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Title:

**Silacrown ethers-clay intercalation materials: application in
potentiometric sensors **for detection of alkali-ions****

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Abstract

Dimethylsila-14-crown-5 (DMS14C5) and dimethylsila-17-crown-6 (DMS17C6) macrocyclic polyethers have been intercalated into montmorillonite layered silicates containing Li^+ , Na^+ or K^+ cations as exchangeable cations. XRD and FTIR spectroscopy offer information on the disposition of the macrocycle in the interlayer and accommodation of cations within the cavity of the polyoxyethylene ligand. ^{13}C , ^{29}Si and ^{23}Na solid-state NMR spectroscopy provides information about the replacement of water molecules from the hydration shell of interlayer cations by the macrocyclic ligand and confirms differences in the interactions depending on the nature of the ligand. The resulting montmorillonite intercalation materials have been tested as active phase of PVC electrodes for the development of potentiometric sensors, in a preliminary attempt to evaluate their electrochemical response towards alkali-metal ions in solution.

Keywords: silacrowns, crown-ethers, montmorillonite, clays, electrochemical sensors

1. Introduction

It is widely known the great tendency of crown-ethers and cryptands to form stable complexes with alkali metal ions in solution as discovered by Charles Pedersen, Donald Cram and Jean-Marie Lehn who received the Nobel Prize in 1987, their work being pioneering in the so-called Supramolecular Architectures.^[1-5] As we reported in 1978,^[6] intercalation of these macrocyclic compounds in layered silicates, such as smectite clay minerals and vermiculites, also leads to the formation of very stable ion-dipole complexes between the macrocyclic compounds and the interlayer exchangeable cations in the interlayer space of those silicates.^[7-9] It has been well established that the resulting intercalation compounds constitute an interesting class of organo-inorganic hybrid materials capable to act as efficient solid electrolytes^[10] and as active phase for composite ion-selective membranes.^[11] In this way, the intercalated macrocyclic compounds can be regarded as ligands for the interlayer cations, which are finally involved in interactions of variable strength allowing tunable ion-mobility materials.^[12-14]

On the basis of the abovementioned previous contribution, we report here the intercalation of related macrocyclic compounds such as silacrown-ethers in homoionic samples of montmorillonite (Figure 1a). Silacrowns are macrocyclic polyether compounds containing silicon heteroatoms in the oxyethylene ring of $R^1R^2Si(OCH_2CH_2)_nO$ ($3 < n < 7$) general formula. In the same way than analog crown-ethers, they also exhibit ability for complexing alkali-metal ions in aqueous solutions achieving new supramolecular entities showing elevated stability that may allow possible applications as active phase of electrochemical sensors due to the inner selectivity of these macrocycles towards complexation of the diverse alkali-cations.^[15-17] The immobilization of silacrowns following sol-gel procedures in silica based hybrid materials has been previously reported as a way for the development of ionselective electrodes showing good long-term stability and an appropriate electroanalytical response for potentiometric detection of alkali ions (i.e., Li^+ , Na^+ and K^+) in aqueous solutions.^[17] There are currently interest in the development of new systems for molecular recognition (detection and sensing)^[18-19] as well as in the use of layered materials, including clay minerals, for the development of new related functional nanoarchitectures.^[20-22]

In this work, the two following silacrowns represented in Figure 1b,c: dimethylsila-14-crown-5 (DMS14C5) and dimethylsila-17-crown-6 (DMS17C6), have been selected for

the preparation of Li^+ , Na^+ and K^+ -montmorillonite intercalation materials that have been further incorporated as active phase of PVC electrodes for the development of ion-sensing devices. The electrochemical response towards alkali-metal ions in solution of these immobilized silacrown compounds, will be here compared to similar materials prepared by intercalation of a crown-ether analog, the 18-crown-6 (18C6), which is one of the most representative crown-ethers, showing well established potentiometric response toward alkali cations.

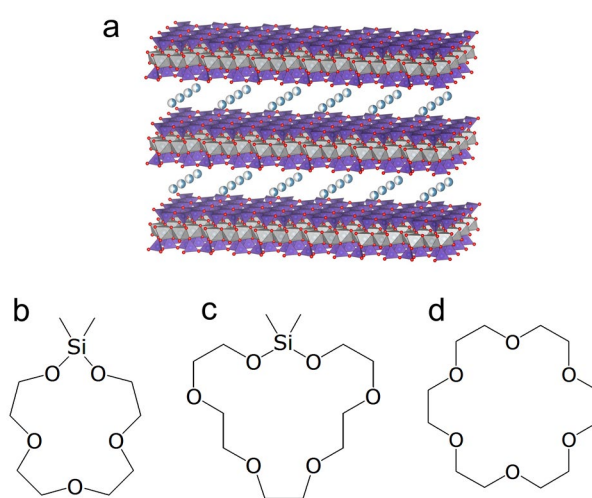


Figure 1. Structures of (a) the clay mineral montmorillonite,^[23] and the (b) DMS14C5, (c) DMS17C6 and (d) 18C6 macrocyclic compounds used in this work.

