microelectrodes in order to determine the average potential drop per gap.

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Poly(ethylene oxide)–Silicate Intercalation Materials

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Intercalation of poly(ethylene oxide), PEO, into 2:1 charged phyllosilicates (montmorillonite and hectorite) has been investigated. A model for PEO–silicate compounds based on the preservation of the helical structure of the polymer is postulated. The results of IR, NMR, and X-ray diffraction studies support this hypothesis. The resulting materials show good chemical and thermal stability, improving the characteristic ion conductivity of the parent silicates. Typical conductivity values associated with the motion of the intracrystalline cations contained in the poly(ethylene oxide)/montmorillonite materials ranges from 10^{-7} to 10^{-4} S cm^{-1} for PEO/Na^+–montmorillonite compounds (400–600 K, measured in a direction parallel to the silicate layers).

Introduction

The ability of poly(ethylene oxide), PEO, to act as solid solvent for different metal salts giving polyelectrolyte materials of great interest in various electrochemical applications, such as solid-state batteries, electrochromic devices, sensors, etc., is widely known.[1–6] Among the factors controlling the ion mobility, the crystallinity of polymers and the nature of the counterion appear to be the most influential features. In this way, inorganic materials such as NASICON or alumina are combined with polymeric oxyethylene compounds giving PEO composite systems with improved mechanical properties and, in some cases, enhancing the inner conductivity of PEO complexes.[7–9]

Conventional PEO salt complexes exhibit ionic conductivity based on both anionic and cationic mobility (ion-pair transport), which can impose limitations for various applications. The capability of certain layer silicates to intercalate a large variety of organic compounds,[10,11] including oxyethylene compounds as crown ethers[12–14] and poly(ethylene glycol),[15–17] opens ways to insert PEO into 2:1 charged phyllosilicates, such as montmorillonite and hectorite. The structure of these silicates consists of layers built up by two tetrahedral silica sheets and a central octahedral sheet of magnesia or alumina (Figure 1). Isomorphous substitutions, mainly in the octahedral sheets, give a negative charge located in the layers which is compensated by cations (exchangeable cations) in the interlayer space. Thus, oxyethylene compounds as intercalates can act as ligands of these interlayer cations, giving rise to stable complexes. These properties have been used to prepare PEO–silicate intercalation materials that we describe in this work.

Preliminary results concerning Li^+-montmorillonite intercalated compounds have been published in a previous note[18] which showed promising properties for PEO–composite materials. The silicate matrix constitutes the counterion, and consequently in PEO–silicate materials the conductivity is exclusively restrained to cations of the interlayer region ($t_- = 0$). In addition to this behavior, the layer structure imposes a marked anisotropy, the conductivity in the direction parallel to the *a,b* plane being about 10^3 times greater than the corresponding conductivity determined along the *c* axis, as we reported previously.[18,19]

This paper concerns the study of the intercalation process of PEO (average molecular mass 10^5) in different homoionic montmorillonites and hectorites, describing their structural features and the properties related to its ionic conductivity.

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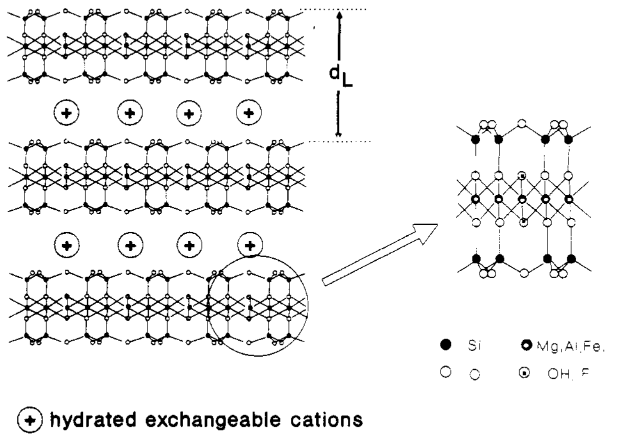

Figure 1. Schematic representation of a 2:1 charged phyllosilicate.

Experimental Section

Materials and Methods. Montmorillonite from Upton (WY) was supplied by Ward's Natural Science Establishment Inc. Cation exchange capacity: 91 mequiv/100 g. Homoionic M^{n+}–montmorillonite samples (M^{n+}: Li^+, Na^+, K^+, NH_4^+, Ca^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+}, $CH_3CH_2CH_2NH_3^+$) were prepared by treatment of the <2-μm-diameter fraction of the mineral particles with the corresponding cation chloride solutions (1 N, for monovalent cations; 0.5 N for polyvalent cations). After complete exchange, the samples were washed with distilled water until free from chloride by the $AgNO_3$ test. Hectorite from Hector (CA) was prepared as homoionic M^{n+}–hectorite following the same procedure described above for montmorillonite samples. In this case, it was necessary to eliminate carbonate impurities by treatment with 0.5 N acetic acid solution. Homoionic hectorite samples were used for NMR spectroscopy due to their low paramagnetic element content.

Polyoxyethylene compounds, $(-CH_2-CH_2-O-)_n$ formulas, of different average molecular weight (poly(ethylene glycol) MW = 6×10^2 and 4×10^3; poly(ethylene oxide) MW = 10^5 and 6×10^5), were supplied either by Merck or by Aldrich Chemical Co., Inc. The solvents used (Carlo Erba, RPE-ACS grade) were dried over molecular sieves.

Powders or self-supporting films (ca. 50 mg) of M^{n+}–silicates were immersed for a variable time (2–5 days) into 25 mL of polyoxyethylene compounds solutions in dry acetonitrile (4.4 g/L, i.e., 0.1 M expressed in terms of oxyethylene units, OEUs) at room temperature (ca. 298 K). The resulting products were repeatedly washed with (i) dry acetonitrile, in order to remove the nonintercalated physisorbed polymer, and (ii) methanol, to desorb the remaining acetonitrile, and then dried under vacuum at about 350 K, until complete disappearance of the solvents as revealed by IR spectroscopy.

The intercalated compounds were characterized by XRD (Philips PW 1710 instrument with a Cu anode and Ni filter), ^{13}C and ^{23}Na MAS NMR spectroscopy (Bruker MSL spectrometer, resonance frequencies 100.63 and 105.85 MHz, respectively), thermal analysis (TGA, DTG and DTA (STATON 750 equipment)), elemental microanalysis (Perkin-Elmer 240C microanalyzer), and IR spectroscopy (Perkin-Elmer 580B double-beam spectrophotometer, and Nicolett 20F far-IR vacuum spectrophotometer). Some experiments of thermal treatments of PEO–silicate materials were carried out in a conventional Pyrex glass cell for IR studies allowing exposure to vacuum (10^{-3} Torr).

