that the extraction of fission product is only due to the intercalated crown ether and not due to other impurities in the host was verified by carrying out the extraction experiments simultaneously under identical experimental conditions on the intercalated material and the parent bentonite sample. It was observed that the parent sample did not exhibit any appreciable uptake (Table 1).

The standard enthalpy change for the extraction of cesium and strontium by Ben-Crown is related to the distribution coefficient by Van't Hoff's relation, eqn. (5):

$$\frac{\partial \log(K_d)}{\partial(1/T)} = \frac{-\Delta H^o}{2.303R} \qquad (5)$$

where R is the gas constant. The plot of $\log K_d$ *versus* $1/T$ is shown in Fig. 8. From the slope of the straight line the enthalpy change accompanying the extraction of cesium and strontium by Ben-Crown was found to be −6.4 and –4.5 kJ mol^{-1}, respectively. The enthalpy of the liquid–liquid extraction of strontium from 4.0 M nitric acid by DCH18C6 present in an alcohol mixture was reported[24] to be −11.8 kJ mol^{-1}, which is more exothermic compared to the present study. This could be due to the utilization of energy for the dehydration of Sr^{2+} before entering into the rigid matrix and for the diffusion of strontium towards the extraction sites in the bentonite phase.

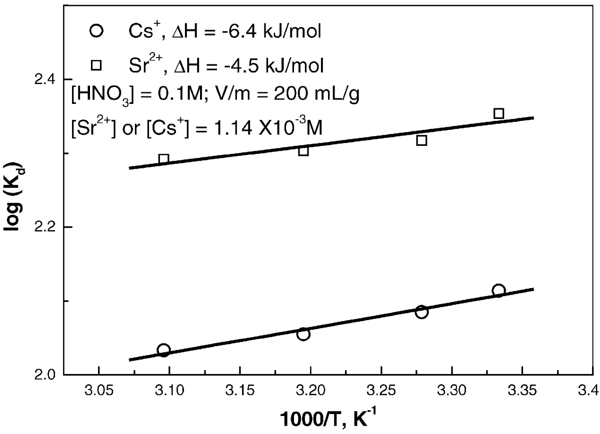


Fig. 8 Variation of $\log K_d$ with $1/T$ for the extraction of cesium and strontium from 0.1 M nitric acid by Ben-Crown.

Conclusions

DCH18C6 has been intercalated in bentonite and the product, Ben-Crown, characterized by various analytical techniques. Microelemental and TG-DTA analysis showed the presence of 0.22 mmol of crown ether present in a gram of Ben-Crown. Some water molecules present in bentonite(Na) were displaced by the crown ether during intercalation, followed by an increase of the interlayer distance by 0.39 nm in Ben-Crown. Unusually high extraction of cesium and strontium was observed at low nitric acid concentrations and in contrast to the extraction behaviour exhibited by crown ether, K_d values for both the metal ions decreased with increase in the concentration of nitric acid. Nitrate in the solution phase does not seem to influence the extraction behaviour; however, the distribution coefficients of cesium and strontium decreased with increase in sodium ion concentration. The mechanism of extraction by Ben-Crown is not clear from the present data and further studies are required to clearly elucidate it. The enthalpy change for the extraction of cesium and strontium by Ben-Crown was found to be −6.4 and −4.5 kJ mol^{-1}, respectively.