The complexation of interlayer cations in montmorillonite by intercalation of silacrowns could be also of interest in view to prepare new organic-inorganic hybrid materials where the presence of these macrocycles could be of potential interest in other applications such as phase transfer reactions^[24] and separation processes.^[25]

2. Experimental

Starting materials

Experiments of intercalation of macrocyclic compounds were performed on the purified $< 2 \mu\text{m}$ fraction obtained from Wyoming montmorillonite (SWy-Na) from Crook County, Wyoming (USA). This is a reference clay mineral with a cationic exchange capacity of 76.4 mEq/100 g, supplied by the Source Clay Minerals Repository of the Clay Minerals Society, Columbia, Missouri.^[26] Intercalation compounds for the solid state NMR characterization study were prepared using a natural montmorillonite free of

paramagnetic impurities known as Gel White (GW) from Georgia Kaolin Company, whose main features were described elsewhere.^[27] Purification and extraction of the natural clay from the raw mineral were carried out as reported elsewhere.^[28] The Na⁺ homoionic samples ([Si_{7.9}Al_{0.1}][Al_{3.06}Fe_{0.32}Mg_{0.66}](OH)₄O₂₀Na_{0.64}) were prepared by treatment of the < 2 μm fraction with 1 M NaCl solution for several times. The macrocyclic compounds used in this work (Figure 1b-d) were 2,2-dimethyl-1,3,6,9,12-pentaoxa-2-silacyclotetradecane (dimethylsila-14-crown-5; DMS14C5) and 2,2-dimethyl-1,3,6,9,12,15-hexaoxa-2-silacycloheptadecane (dimethylsila-17-crown-6; DMS17C6), as well as the 18-crown-6 macrocyclic polyether of (CH₂CH₂O)₆ formula, used for comparative purposes. All of them are commercial products provided either by Lancaster (silacrowns), and by ABCR (crown-ether) that have been here used as received without further purification.

Preparation of the intercalation compounds

The intercalation compounds result from the clay mineral prepared as films by slow evaporation of water from a 2% montmorillonite suspension in distilled water. The films were kept in contact with the corresponding solution of the macrocyclic compounds in methanol (Aldrich) (10⁻¹ M) during 24 h at room temperature, and then they were washed with anhydrous methanol to remove the macrocycles excess (i.e. the non-intercalated macrocycle), and finally they are air-dried at the air atmosphere at room temperature. Homoionic K⁺- (mont-K) and Li⁺-montmorillonite (mont-Li) films were prepared from the Na⁺-montmorillonite (mont-Na) films kept in contact with 1 M KCl (Riedel-deHaën) and LiCl (Merck) methanol solutions, respectively during 24 h. After washing and drying, the content in adsorbed macrocyclic compounds were determined by elemental microanalysis using a LECO instrument CHNS-932 model. For the NMR study, the samples were prepared following the same procedure but using Gel White (GW) instead of mont-Na.

Characterization

X-ray diffractograms (XRD) of oriented films were obtained with a Philips PW 1710 instrument equipped with a Cu cathode and Ni filter. Infrared spectra were recorded from the self-supported films using a Nicolet FTIR spectrophotometer 20SXC model operating in the 4000-200 cm⁻¹ region. The ²⁹Si and ¹³C NMR spectra were obtained using a Bruker MSL-400 spectrometer of high field (resonance frequency: 9.4 Tesla).

The TGA/DTA results were obtained under conditions of dynamic air flow (10 ml/min), with a heating speed of 10°C/min using a SEIKO model TG/DTA 320U.

Preparation and evaluation of electrodes modified with the intercalation compounds

Modified PVC membrane electrodes were prepared from the following components: 50 mg of poly(vinyl chloride) (PVC, high molecular weight from Fluka), 96 μ l of dibutyl phthalate (DBP, from M&B) and 750 μ l of tetrahydrofuran (THF, from Carlo Erba). The intercalation materials (50 mg) were incorporated to this mixture and homogeneous suspensions were obtained by stirring in a vortex. The modified PVC membranes were prepared by suspending 40 μ l of the mixture at the end of a polypropylene tube (diameter 2.5 mm) and allowing the solvent to evaporate for 24 h. The potentiometric membrane electrodes were finally constructed by filling the tube with a 10^{-3} M alkali metal chloride solution (NaCl, LiCl or KCl depending on the ion to be measured) as internal reference solution, and inserting a miniaturized homemade Ag/AgCl electrode in the tube as internal reference. Prior to measurements the modified PVC membrane electrodes were ion-conditioned in 0.1 M NaCl, LiCl or KCl aqueous solutions for 6 days. The measurements were carried out using a pH-meter Orion, Research Expandable Ion Analyzer EA920. A conventional two-electrode configuration was used where the silacrown-based PVC sensors acted as the working electrode and the potential outputs were measured against a commercial Ag/AgCl reference electrode from Crison.