The electrical conductivity was measured in the 300–700 K temperature range with a Solartron 1174 frequency response analyzer connected to a Solartron 1286 electrochemical interface. Applied signal amplitude was 100 mV in the nominal frequency range 10 mHz to 0.5 MHz. Pellets were made by pressing the samples (films) at 700 MPa: in this way the system is preferentially orientated, the current flux being either perpendicular (30–40-μm thickness) or parallel (2-mm thickness) to the plane defined by the layered materials, i.e., the *a,b* plane. The pellets were placed in a specially constructed cell, that allowed temperature control and maintenance of a dry nitrogen atmosphere during the measurements. Two identical electrodes are formed by sputtering of a silver and chromium mixture over the two opposite flat surfaces of the samples (for perpendicular measurements) or over two sides of the rectangular samples (for parallel measurements). The current was collected by means of platinum grids pressed against the two selected electrodes.

The adsorption isotherms were carried out by treatment of 25 mg of either Na^+– or Ba^{2+}–montmorillonites in an airtight flask with 20 mL of poly(ethylene oxide) (PEO of MW = 10^5) in acetonitrile solutions, ranging from 10^{-5} to 10^{-1} M (expressed in terms of oxyethylene units) at 298 ± 0.1 K placed in a constant-temperature air-bath. The selected time was 1 week, which largely exceeds the time necessary to reach the equilibrium. Afterward, the samples were washed with dry acetonitrile to eliminate excess polymer, and finally polymer content was determined by chemical microanalysis.

Microcalorimetric determinations were performed at 298 ± 0.01 K in a LKB 2107 adsorption microcalorimeter. About 40 mg of Na^+–montmorillonite is placed in the microcalorimetric sorption cell, and a flow of solvent (methanol or acetonitrile) is passed through the sample until the equilibrium temperature is reached. Then, the poly(oxyethylene) (MW = 4×10^3) dissolved either in acetonitrile or in methanol (10^{-2} M, referred to OEUs), is pumped to the sample (adsorption reaction). In the same way, at equilibrium, i.e., when no net heat is evolved or adsorbed, the pure solvent is pumped through the intercalated compound to produce the desorption of the physisorbed polymer. The energy involved in these processes is determined by comparison of the calorimetric response to previous electrical calibrations. The corresponding enthalpy values are determined from the energy balance between adsorption and desorption energies, taking into account the amount of intercalated polymer found from the elemental microanalysis of the resulting samples.

Results and Discussion

(1) Intercalation of PEO. Preliminary series of experiments to intercalate PEO (MW = 10^5) into Na^+–montmorillonite (as self-supporting films), were carried out using different polar solvents (H_2O, MeOH, acetonitrile, mixtures 1:1 of H_2O/MeOH and MeOH/acetonitrile). The nature of solvents is crucial to facilitate the insertion of organic materials between the silicate layers, the polarity of the medium being a determining factor for intercalations.[10,11] The high polarity of water causes swelling of Na^+–montmorillonite provoking the cracking of the films. Methanol is not suitable as a solvent for high molecular weight PEO, whereas water/methanol mixtures appear to be as useful for intercalations, although the cracking of the resulting materials is frequently observed. PEO intercalated compounds derived from the homoionic M^{n+}–montmorillonite and M^{n+}–hectorite, can be satisfactorily obtained using anhydrous acetonitrile or MeOH/acetonitrile mixture as solvents.

The resulting PEO–silicate materials show good stability toward treatment with different solvents (acetonitrile, methanol, ethanol, water, etc.), in experiments carried out at room temperature for long time periods (>24 h). In addition, the lack of PEO replacement by organic compounds having high affinity toward the parent silicate, such as dimethyl sulfoxide and crown ethers, indicates again the high stability of PEO-intercalated compounds. On the other hand, treatment with salt solutions provokes the replacement of the interlayer cations without loss of PEO. For instance, Na^+ ions in PEO/Na^+–montmorillonite are easily replaced by NH_4^+ or $CH_3(CH_2)_2NH_3^+$ ions, after treatment (2 h) at room temperature with aqueous solution of their chloride, perchlorate and thyocianate salts (1 N solutions), in a reversible process.

Experiments carried out using poly(oxyethylenes) of different chain length, from MW = 6×10^2 to MW = 6×10^5 show intercalation rates in Na^+–montmorillonite which vary inversely with the average molecular weight of the polymers (Table I). The maximum amount of intercalated

Table I. Adsorbed Amounts[a] of Different Average Molecular Weight Poly(oxyethylene) Compounds (PEGs and PEOs) in Na^+-Montmorillonite after 3 and 7 days of Treatment in Acetonitrile Solutions (0.1 M, Expressed in OEUs)

time of treatment (days)	av mol mass			
	6×10^2	4×10^3	1×10^5	6×10^5
3	513	464	170	145
7	537	642	706	375

[a] (mequiv of OEU/100 g)

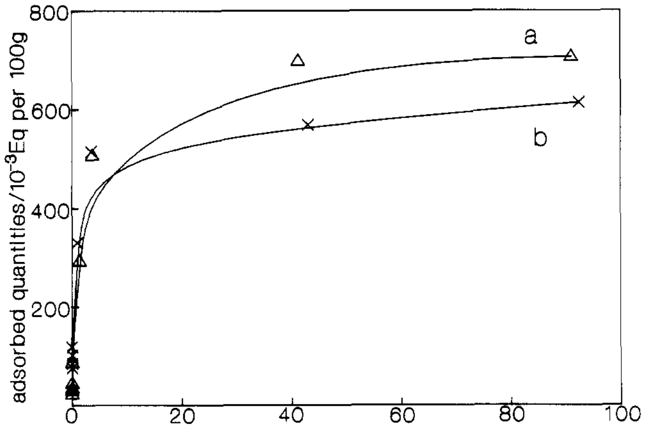

Figure 2. Adsorption isotherm at 298 ± 0.05 K of PEO from acetonitrile solutions. (a) Na^+–montmorillonite; (b) Ba^{2+}–montmorillonite.

poly(oxyethylene) compounds of high molecular weight is found for PEO of MW = 10^5. One can consider that the largest poly(oxyethylene) compounds are too large to be homogeneously arranged in the intracrystalline region of a phyllosilicate with a particle size distribution <2 μm, and consequently its diffusion is strongly limited giving composite materials with segregated phases.