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References

1 (*a*) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017; (*b*) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb and J. J. Christensen, *Chem. Rev.*, 1985, **85**, 271; (*c*) A. H. Bond, M. L. Dietz and R. Chiarizia, *Ind. Eng. Chem. Res.*, 2000, **39**, 3442.
2 E. P. Horwitz, M. L. Dietz and D. E. Fisher, *Solv. Extr. Ion Exch.*, 1991, **9**, 1.
3 E. P. Horwitz, M. L. Dietz, H. Diamond, R. D. Rogers and R. A. Leonard, in *Chemical Pretreatment of Nuclear Wastes for Disposal*, ed. E. P. Schulz Horwitz, Plenum, New York, 1994, pp. 81–99.
4 M. Rodriguez, J. A. Suhrez and A. G. Espartero, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1996, **369**, 348.
5 E. P. Horwitz, M. L. Dietz and D. E. Fisher, *Solv. Extr. Ion Exch.*, 1990, **8**, 557.
6 Y. Kikuchi and Y. Sakamoto, *Anal. Chim. Acta.*, 2000, **403**, 325.
7 E. P. Horwitz, M. L. Dietz and D. E. Fisher, *Anal. Chem.*, 1991, **63**, 522.
8 R. M. Barrer, *Zeolite and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1978, p. 339.
9 E. J. Nowak, in *Scientific Basis for Nuclear Waste Management II*, ed. C. J. M. Northrup, Jr., Plenum Press-, New York, 1980, p. 403.
10 (*a*) A. Dyer, J. K. K. Chow and I. M. Umar, *J. Mater. Chem.*, 2000, **10**, 2734; (*b*) A. Chakir, J. Bessiere, K. E. Kacemi and B. Marouf, *J. Hazard. Mater. B.*, 2002, **95**, 29; (*c*) I. C. Bourg, A. C. M. Bourg and G. Sposito, *J. Contam. Hydrol.*, 2003, **61**, 29.
11 (*a*) B. Riebe, J. Bors and S. Dultz, *J. Contam. Hydrol.*, 2001, **47**, 255; (*b*) J. Bors, S. Dultz and B. Riebe, *Appl. Clay Sci.*, 2000, **16**, 1; (*c*) S. Dultz and J. Bors, *Appl. Clay Sci.*, 2000, **16**, 15; (*d*) J. Bors, S. Dultz and B. Riebe, *Eng. Geol.*, 1999, **54**, 195.
12 E. Ruiz-Hitzky and B. Casal, *Nature (London)*, 1978, **276**, 596.
13 (*a*) B. Casal, E. Ruiz-Hitzky and M. Serratosa, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2225; (*b*) P. Aranda, J. Galvan, B. Casal and E. Ruiz-Hitzky, *Electrochim. Acta*, 1992, **37**, 1573; (*c*) P. Aranda, B. Casal, J. J. Fripiat and E. Ruiz-Hitzky, *Langmuir*, 1994, **10**, 1207; (*d*) E. Ruiz-Hitzky, J. C. Galvan, J. Merino, B. Casa, P. Arandab and A. Jimenez-Moralesb, *Solid State Ionics*, 1996, **85**, 313.
14 (*a*) T. J. Pinnavaia, *Science*, 1983, **220**, 365; (*b*) R. Burch, *Catal. Today*, 1988, **2**(2–3), 1 (special issue on pillared clays); (*c*) R. S. Varma, *Tetrahedron*, 2002, **58**, 1235.
15 (*a*) A. Dyer and T. Gallardo, in *Recent Developments in Ion Exchange 2*, eds. P. A. Williams and M. J. Hudson, Elsevier Applied Science, London, 1990, p. 75; (*b*) P. Sylvester and A.

Clearfield, *Sep. Sci. Tech.*, 1998, **33**, 1065; (*c*) C. A. Papachristodoulou, P. A. Assimakopoulos, N. H. Gangas and D. T. Karamanis, *Microporous Mesoporous Mater.*, 2000, **39**, 367.

16 (*a*) B. A. Moyer, W. J. McDowell, R. J. Ontko, S. A. Bryan and G. N. Case, *Solv. Extr. Ion Exch.*, 1986, **4**, 83; (*b*) W. J. McDowell, *Sep. Sci. Tech.*, 1988, **23**, 1251; (*c*) M. L. Dietz, E. P. Horwitz and R. D. Rogers, *Solv. Extr. Ion. Exch.*, 1995, **13**, 1.

17 R. Cason and L. W. Reed, *Proc. Okla. Acad. Sci.*, 1977, **57**, 116.

18 (*a*) R. Green-Kelly, *Clay Miner. Bull.*, 1952, **1**, 221; (*b*) R. C. McKenzie, *Differential Thermal Analysis*, Academic Press, London & New York, 1970.

19 R. Chiarizia, E. P. Horwitz and M. L. Dietz, *Solv. Extr. Ion. Exch.*, 1992, **10**, 337.

20 R. Harjula, *Ph.D. Thesis*, University of Helsinki, Helsinki, Finland, 1993 (Reports in Radiochemistry Series 8/1993).

21 (*a*) J. Lehto and R. Harjula, *Sol. Extr. Ion Exch.*, 1987, **5**, 343; (*b*) J. Lehto, R. Harjula and J. Wallace, *J. Radioanal. Nucl. Chem.*, 1987, **111**, 297; (*c*) J. Lehto, R. Harjula and A.-M. Girard, *J. Chem. Soc., Dalton Trans.*, 1989, 101; (*d*) R. Harjula, J. Lehto, J. H. Pothuis, A. Dyer and R. P. Townsend, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1877.

22 (*a*) E. Srasra, *Appl. Clay Sci.*, 2000, **17**, 71; (*b*) R. V. Francisco, *Quim. Nova*, 2001, **24**, 345.

23 (*a*) M. V. Sivaiah, K. A. Venkatesan, R. M. Krishna, P. Sasidhar and G. S. Murthy, *Colloids Surf., A*, 2004, **236**, 149; (*b*) S. S. Kumar, M. V. Sivaiah, K. A. Venkatesan, R. M. Krishna, G. S. Murthy and P. Sasidhar, *J. Radioanal. Nucl. Chem.*, 2003, **258**, 321.

24 A. Kumar, P. K. Mohapatra, P. N. Pathak and V. K. Manchanda, *Talanta*, 1997, **45**, 387.