3. Results and discussions

Intercalation of silacrowns

According to the XRD results (Figure 2), the basal spacing increase (Δd_L) (Table 1) of montmorillonite indicates the ability of silacrowns to intercalate all the selected homoionic samples of the layer silicate. The resulting intercalation compounds exhibit relatively good crystalline organization along the *c*-axis, as deduced from the presence of several *00l* rational orders in the XRD patterns (Figure 2). In a similar way to that reported for the intercalation of different crown-ethers in layered clays, the value of about 0.4 nm corresponds to the thickness of the macrocycles in a pseudo-planar disposition covering the interlayer surface of the phyllosilicates.^[6-7] As deduced from

the spectroscopic results (*vide infra*) the macrocycles act as ligands of the interlayer cations replacing the coordination shell of water molecules. In this way, these interlayer cations coordinate through ion-dipole interactions to oxygen atoms either from the macrocycles or from the basal planes of the silicates. The size of cations relative to the cavity size of the macrocycle is crucial for the accommodation of cations within the oxyethylene ligand.^[7] To propose intracrystalline molecular arrangements of macrocycles and cations, it should be also considered the possibility that the dehydrated cation may fit the pseudo-hexagonal holes of the smectite. For small and medium size cations, their partial inclusion within this type of structural cavities can produce a decrease of the Δd_L values with respect to bigger cations.

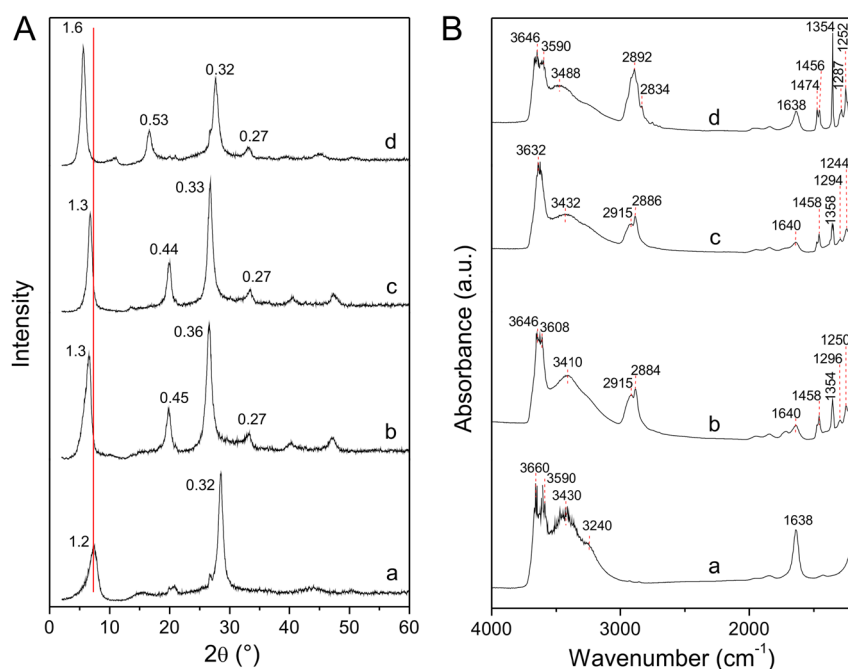


Figure 2. (A) XRD patterns and (B) FTIR spectra of starting mont-Na (a) and the three different intercalated compounds: DMS17C6/mont-Na (b), DMS14C5/mont-Na (c) and 18C6/mont-Na (d).

Table 1. Basal spacing increases (Δd_L), actual (X_m) and theoretical (X_t) intercalated amount (expressed in mmol per 100 g of clay) of DMS17C6, DMS14C5 and 18C6 macrocyclic ligands as a monolayer in the interlayer region of mont-Li, mont-Na and mont-K.

Interlayer cation (ionic radius)	Macrocyclic ligand								
	DMS17C6			DMS14C5			18C6		
	X_t	X_m	Δd_L (Å)	X_t	X_m	Δd_L (Å)	X_t	X_m	Δd_L (Å)
Li^+ ($r_i = 0.60$ Å)	66.5	49	4.5	76.1	37	4.2	63.2	44	5.8
Na^+ ($r_i = 0.95$ Å)	66.5	49	3.9	76.1	62	3.6	63.2	79	6.3
K^+ ($r_i = 1.33$ Å)	66.5	63	4.0	76.1	46	3.8	63.2	69	4.5

Table 2. FTIR bands (in cm^{-1}) assignment in the 4000-800 cm^{-1} region for the starting Na-montmorillonite and the intercalated macrocyclic compounds in this homoionic clay mineral.

mont-Na	DMS14C5/ mont-Na	DMS17C6/ mont-Na	18C6/mont-Na	Assignment
3660 3590 3430 3240	3632 3432	3646 3608 3410	3636 3488	$\nu_{\text{O-H}}$ (H_2O , M-OH silicate)
---	2915 2886	2915 2884	2852 2834	$\nu_{\text{C-H}}$ (Si-R) $\nu_{\text{C-H}}$ (-O-CH ₂ -CH ₂ -)
1638	1640	1640	1638	δ_{HOH} (H_2O)
---	1458	1458	1474 1456	δ_{CH_2} (Si-R)
---	1358	1354	1354	$\delta_{\text{CH}_2, \text{w}}$ (-CH ₂ -O-)
---	1294	1296	1287	$\delta_{\text{CH}_2, \text{t}}$
---	1244	1250	1252	$\delta_{\text{CH}_2, \text{w}}$ $\delta_{\text{Si-C}}$ (Si-CH ₃)
---	1203	1203	---	$\nu_{\text{as Si-O}}$ (SiOSi)
---	1124	1124	---	$\nu_{\text{s Si-O}}$ (SiOSi)
1190-890	1190-890	1190-890	1190-890	ν_{SiOM} (silicate)
851	849	845	843	$\nu_{\text{Si-O}}$ (silicate)
799	799	799	799	$\nu_{\text{Al-O-Al}}$ (silicate)