Adsorption Isotherms. The experimental conditions adopted for preparation of PEO–silicate intercalation materials is based on results deduced from the PEO adsorption isotherms in M^{n+} montmorillonites. Figure 2 shows the adsorption isotherms at 298 ± 0.1 K from acetonitrile solutions of PEO (MW = 10^5) on different cation exchanged montmorillonites (Figure 2 shows isotherms on Na^+- and Ba^{2+}-exchanged montmorillonites which have been selected as examples). They fit the L-type isotherms according to the Giles et al.[20] classification for solid–liquid interface adsorption processes. The slope drops sharply to zero at full surface coverage, this being characteristic of processes with high adsorbate–adsorbent affinity. In the case of samples treated with the lowest concentrations of polymer, the adsorption of poly(ethylene oxide) is practically complete, and consequently, both small and large polymer chains are indistinctly adsorbed. The X-ray diffraction patterns of these samples show an increase in the crystal order of the intercalated compound when the concentration of polymer increases. The best ordered phases correspond to the "plateau" points. Nevertheless, if the equilibrium concentration is higher than 10^{-1} M, then several peaks assigned to the crystalline polymer are added to those of the intercalation compounds in the X-ray diffraction pattern. This excess of PEO, adsorbed on the external surface of the silicate particles, can be eliminated by prolonged washing.

Table II. Values of the Increase of Interlayer Distances (Δd_L),[a] Amounts of Intercalated PEO (x_m), and OEU/Interlayer Cation Ratio in M^{n+}-Montmorillonites

M^{n+}	Δd_L (Å)	x_m (mequiv of OEU/100 g)	OEU/cation ratio
Li^+	7.6	620	6.8
Na^+	8.0	706	7.7
K^+	8.0	684	7.5
NH_4^+	8.3[b]	803	8.8
$PrNH_3^+$	7.5	557	6.1
Ca^{2+}	5.1[c]	429	9.4
Ba^{2+}	7.8	613	13.5
Al^{3+}	8.1[b]	536	17.7
Cr^{3+}	7.9[b]	586	19.3

[a] Average interlayer distances as determined from 001 X-ray reflections; $\Delta d_L = d_L - 9.6$ Å. [b] Δd_L corresponding to the intercalated phase coexisting with the nonintercalated parent silicate. [c] Δd_L corresponding to a regularly stratified material.

Table II shows the maximum values (x_m) of adsorbed PEO in different homoionic montmorillonites. These values are in the 430–700 mequiv of OEU/100 g range, depending on the nature of the interlayer cation, the highest values corresponding to the monovalent cation exchanged montmorillonites. It is important to note that the interactions between oxyethylene units and ions in conventional PEO–salt complexes produce a closely packed coil of chains.[4,21] It is reasonable to assume a similar behavior for PEO–interlayer cations interactions. Typical values in the 600–700-mequiv range of intercalated oxyethylene units (OEU) per 100 g of monovalent ion-exchanged silicate are deduced from the elemental carbon analysis. So, the OEU/M^+ ratio is approximately 7, which is in the range usually selected for conventional solid electrolytes based on PEO–salt complexes.[1,4] In 2:1 charged phyllosilicates the surface area accessible to organic intercalates is about 760 m^2/g, and for M^+-montmorillonites the area available is 73.4 $Å^2$ per cation.[22] The projected area of seven OEUs (average OEU/monovalent interlayer cation ratio; see Table II) calculated for a helical structure of the polymer is around 72 $Å^2$. Thus, practically all the interlamellar silicate surface is covered by a monolayer of PEO entities in a close-packing arrangement.

Microcalorimetry. The thermodynamic behavior of complexing reactions of poly(ethylene oxide) with metal salts in homogeneous media has been investigated by Buschmann.[23] These reactions show enthalpy values close to zero for a large variety of cations in experiments carried out with salts dissolved either in methanol or in aceonitrile. We have found that the intercalation of PEO in a Na^+–montmorillonite both from methanol and from acetonitrile solvents constitutes a heterogeneous process of exothermic character. The enthalpies, related to one adsorbed oxyethylene unit, are −4.3 (from methanol) and −3.2 kJ/mol (from acetonitrile), respectively. It is difficult to determine if the main energetic effect corresponds to PEO–interlayer cation interactions, because other contributions (layer expansion, van der Waals contacts between the silicate sheet and PEO chains, etc.) could be also involved. Nevertheless, we can suppose that PEO–interlayer cation associations are of significant importance in the total energetic balance, as was observed in the intercalation of some poly(oxyethylene) macrocyclic compounds (crown ethers) and also in homoionic 2:1 charged silicates. Highly exothermic reactions are found when these strong cation

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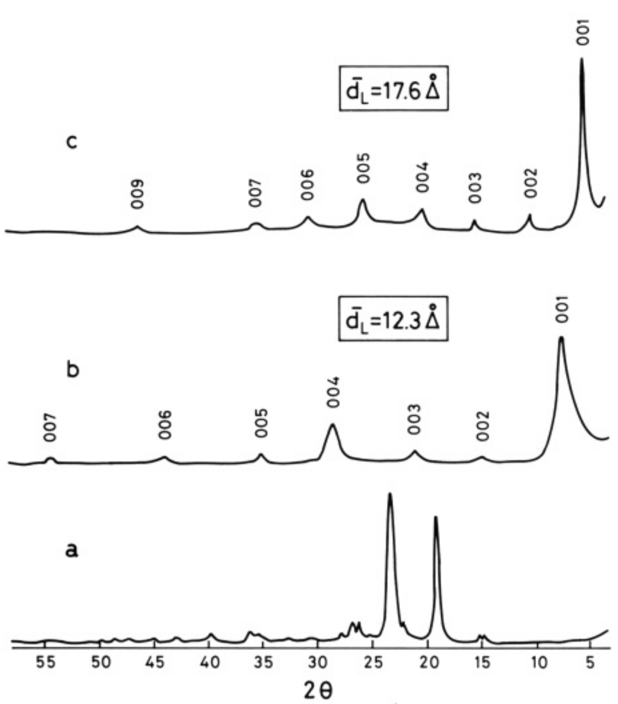

Figure 3. X-ray diffraction patterns of (a) pure PEO; (b) hydrated Na^+–montmorillonite, and (c) PEO/Na^+–montmorillonite compound.

complexing agents intercalate those silicates, the most important contribution being related to the crown ether–cation interactions.[24]

(2) Characterization. *X-ray Diffraction.* Figure 3 shows the XRD patterns of Na^+–montmorillonite and its PEO intercalation compound, selected as examples, together with the corresponding diffractogram of crystalline PEO. The intercalation of PEO is clearly inferred from the X-ray diffraction data. The interlayer distances (c lattice spacing) are deduced from the d_{00l} spacings, which are obtained using the first rational orders (usually from 7–10 orders) corresponding to the 00*l* reflections. If the polymer is regularly intercalated, the d_{00l} values are close to 17.5 Å in comparison with 12 Å found in the starting host silicate (hydrated sample containing a monolayer of H_2O). Thus, taking into account the thickness of the layer (about 9.5 Å), the increase of the interlayer distance (Δd_L) is near 8 Å, which corresponds to the thickness of the intercalated polymer.