The molecular areas of the silacrowns, calculated from the molecular models, are 0.82 nm² and 0.94 nm² for DMS14C5 and DMS17C6, respectively. Taking into account the surface available in the interlayer space (ca. 750 m²/g),^[29] the maximum amount of silacrowns that can be intercalated in a monolayer arrangement is of around 75 and 65 mmol per 100 g of clay for DMS14C5 and DMS17C6, respectively. The experimental values of the intercalated amount of silacrowns deduced from the CHN elemental analyses are in the 40-60 mmol/100 g range, being in all the cases below the calculated amounts, which confirms therefore the planar disposition of macrocycle molecules in monolayer within the interlayer space of montmorillonite. The different models corresponding to possible dispositions of the silacrown macrocycles and the interlayer cations are schematically represented in Figures 3b and c.

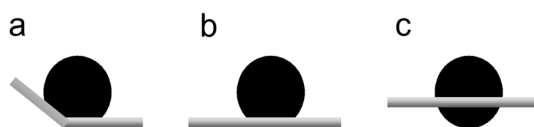


Figure 3. Schematic representation of structural models corresponding to possible dispositions of the macrocyclic compounds depending of the interlayer cation size (black spheres).

The corresponding values of Δd_L and the intercalated amounts obtained for the 18C6-montmorillonite compounds are in good agreement with data already reported.^[7, 30-31] In these intercalation compounds the content in 18C6 macrocyclic ligands can reach values of ca. 80 mmol/100g, *i.e.* overpassing the theoretical amount for the monolayer in a planar disposition of the macrocycle (ca. 65 mmol/100g). In this case the Δd_L values (ca. 0.6 nm) are higher than those found for the silacrowns, being proposed a molecular arrangement of the 18C6 ligand with a distorted conformation as indicated in Figure 3a.^[7, 30-31]

The FTIR spectra (Figure 2B) were registered from the same montmorillonite films before and after treatment with the macrocycles in solution. In Table 2 are tentatively assigned the IR absorption bands of the different spectra registered in the 4000-1200 cm⁻¹ region. In the same way as reported for crown-ethers and cryptand intercalations, the spectra of the silacrown-montmorillonite materials show a strong decrease in intensity of the bands assigned to water molecules belonging to the hydration shell of

cations in the starting samples, after intercalation of the macrocycles. This feature and the modification of bands associated with the macrocycles agree with the assignment of ligand-cation interactions in the interlayer space of the silicate.^[7, 30-31]

On the other hand, significant information about the structural arrangement of the intercalated macrocyclic compounds has been deduced from IR dichroism studies. As it is well known, this type of studies represent a useful tool for precise determination of the relative orientation of intercalated species into layered host lattices, such as smectite clay minerals.^[32] Certain crown-ethers show a marked dichroic effect of the IR $\nu_{\text{CH}_2, \text{r}}$ band, that appears in the 800-900 cm^{-1} region, when they are intercalated in layered silicates.^[7, 30] This effect allows clarifying the orientation of the ligand relative to the silicate layers, corroborating, in some cases, the structural features based on the XRD patterns. Assuming that the $-\text{CH}_2-$ groups of silacrowns are distributed uniformly around the cavity of the ligand, a parallel orientation of the macrocyclic ring relative to the silicate layers means that the dipole moment changes associated with $\nu_{\text{CH}_2, \text{r}}$ vibrations had to be perpendicular to the plane defined by the silicate (Figure 4). Consequently, the corresponding IR absorption bands (Figure 5) must increase in intensity with an increase in the angle between the incident beam and the plane defined by the oriented aggregated sample (positive dichroism). Figure 5 shows the FTIR spectra of the different ligands, DMS17C6, DMS14C5 and 18C6 intercalated in Na-montmorillonite registered at different orientations (0° and 40°) of the incident IR beam and the plane defined by the silicate. It can be observed that the bands present a positive dichroic effect for both intercalated silacrowns, i.e. the DMS17C6/mont-Na and DMS14C5/mont-Na complexes. However, in the intercalated 18C6 macrocycles the intensity of the bands remains invariable after modification of the incidence angle of the IR beam (Figure 5C). In conclusion, these results indicate that both silacrowns are intercalated adopting a parallel disposition of the macrocyclic cavity with respect to the silicate layers, whereas 18C6 crown-ether adopt another configuration, in good agreement with the basal spacing values deduced from XRD patterns.

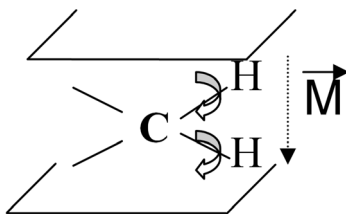


Figure 4. Schematic representation of dipolar moment vector (M) associated with methylene groups belonging to a polyoxyethylene macrocyclic compound oriented in planar arrangement with respect to the silicate layers, explaining the dichroic effect of the γ_{CH_2} (r) vibration band.

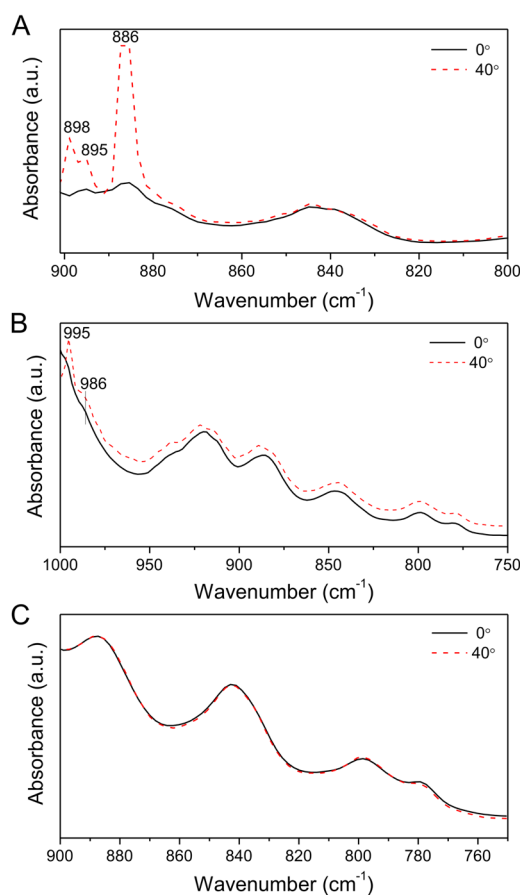


Figure 5. Dichroic effect in the γ_{CH_2} IR vibration band of different macrocyclic compounds intercalated into mont-Na: (A) DMS17C6, (B) DMS14C5, and (C) 18C6.

The ^{13}C , ^{23}Na and ^{29}Si solid state Nuclear Magnetic Resonance (NMR) characterization of smectites-macrocyclic compounds was carried out in intercalation compounds prepared from the Na^+ -exchanged Gel White (GW) instead of Wyoming montmorillonite as the former is practically free of paramagnetic Fe(III) species, which allows the correct acquisition of NMR spectra. The ^{13}C and ^{23}Na spectra of the neat GW

clay and those of the ones corresponding DMS14C5/GW, DMS17C6/GW, and this last sample after heating at 200°C for 1 hour in air are collected in Figure 6.

In the ^{13}C NMR spectra (Figure 6A), the characteristics signals of C atoms of ether functionalities present in the silacrowns are observed between 60 and 70 ppm,^[33] though it is not possible to distinguish the signal corresponding to the methyl groups expected to be close to 0 ppm and observed with low intensity in other hybrid materials prepared from silacrowns within a polysiloxane matrix.^[17] The signals are clearly asymmetric, indicating the presence of various environments for the C from oxyethylene units, and in the spectrum of the DMS14C5/GW intercalation compound there are clearly defined two peaks, which could be consequence of interactions with the interlayer cations.^[34] After thermal heating of the DMS17C6/GW compound for removal of water molecules the spectrum shows only slight differences. In the ^{29}Si NMR spectra (not shown) it is observed only the characteristics peaks of the silicate host matrix in the -95 ppm region, making no possible further information in relation to the macrocyclic compound whose signal should appear close to 0 ppm.^[33]

Concerning the ^{23}Na NMR spectra, it is important to be aware of the key role of water present in the sample as the signals associated with this nucleus are highly sensitivity to oxygen coordination and, therefore, with the water molecules environment in montmorillonite and other 2:1 related phyllosilicates.^[31, 35-36] In this way, the signal of Na^+ ions in Laponite[®] (a synthetic saponite) layered clay showing structural arrangement similar to the montmorillonite here used, shifts from values around 0 ppm, when the interlayer Na^+ ions are fully hydrated (two layers of water), to -9 ppm, when the Na^+ cations are simultaneously associated with a monolayer of water and the oxygens of the silicate sheet, and event to more negative chemical shift values, observing the appearance of various signals when the content in water decrease and there are interaction with oxygens from the two silicate sheets.^[31, 36] It has been reported that when crown-ethers and other polyoxyethylene species are intercalated in smectites they coordinate the interlayer Na^+ ions replacing water molecules introducing changes in the chemical shift of the Na nucleus with the intercalated species.^[9, 31] From the spectrum in Figure 6B it is confirmed that GW montmorillonite shows a slightly asymmetric and sharp signal centered at -14.5 ppm, indicating that Na^+ cations are in interaction with a monolayer of water and the oxygens belonging to one of neighboring

silicate sheets. As occurs in crown-ethers, after intercalation of DMS14C5 and DMS17C6 silacrowns the signal slightly shifts towards more negative values (-15.2 and -16.8 ppm for DMS14C5 and DMS17C6, respectively) as water molecules are removed and then the cations are in direct interaction with the intercalated macrocyclic compound.^[31] In the same way, if these macrocycles behave as crown-ethers it could be also proposed stronger interactions in the case of the DMS17C6, being explained by the possibility of interaction with five oxygen atoms instead of four.^[9] After removal of water molecules, two signals are observed in the spectrum of the DMS17C6/GW (Figure 6B d), the one ascribed to Na⁺ associated with the macrocycle now appearing at -20.0 ppm, whose change towards upfield chemical shift indicates a stronger interaction.^[9] It is also observed the presence of a signal at -30.2 ppm, characteristics of Na⁺ cations in interaction with the oxygen atoms of the silicate layers.^[31]