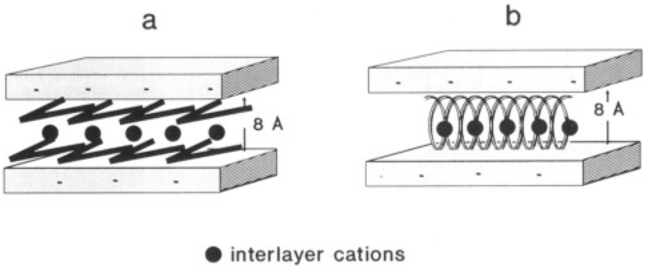

Figure 4. Schematic representation of PEO intercalation models in phyllosilicates: (a) double-layer planar zigzag disposition; (b) helicoidal conformation of PEO chains.

As mentioned above (Table II), PEO/M^{n+}–montmorillonite intercalated materials with $n = 1$ (n = interlayer cation charge), show well-ordered 001 reflections in the X-ray diffraction patterns (except for PEO/NH_4^+ montmorillonite), whereas for $n = 2$ and $n = 3$, interstratified materials are obtained (except for PEO/Ba^{2+}–montmorillonite). The nonordered phases show two groups of peaks, corresponding both to those reflections of the parent nonintercalated silicate and to those reflections assignable to the intercalated compound. The interstratified materials contain an appreciable quantity of residual water molecules coordinated to the interlayer cations, as evidenced by IR spectroscopy. Di- and trivalent interlayer cations having high hydration energy prevent the direct oxyethylene group cation association. The shifts observed for the characteristic IR frequency bands (stretching and bending) suggest hydrogen bonding interactions between the water belonging to the coordination shell of the interlayer cations and the oxyethylene units of the polymer. The existence of water bridges was also observed by Parfitt and Greenland[16] in low molecular weight poly(ethylene glycol)–montmorillonite intercalated compounds, prepared from polymer water solutions. Thus, it appears that hydrogen bonding interactions involving interlayer cations and oxyethylene groups results in incomplete water replacement by the polymer, giving rise to interstratified materials. In addition, POE/NH^+–montmorillonite compounds are also interstratified materials where hydrogen bonding interactions between ammonium ions and oxyethylene units are evidenced by IR spectroscopy.

Well-ordered PEO–silicate intercalated compounds are formed when water molecules belonging to the coordination shell of low hydration energy interlayer cations are replaced by the polymer. In a similar way that occurs in crown ether–phyllosilicate intercalations[12–14,25] the oxyethylene units are directly coordinated to the cations. In PEO–silicate compounds the interlayer expansion values are close to 8 Å (Table II), which are compatible with two possible polymer arrangements in the interlayer region (Figure 4). First, we can suppose a planar zigzag conformation of PEO chains (Figure 4a), similar to that observed in some Hg salt/PEO complexes.[26–28] In this case, two layers of polymer are needed to produce the 8 Å of expansion, as occurs in the intercalation of ethylene glycol molecules in homoionic montmorillonites.[29,30] The second possibility corresponds to a preservation of the PEO helical conformation in the interlayer region, as illustrated in Figure 4b, with the axis of the polymer chain oriented parallel to the silicate layers, i.e., to the *a*,*b* plane, and a theoretical layer expansion also close to 8 Å. This arrangement is compatible with interlayer cations more or less placed into the polymer helix, depending on their size. The last situation seems more plausible, because only one "plateau" is observed in the adsorption isotherms, and it can be assigned to a PEO monolayer. Two "plateaux" would be expected if a zigzag double polymer layer was intercalated; ethylene glycol intercalations belong to this type of isotherm with two steps.[29,30] In addition, the proposed structure involving helical conformations is compatible with the structural parameters of crystalline $[P(EO)_nM^+]X^-$ complexes[3] and is also supported by IR and NMR spectroscopies.

Thermal Analysis. Figure 5 shows the TGA and DTA curves recorded in the 300–1000 K range (under N_2 at-

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Table III. IR Vibration Frequencies and Its Assignation for PEO, PEO/Metal Salt Complexes, and PEO/M^{n+} Montmorillonite Compounds

PEO/Li^+ mont[a]	PEO/Na^+ mont[a]	PEO/Ba^{2+} mont[a]	18C6/Ba^{2+} mont[a,c]	PEO (10^5)[a]	PEO–NaSCN[a,d]	PEO–RbSCN[a,d]	assignation[e]
3625 (s)	3625 (s)	3625 (s)	3630 (s)				ν_{OH} (silicate)
3430 (m)	3440 (w)	3425 (m)					ν_{OH} (H_2O, silicate)
3260 (sh)	3269 (sh)	3250 (sh)					
2910 (m)	2915 (m)	2910 (m)	2930 (m)	2940–2800[b]			
2870 (m)	2875 (m)	2880 (m)	2900 (m)	2735 (w)			ν_{CH} (–CH_2–)
				2695 (w)			
1645 (vw)	1647 (vw)	1645 (vw)	1630 (vw)				δ_{HOH} (H_2O, silicate)
1469 (m)	1470 (m)	1465 (m)	1480 (m)	1466 (m)	1466 (m)	1464 (m)	δ_{CH_2} (asym)
1454 (m)	1455 (m)	1455 (m)	1455 (m)	1453 (m)	1450 (m)	1447 (m)	
1353 (m)	1360 (sh)			1359 (m)	1350 (s)		δ_{CH_2} (w) sym
	1352 (m)	1353 (m)	1360 (s)	1342 (m)	1340 (s)	1347 (s)	asym
1298 (m)	1294 (m)	1298 (m)	1300 (m)	1283 (m)	1287 (m)	1285 (m)	
1280 (w)	1274 (w)	1290 (m)			1275 (w)		δ_{CH_2} (t) sym
			1265 (m)		1260 (m)		asym
1247 (m)	1248 (m)	1250 (m)		1240 (m)	1238 (s)	1246 (s)	
975–1175 (vs)	975–1175 (vs)	975–1175 (vs)	975–1175 (vs)				ν_{SiO} (silicate)
940 (m)	947 (m)			957 (s)	955 (s)	953 (s)	
				946 (m)	945 (s)		
848 (m)	846 (m)	845 (m)		842 (s)	850 (m)	844 (m)	δ_{CH_2} (r)
					832 (m)		
					824 (m)		

[a] All frequency values expressed in cm^{-1}. [b] A very broad and strong band centered at 2890 cm^{-1}. [c] From ref 32. [d] From ref 36. [e] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