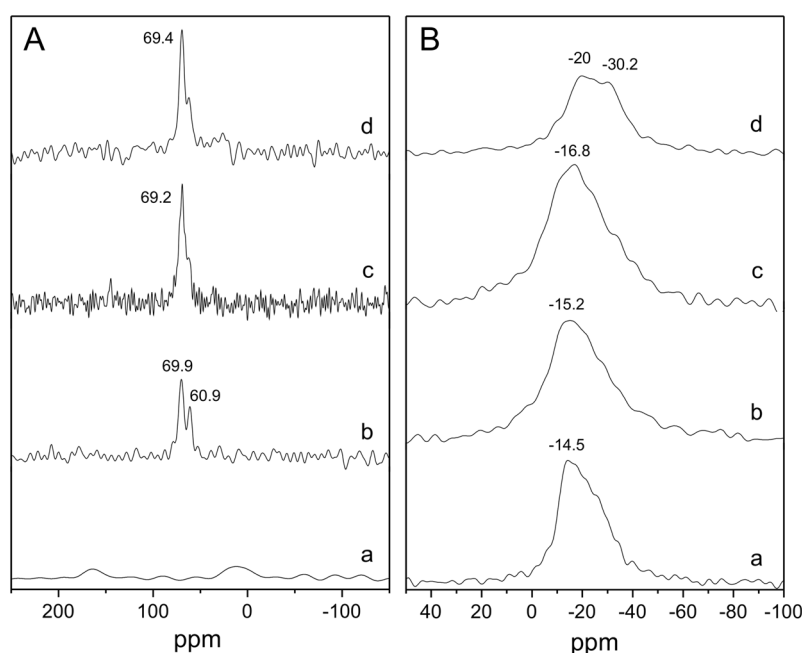


Figure 6. (A) ¹³C and (B) ²³Na NMR spectra of (a) GW Na-montmorillonite and the intercalation compounds prepared from it: (b) DMS14C5/GW (c) DMS17C6/GW, and (d) the heating product of DMS17C6/GW at 200°C for 1 hour in air flux.

The DTA and TGA curves of the silacrown-montmorillonite intercalation compounds show different mass loss steps in the 20-1000°C temperature range (Figure 7). The mass loss between room temperature and about 150°C associated with an endothermic event corresponds to desorption of water molecules physically adsorbed on the clay mineral

host. Clearly the content of water is lower in the intercalation compounds (typically in the 2.5-4 % range) than in the neat clay (approx. 7%), confirming the hydration shell of interlayer cations are replaced by the intercalated macrocyclic compounds. The mass loss in the 200°C to 450°C temperature range is associated with the removal of the intercalated macrocyclic compounds by combustion as indicated by the presence of two exothermic effects and values close to the organic content determined from CHN elemental analysis (Table 3). There are small differences in the total mass loss and the characteristics of the exothermic events with the nature of the intercalated macrocycle though they show similar profiles especially in the case of the two silacrown-based hybrids. The last endothermic event around 670°C corresponds to the loss of water by dehydroxylation of the silicate host matrix.

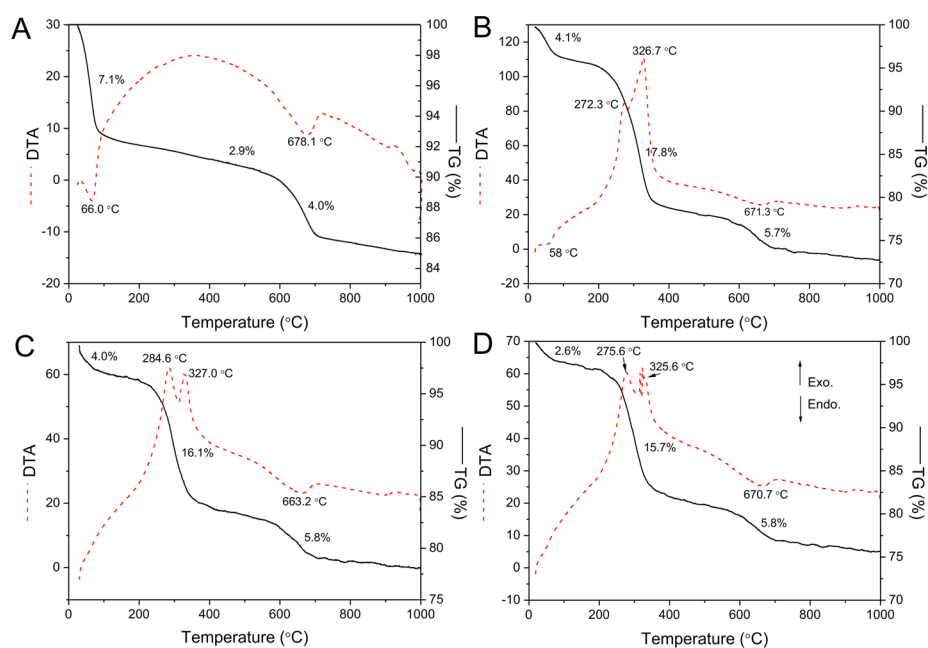


Figure 7. TGA (solid line) and DTA (dashed line) curves of (A) the starting mont-Na and the intercalation compounds (B) 18C6/mont-Na, (C) DMS14C5/mont-Na, and (D) DMS17C6/mont-Na.

Table 3. Mass loss in the 200-450°C temperature range determined from TG curves and total content of macrocycles determined from CHN elemental analysis.

Intercalation compound	Mass loss from TG (g/100g)	Macrocycle content (g/100g)
DMS17C6/mont-Na	15.7	15.6
DMS14C5/mont-Na	16.1	13.4
18C6/mont-Na	17.8	17.2

Electroanalytical performance of silacrown/montmorillonite based PVC electrodes

As mentioned above, silacrowns have the ability to form stable molecular complexes with alkali or alkaline earth salts in solution as well as in the solid state^[15, 37] and such a feature can be profited to develop sensor devices for the electroanalytical determination of these types of ions. For instance, a vinyl-modified silacrown was incorporated in PVC membranes, in order to develop a potentiometric ion-selective electrode for sodium ions.^[16] DMS17C6 was also entrapped within a polysiloxane matrix derived from the 3-(trimethoxysilyl) propyl methacrylate (MAPTS) and tetramethoxysilane (TMOS) alkoxysilanes doped with graphite particles, in order to develop bulk-modified potentiometric electrodes.^[17] In this case, the sensor did not show specificity for a unique cation, but it was promising for integration in arrays of non-specific electrodes whose responses are evaluated by artificial intelligence methods. The intercalation materials here prepared by silacrowns complexation of clay interlayer cations in montmorillonite can be also proposed as ion-sensing phase in potentiometric electrodes. In this way, PVC membranes are modified with the silacrown-based intercalation compounds, in which the silicate counterpart may have a protective effect on the ionophore, avoiding its leaching from the membrane. The intercalation compounds prepared from Na-montmorillonite have been employed for this evaluation. The resulting modified PVC membrane electrodes, including DMS17C6/mont-Na DMS14C5/mont-Na and 18C6/mont-Na, have been tested in aqueous solutions of LiCl, NaCl or KCl in concentrations ranging from 10^{-6} to 10^{-1} M. As shown in Figure 8, the resulting potentiometric curves show a positive slope in the linear range, as expected for the determination of cationic species, although in all cases the tested electrodes provide subnerstian responses, giving slope values below the theoretical value of +59 mV/decade for monovalent cations.

The slope values, detection limits and the range of linear response obtained by each sensor in the different measured solutions are summarized in Table 4. These results are in agreement with the known selectivity of the studied macrocyclic compounds towards a given alkali metal ion, which is due to the size of the macrocycle cavity. Although the values are similar for all the studied systems, the DMS17C6/mont-Na based electrode shows a slightly higher slope value of +42.7 mV/decade and a better detection limit in the measurement of Na^+ , around 1.05×10^{-4} M. In contrast, when the electrode includes the crown-ether 18C6, the measurement of K^+ gives rise to a slope value of 43.1 mV/decade that is only slightly higher than that obtained for Na^+ , but it shows a lower

detection limit of 7.5×10^{-5} M. This fact is in agreement with the higher affinity of the 18C6 crown-ether for potassium ions, since the ionic radius of K^+ fits well with the cavity of this macrocycle.^[38] The DMS14C5/mont-Na based electrode provided the best detection limit (8.7×10^{-5} M) in the measurement of Na^+ , but similar slope values were obtained for Na^+ and K^+ . Given that this macrocycle shows a smaller cavity than DMS17C6, the good sensitivity of the DMS14C5 based sensor towards K^+ was not expected. This fact could be attributed to the contribution of the non-selective cation exchange ability of the silicate, which could reduce the selectivity related to the cavity size of the silacrown. These results suggest that improvements in the preparation of the intercalation materials as well as in the electrode construction are required to enhance the electroanalytical performance of the resulting sensors. Nevertheless, these preliminary studies confirm that the intercalation of silacrowns and related compounds in the interlayer galleries of montmorillonite does not affect the ion-complexation ability of macrocycles, being possible to apply the resulting compounds as the ion-sensing phase of potentiometric electrodes for determination of alkali metal ions, preferably taking part in electrode arrays combined with artificial intelligence methods that can benefit from the partial selectivity of these electrodes to different ions.^[39]