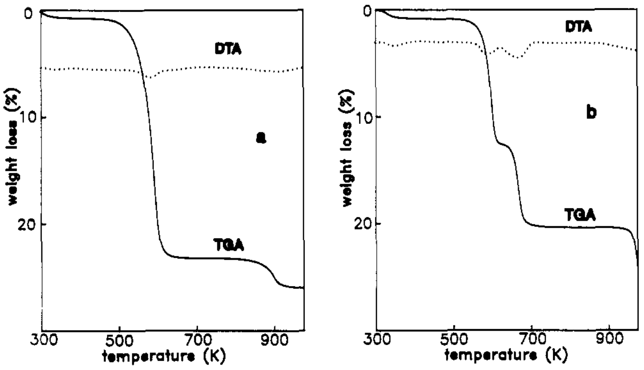

Figure 5. TGA and DTA curves in the 300–1000 K temperature range (obtained under N_2 atmosphere) of PEO/Na^+–montmorillonite (a) and PEO/Ba^{2+}–montmorillonite (b) intercalation compounds.

mosphere), corresponding to the selected examples of PEO/M^{n+}–montmorillonites compounds (M = Na^+ and Ba^{2+}). The two intercalated compounds, both show a small weight loss (<1%) at about 270 K, assigned to the elimination of remaining water; this value is much less than the value found for the starting homoionic montmorillonites (≈10%). Near 600 K intercalated organic matter starts to be lost in one or two steps for sodium or barium silicate intercalation compounds, respectively. This corresponds to a complete PEO elimination (23.1% and 20.0% of weight loss, respectively) in agreement eith the initial organic content determined by microanalysis (24.1% and 21.3%, respectively). The total weight loss for the sample heated in absence of oxygen corresponds to loss of 97% of the PEO, and an endotherm peak at 661 K can be correlated with the polymer pyrolysis.

The DTA data show endothermic effects attributed to the pyrolysis of the intercalated polymer. It is known that pure PEO can have an additional thermal effect, consisting of an endothermic peak close to 340 K corresponding to its melting point.[31] Contrarily to "conventional" PEO salt complexes, in the intercalated compounds the endothermic signal associated with the melting point of PEO is not observed, as a result of a different PEO aggregation state. In those samples containing an excess of PEO (intercalated and physically adsorbed on the external particle surfaces), DTA curves show a peak at 339 K corresponding to the melting point of crystalline PEO, together with three peaks (also endothermic signals) in the 575–625 K temperature range, which are associated with pyrolysis processes of PEO in different environments.

IR Spectroscopy. The replacement of the natural hydration sphere of the interlayer cations produced by the intercalation of PEO is evidenced by IR spectroscopy. A representative sample is illustrated in Figure 6, showing the IR difference spectrum obtained by subtracting the IR Li^+–montmorillonite film spectrum from the IR spectrum of this sample treated with PEO (Figure 6a). In this spectrum, one can see in the "negative absorbance" region the bands corresponding to the ν_{OH} and the δ_{HOH} vibrations of water molecules in the original starting silicate, indicating the loss of these molecules as a consequence of the insertion of PEO. In the "positive absorbance" region, the observed IR absorption bands correspond to the characteristic vibrations of the intercalated polymer, although compared to the IR of pure PEO (Figure 6b), some changes in the stretching and deformation vibration bands of the methylene groups are observed. In general, a similar spectroscopic behavior was found when strong complexing agents, such as macrocyclic polyethers (crown ethers and cryptands) were intercalated.[12,13,32] In this case, the IR spectroscopic changes mainly observed in deformation vibration bands (1200–1500-cm^{-1} region, Table III) were related to interactions between interlayer cations and electron lone pairs belonging to adjacent oxygen atoms of the oxyethylene ligands.

Concerning the stretching vibrations bands, the broad $\nu_{CH}(CH_2)$ band centered at 2890 cm^{-1} in pure PEO (Figure 6b), is resolved into two well-defined bands of moderate intensity when the polymer is intercalated (Figure 6a). The associated frequencies (approximately 2910 and 2875 cm^{-1}, respectively) are insensitive to the nature of the interlayer cations, as indicated in Table III. In addition

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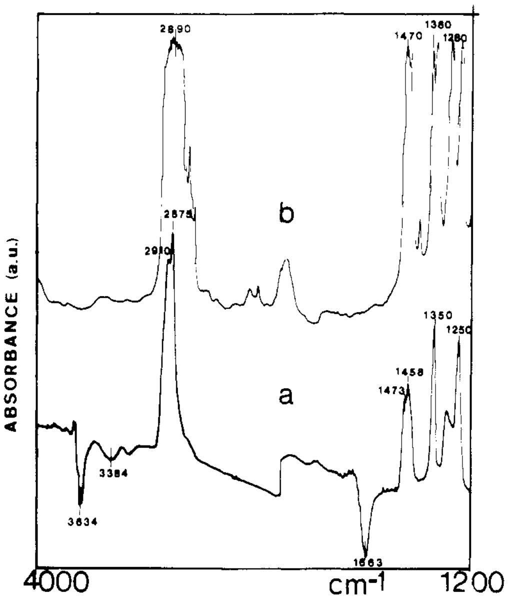

Figure 6. (a) IR difference spectrum (4000–1200-cm^{-1} region) obtained from a same Li$^+$–montmorillonite film before and after intercalation of PEO. (b) IR spectrum of pure PEO (4000–1200-cm^{-1} region).

to these small frequency changes, some shape modifications are also observed depending on the nature of the interlayer metal ion. Both types of changes were described for crown ether intercalations and interpreted in terms of different degrees of interaction between cations and oxyethylene groups[32].

Vibrational studies of pure PEO and PEO/metal salt complexes in the 1500–500-cm^{-1} region allowed the proposal of different polymer chain conformations.[33-37] The analysis of CH_2 deformation bands of O–$(CH_2)_2$–O groups reveals trans or gauche conformations, and consequently it was possible to ascribe a helical structure for PEO/alkaline-metal salt complexes, or alternatively, a planar zigzag conformation in some PEO/Hg salt complexes. In the last case the helical structure is lost, and a characteristic IR band at 1322 cm^{-1}, assigned to $\delta_{CH}(CH_2)$ vibrations of O–$(CH_2)_2$–O groups in the trans conformation, is observed.

In PEO intercalation compounds the assignment (Table III) of bands appearing in the 1500–800-cm^{-1} region are in good agreement with the spectral behavior observed for PEO/alkaline-metal salt complexes, suggesting a gauche configuration and showing that the matrix structure of PEO is preserved after intercalation. In particular, the presence of the two bands close to 945 and 850 cm^{-1} assigned to rocking CH_2 modes,[36] observed in the IR spectra of PEO-intercalated complexes, as well as in PEO–salt complexes, supports the structural model that we propose (Figure 4b). In addition, appreciable shifts of wagging (1350, 1360 cm^{-1}) and twisting (1295, 1280, 1250 cm^{-1}) vibration modes are of comparable magnitude in both types of complexes, PEO–alkaline salt or PEO–silicate compounds. These changes are also dependent on the nature of the associated cation (Table III).