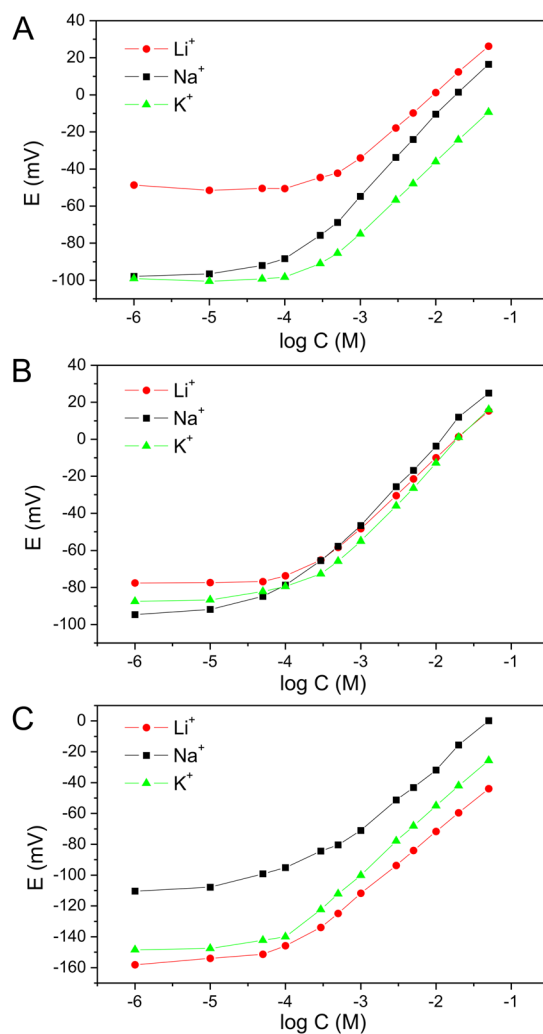


Figure 8. Potentiometric response of the PVC electrodes modified with (A) DMS17C6/mont-Na, (B) DMS14C5/mont-Na and (C) 18C6/mont-Na towards K^+ , Li^+ , and Na^+ cations.

Table 4. Slope values in the linear response range and detection limits of different PVC electrodes based on the macrocycle/mont-Na intercalation compounds.

	Detection Limit / M			Slopes Value /mV dec ⁻¹			Linear range / M		
	Li^+	Na^+	K^+	Li^+	Na^+	K^+	Li^+	Na^+	K^+
DMS17C6 /mont-Na	3.3×10^{-4}	1.05×10^{-4}	2.3×10^{-4}	35.7	42.7	39.1	$5 \times 10^{-4} - 5 \times 10^{-2}$	$5 \times 10^{-4} - 5 \times 10^{-2}$	$5 \times 10^{-4} - 5 \times 10^{-2}$
DMS14C5 /mont-Na	1.9×10^{-4}	8.7×10^{-5}	1.8×10^{-4}	38.7	41.7	41.6	$5 \times 10^{-4} - 5 \times 10^{-2}$	$3.2 \times 10^{-4} - 2 \times 10^{-2}$	$5 \times 10^{-4} - 5 \times 10^{-2}$
18C6 /mont-Na	1.2×10^{-4}	1.6×10^{-4}	7.5×10^{-5}	40.7	42.1	43.1	$3.2 \times 10^{-4} - 5 \times 10^{-2}$	$5 \times 10^{-4} - 5 \times 10^{-2}$	$10^{-4} - 5 \times 10^{-2}$

4. Conclusions

The basic outline already followed for the preparation of intercalation compounds in layered silicates involving diverse macrocyclic compounds belonging to the crown-ether family, can be successfully applied for the synthesis of analogous silacrown-ethers/clay nanoarchitectures. In this way, the DMS14C5 and DMS17C6 silacrowns have been easily intercalated in homoionic montmorillonites from methanol solutions, the resulting hybrid materials showing the inner characteristics introduced by these macrocycles as complexing ligands for alkali-metal ions. From the XRD patterns and the study of dichroism associated to infrared absorption bands it can be deduced that both macrocycles adopt a planar disposition on the interlayer space of the silicate. Such a disposition is different to that shown by the conventional analog crown-ether (18-crown-6), which can adopt a distorted arrangement when it is intercalated. From the NMR solid-state spectroscopy study it has been confirmed the replacement of water molecules from the hydration shell of interlayer cations by the intercalated ligands. Moreover, differences in the chemical shift of the ^{23}Na NMR signals in DMS14C5 and DMS17C6 intercalation compounds confirms the existence of interactions between the macrocycle and the interlayer cations.

These intercalation materials have been preliminarily tested as PVC-based electrodes suitable for the potentiometric determination of alkaline cations in aqueous solutions. These sensors show similar behavior (e.g. detection limit values) than conventional 18-crown-6, and also a close sensitivity towards the three tested alkaline cations with comparable slope values, which would give rise to interference when measuring in mixed solutions. Selectivity studies or the optimization of the PVC membrane composition will be necessary to evaluate the practical usefulness of these silacrowns-clay electrodes. The sensors would be also suitable for integration in electrode arrays combined with artificial intelligence methods, which can evaluate their potentiometric responses even when interference occurs.

It can be postulated that silacrowns, as lower polar macrocycles showing lower solubility than analog crown-ethers, can represent an advantage disfavoring the leaching of this active phase when used in electrodes for detection of cations in aqueous solutions. Finally, it should be signaled the opportunity of application of these new hybrids in other fields. For instance, the use as phase transfer catalysts of silacrowns^[24] could be here profited as supported systems where the clay substrate, usually inert in

organic reactions, could offer a relatively high exposure of the immobilized macrocycle and facilitating its recovery after reaction. Another possible application could be as stationary phase in liquid chromatography, taking into account that polymeric silacrowns have been successfully tested as capillary modified systems showing polarity and selectivity characteristics comparable to those of Carbowax 20M.^[25]

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GRAPHICAL ABSTRACT