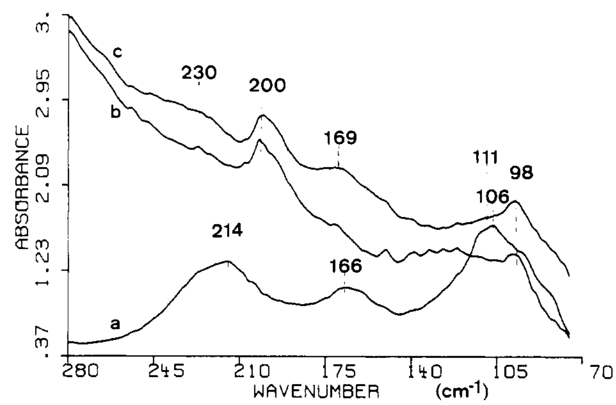

Figure 7. Far-IR spectra (280–70-cm^{-1} region) of pure PEO (a), Na$^+$–montmorillonite (b), and PEO/Na$^+$–montmorillonite (c) compounds.

The ν_{CO} stretching modes involving C–O–C entities that should be observed in the 1200–900-cm^{-1} region[36] are screened by the very intense ν_{SiO} stretching vibration bands (silicate framework), restricting further information.

Far IR spectra of PEO–silicate compounds could be an useful method to probe polymer-cation interactions. Figure 7 shows the IR spectra in the 280–70 cm^{-1} region of (a) pure PEO, (b) Na$^+$–montmorillonite, and (c) PEO/Na$^+$–montmorillonite compound. It is known that PEO bands observed at 214, 166, and 106 cm^{-1} change after association of the polymer with metal ions. Thus, in PEO/Na$^+$X$^-$ complexes these characteristic bands, assigned to C–O–C bending and C–O or C–C rotational motions coupled to the cation motions, appear in the 266–240 (sh), 170–180 (sh), and 102–107 (w) cm^{-1} ranges, depending on the nature of the counterions.[36] In the PEO/silicate compound, these bands are observed as broad and low intensity bands at 230, 169, and 111 cm^{-1}, indicating a similar behavior to that observed for PEO–salt complexes. The bands at 200 and 98 cm^{-1} present in PEO/silicate compounds can be assigned to vibrations of Na$^+$–montmorillonite. The former is a characteristic band of dioctahedral layer silicates,[38] observed in homoionic montmorillonites by Chourabi.[39] Concerning the 98-cm^{-1} band, it is difficult to ascribe this to framework vibrations, although it could be related to Na$^+$ motions, in agreement with the spectra reported[39] for a Na$^+$–montmorillonite (from Campberteau) that shows a very broad absorption band centered at 100 cm^{-1}. PEO intercalation produces slight modifications of this last band.

NMR Spectroscopy. Solid-state high-resolution NMR spectroscopy was applied to study PEO/M^{n+}–silicate complexes on homoionic hectorite samples instead of M^{n+}–montmorillonite because the latter silicate contains paramagnetic Fe^{3+} impurities perturbing NMR signals.

The ^{13}C CP MAS NMR spectrum of pure PEO (Figure 8a) shows two signals at 70.6 and 71.9 ppm respectively, the first corresponding to a relatively narrow peak. It has been reported[40] that for PEO/solvent systems a ^{13}C NMR signal appears in the 71.5–72.4 ppm range, depending both on its concentration and on the trans–gauche average conformations of the polymer in solution. For crystalline PEO, presenting a helicoidal structure (only gauche

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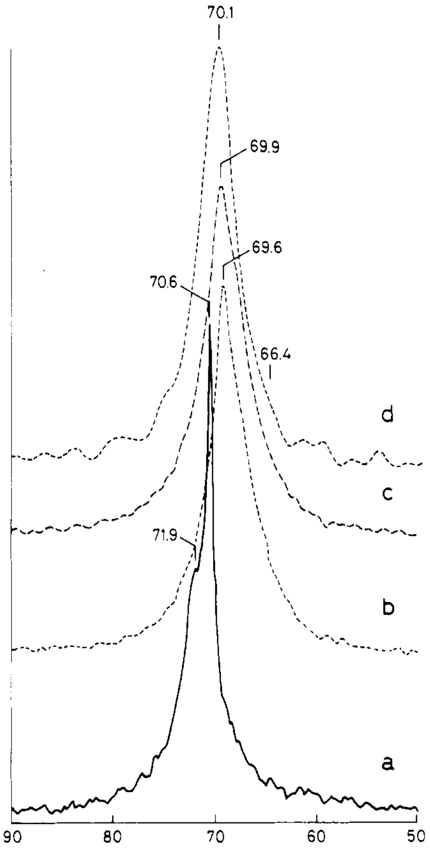

Figure 8. ^{13}C NMR spectra of pure PEO (a), PEO/Na^+–hectorite (b), PEO/K^+–hectorite (c), and PEO/Ba^{2+}–hectorite (d) compounds.

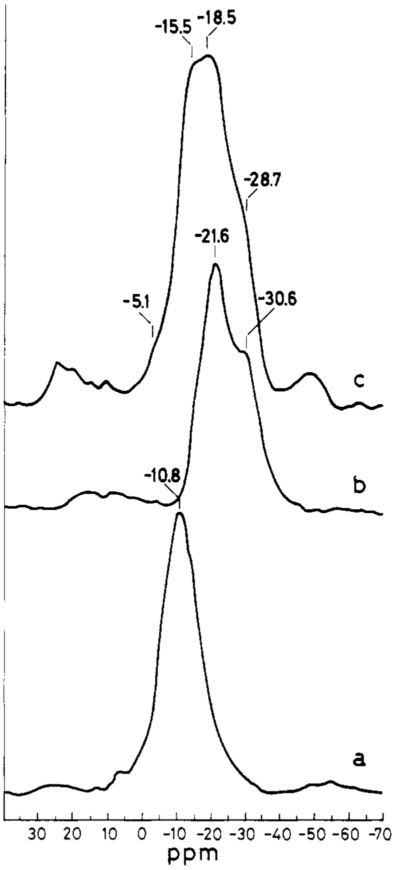

Figure 9. ^{23}Na NMR spectra of PEO/Na^+–hectorite compound (a), fully dry Na^+–hectorite (b), and partial hydrated (50% relative humidity) Na^+–hectorite (c).

CH_2–CH_2 conformations), is expected to give a single signal. The existence of two peaks can be alternatively attributed to (i) interactions between different chains of the polymer in solid state or (ii) the presence of some methylene groups in the trans conformation, that should be associated to the downfield signal. In the PEO/Na^+–hectorite, PEO/K^+–hectorite, and PEO/Ba^{2+}–hectorite compounds only one peak close to 70 ppm is observed (Figure 8, parts b, c, and d, respectively). We can assign these peaks to a gauche conformation of methylene groups, suggesting that the helicoidal conformation is maintained after intercalation. The small chemical shift changes found for intercalation compounds containing different interlayer cations could be associated with weak interactions between the oxyethylene groups of the polymer and those interlayer cations. The ^{13}C NMR chemical shifts may not be a good indicator of the extent of interaction between the ether oxygens and the interlayer ions. Nevertheless, these interactions can be revealed either by ^{17}O or by other NMR active nuclei corresponding to interlayer cations. In this way, we have applied ^{23}Na NMR spectroscopy to characterize PEO/Na^+–hectorite compound, which shows a peak at −10.8 ppm (Figure 9a). In Na^+–hectorite, the ^{23}Na NMR spectrum shows different signals depending on the environment of sodium ions: (i) two peaks at −21.6 and −30.6 ppm, respectively, are observed (Figure 9b) in dry Na^+–hectorite (sodium ions in interaction with the oxygen atoms beloning the silicate layers), and (ii) a broad signal containing several peaks (−5.1, −15.5, −18.5, and −28.7 ppm) in Na^+–hectorite hydrated samples equilibrated with 50% of relative humidity (Figure 9c). Thus, it can be deduced an increase in the homogeneity of the Na^+ ion environment that the intercalation of PEO leads to and simultaneously to a decrease of Na^+ interactions with the oxygens belonging to the silicate layers. It is important to note that a sodium complexing agent such as dibenzo-24-crown-8 intercalated in Na^+–hectorite presents a very similar ^{23}Na NMR signal ($\delta = -10.3$ ppm).[24]

Ionic conductivity. M^{n+}–montmorillonite samples in equilibrium with the atmospheric moisture have water molecules associated with the interlayer cations (Figure 1) which show high degrees of dissociation,[41] and consequently these materials present protonic conductivity.[42] A typical Cole–Cole impedance diagram of these samples (Figure 10a) consists of a semicircle at high frequencies followed by a "tail". That semicircle can be ascribed mainly to ionic conductivity of M^+ interlayer cations associated to water molecules, although a little contribution of H^+ species could be also participate in the mechanism of the electrical conductivity. The intercept point of the semicircle with the real axis (Z') at low frequency gives the ionic resistance (R_i) value and therefore the specific conductivity (10^{-5}–10^{-7} S/cm at room temperature, depending on the water content and on the nature of the interlayer M^{n+} cation).

When the M^{n+}–montmorillonites are dried, either by passing a continuous flux of dry nitrogen or by exposing the sample to dynamic vacuum, or when they are heated (≈400 K), the loss of water molecules produces a significant change in the electrical properties, and under these conditions it is not possible to obtain well-defined Cole–Cole diagrams. This fact can be related to water elimination from the coordination shell of interlayer cations, producing

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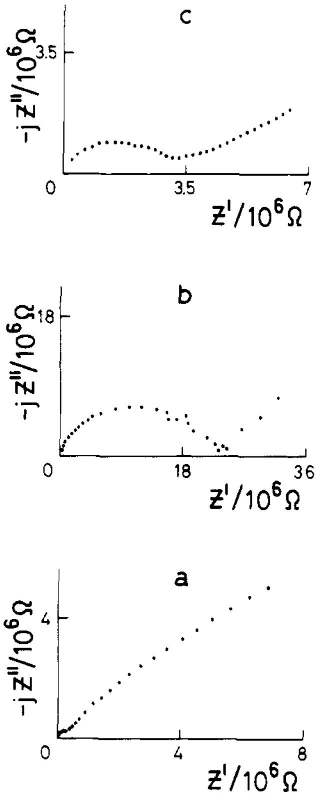

Figure 10. Impedance plots and ionic resistance (R_i) values corresponding to the following samples: (a) hydrated Na^+–montmorillonite (293 K), R_i = 1.26 × 10^5 Ω; (b) heated Li^+–montmorillonite (700 K), R_i = 2.5 × 10^7 Ω; (c) PEO/Na^+–montmorillonite (504 K), R_i = 3.47 × 10^5 Ω.

a strong association between these cations and the oxygen atoms belonging to the interlayer silicate surface. Consequently, these metal ions remain entrapped in an constrained system that prevent their mobility, necessitating thermal treatments (temperatures up to 600 K) to detect ionic conductivity (10^{-8}–10^{-9} S/cm at 650 K) ascribed to the M^{n+} ions (Figure 10b). The corresponding activation energy for Li^+ and Na^+ montmorillonites in the 650–700 K range can be estimated to be close to 1 eV.

PEO intercalation in M^{n+}–silicates produces cation environment modifications that allow appreciable ionic conductivity (Figure 10c) at lower temperatures. In this way, in PEO-intercalated compounds, the organic polymer acts as a pillar, causing a permanent separation between the silicate layers, and consequently reduces the mobility restrictions of cations. In addition to the "pillar effect", factors associated with the relaxation of the polymer chain can also increase the cation mobility as proposed for conventional PEO–salt complexes.[4,5,43] In the 400–700 K temperature range, Li^+ and Na^+ ion conductivities, measured in the parallel or perpendicular direction to the plane defined by the layers in PEO/M^{n+} montmorillonite (M^{n+} = Li^+, Na^+) compounds, are compared in Figure 11. The conductivity increases with temperature until a maximum value around 550 K and after this value strongly decreases until reaching the characteristic conductivity of the parent nonintercalated silicate. PEO–silicate compounds show impedance diagrams as represented in Figure 10c. Depressed capacitive arcs are observed, probably due to the surface roughness of the measured samples (pellets) and/or to the coexistence of more than one semicircle contained in the experimental plot. Sometimes, clearly evidenced is the presence of two semicircles composing the observed capacitive arc, the explanation consisting of the two following contributions:[19] (i) ionic conductivity in the bulk and (ii) ionic conductivity in the intergranular region between particles (remember that these materials are constituted by aggregation of microcrystalline <2-μm particles). In these cases, the spectra deconvolution by using the Boukamp's simulation method allows a deeper knowledgement of the electrical behavior of oxyethylene intercalation compounds, as we reported elsewhere.[19]

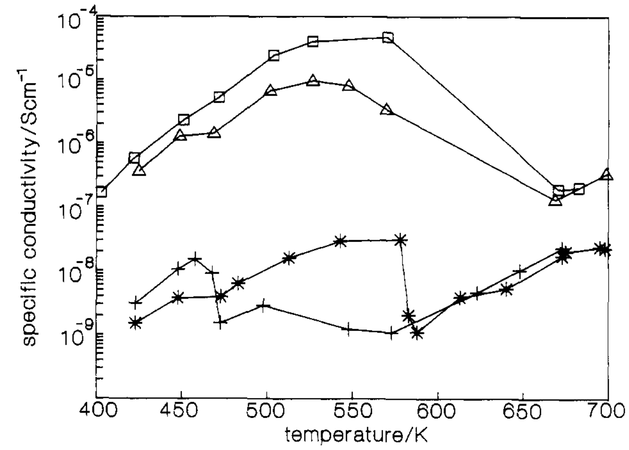

Figure 11. Specific conductivities represented as a function of the temperature for PEO/Na^+–montmorillonite and PEO/Li^+–montmorillonite compounds. Measurements carried out in perpendicular (+ and ×) and parallel (□ and △) directions to the silicate layers, respectively.

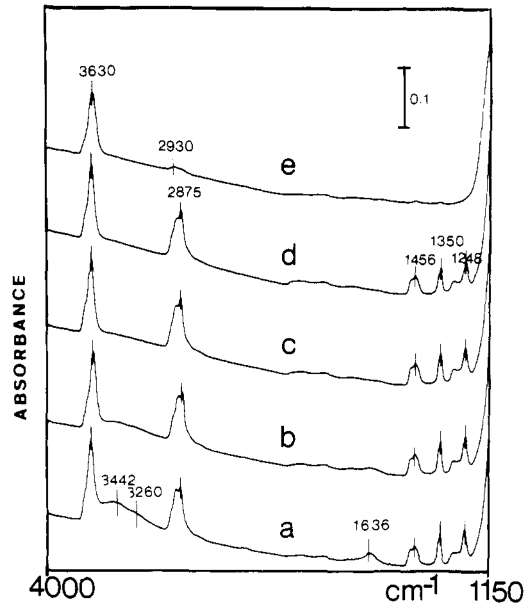

Figure 12. IR spectra (4000–1500-cm^{-1} range) of PEO/Na^+–montmorillonite (a) after thermal treatments (under vacuum) at 338 (b), 473 (c), 533 (d), and, 593 K (e).

As above indicated, thermal analysis demonstrated the stability of the PEO–silicate compounds under 600 K. In addition, IR absorption spectroscopy applied to PEO/Na^+ montmorillonite compounds (films, Figure 12) shows that bands assigned to the intercalated polymer remain unaltered up to 580 K, but at higher temperatures a significant and progressive decrease in intensity of these bands is observed. Thus, at ≈600 K the intercalated material is eliminated, giving a "collapsed" phase of the starting montmorillonite, as deduced from the corresponding XRD patterns (d_L = 9.7 Å). These results agree with the thermal

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behavior associated with the ionic conductivity.

Comparing the specific conductivity found for Li$^+$ and Na$^+$ ions in PEO-intercalated silicates, it appears that sodium ions exhibit higher conductivity than lithium ions (10^{-4} vs 10^{-5} S/cm). Similar behaviors are reported for β-alumina[44] and for some PEO-salt complexes.[1] In our case, this can be accounted for by the ability of lithium ions to move from the interlayer region to vacancy sites located in the octahedral silicate layers. This property, called the "Hoffman-Klemem effect",[45] takes place upon thermal treatment of some Li$^+$-exchanged dioctahedral phyllosilicates, as is the case with our montmorillonite samples. A consequence of this, is the immobilization of a fraction of charge carriers (Li$^+$) in the core of the silicate.

Conclusions

Many authors devoted much work to improve electrical properties of PEO-salt complexes acting as solid polyelectrolytes.[4,5] So, mixtures of PEO with various electrolytes have been investigated in order to reduce crystallinity, increase flexibility of the polymer chains, and increase the number of charge carriers. Enhancement of conductivity is produced when plasticizer molecules are added to the system, but these molecules are susceptible to leakage. Incorporation of ceramic additives such as alumina increases the amorphous phase ratio of PEO, favoring ion transport.[7-9] Thus, the great relevance of the PEO aggregation state is apparent, the intercalation being an alternative way to break the crystalline state of the polymer. PEO-silicate compounds show conductivity values lower than conventional PEO-salt complexes, although they present better thermal stability and reach good ion conductivity over a broader temperature range. In PEO intercalation materials only the cations are able to move, avoiding problems of formation of ion pairs, and consequently transport number is equal to one ($t_+ = 1$), which is of interest in the study of ion-transport phenomena in polymer electrolyte systems. Finally, intercalation of PEO in layered solids opens the way to new polyelectrolyte materials using host lattices with electronic conductivity, giving solids exhibiting mixed ionic electronic conductivity. Following this approach, PEO intercalations in hydrated vanadium pentoxide have been recently reported.[46,47]

Acknowledgment. Financial support from the Fundación Ramón Areces (Project Membranas con transportadores macrocíclicos específicos) and from the CICYT, Spain (Projects MAT 90-725 and MAT-91-0952-CO4-02) are gratefully acknowledge. We are indebted to Dr. Blanca Casal and to Dr. Juan Carlos Galván for helpful discussions. We also thanks Dr. Jesús Sanz for his assistance in NMR studies.

Registry No. PEO, 25322-68-3; Li$^+$, 17341-24-1; Na$^+$, 17341-25-2; K$^+$, 24203-36-9; NH$_4^+$, 14798-03-9; Ca^{2+}, 14127-61-8; Ba^{2+}, 22541-12-4; Al^{3+}, 22537-23-1; Cr^{3+}, 16065-83-1; CH$_3$CH$_2$CH$_2$NH$_3^+$, 17033-39-5; H$_2$O, 7732-18-5; MeOH, 67-56-1; montmorillonite, 1318-93-0; hectorite, 12173-47-6; acetonitrile, 75-05-8; ethanol, 64-17-5; dimethyl sulfoxide, 67-68-5.

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Dimesogenic Compounds Consisting of Two Aromatic Ester or Amide Type Mesogenic Units Having Trifluoromethyl Substituents at Terminal Phenylene Rings and a Central Dimethylenetetramethyldisiloxyl Spacer

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A series of new dimesogenic compounds whose mesogens are diad or triad aromatic ester or amide or esteramide types having trifluoromethyl substituents at the para position of terminal phenylene rings were synthesized. The two mesogenic units are interconnected through the central spacer of 1,3-dimethylenetetramethyldisiloxyl ($-CH_2Si(CH_3)_2-O-Si(CH_3)_2CH_2-$) structure. Their liquid-crystalline properties were studied by differential scanning calorimetry (DSC) and on a cross-polarizing microscope. The compounds having diad aromatic ester or amide type mesogens are monotropically mesomorphic, whereas those having triad mesogens are enantiotropically mesomorphic. All of the compounds form the S$_A$ phase according to their observed optical textures. The CF$_3$ terminal substituent in the mesogenic units together with the disiloxyl spacer appears to favor the formation of a smectic phase.

Introduction

Thermotropic compounds having two identical mesogenic units attached to both ends of a central flexible spacer are interesting not only as a new class of liquid-crystalline compositions[1-13] but also as models[14-16] for main-chain liquid-crystalline polymers (LCP)[17-20] which

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