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Research paper

Cyclic carbonate–sodium smectite intercalates

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ABSTRACT

Five-membered cyclic organic carbonates (COC) are of interest for their ability to modify the surface properties of smectites and enhance the hydraulic resistance of bentonites to saline leachates. The mechanism of interaction of glycerol carbonate (GC) and several other hydroxyl containing cyclic organic carbonates (generally having progressively greater molecular masses) with sodium montmorillonite (Na^+-Mt) was studied using powder X-ray diffraction and infrared spectroscopy. The 001 reflection for GC/Na^+-Mt intercalates varied with the amount COC added, and the measured d_{001} value increased from 1.29 nm to as large as 2.22 nm at equal-mass coverage of the COC to Na^+-Mt. In general, when intercalated, the cyclic carbonyl (C═O) stretch and the fundamental hydroxyl (O–H) stretch bands of COC derivatives were red-shifted with respect to these bands for neat COC, indicating strong ion-dipole interaction of the carbonyl group with interlayer Na^+, and H-bonding of the OH group with both interlayer water and Mt surfaces. A stable and highly ordered intercalate was produced at a 1:1 mass loading with Mt in which about 6 GC molecules per unit cell (~7 molecules per Na^+ ion) replaced most of the interlayer water.

1. Introduction

A high swell capacity and low saturated hydraulic conductivity make sodium bentonite useful as a component in geosynthetic clay liners (GCL) (Eglofgstein, 2001; Bouazza, 2002; Gates et al., 2009). However, bentonites undergo significant increases in saturated hydraulic conductivity when exposed to saline leachates arising from osmotically induced desiccation and associated changes in texture (Quirk and Schoffield, 1955; Guyonnet et al., 2005), thereby enabling these leachates to potentially contaminate underlying sediments and groundwater. GCL performance is thus often limited by the ability of the bentonite component to swell and form and maintain strong gels (Bouazza and Gates, 2014).

Various types of modifications have been developed to improve the chemical and functional capabilities of bentonite, ranging from doping with soda-ash (Harvey and Lagaly, 2006), the addition of polymers (Theng, 2012) to modifying with organo-surfactants (Yang and Lo, 2004) or with solvents (Onikata, 1999), and some of these methodologies have been applied to GCLs (Eglofgstein, 2001; Katsumi et al., 2008; Scalia et al., 2014).

In particular, five-membered cyclic organic carbonate (COC), a class of polar aprotic solvents, have been shown to have unique properties such as high polarity and a propensity for coordinating with metal cations via cation-dipole interactions (Yamanaka et al., 1974; Chernyak, 2006). In addition to high solvency, COC molecules also possess low flammability, high boiling and flash points, low odour levels, low vapour pressure (Verevkin et al., 2008) and generally low toxicities (Anonymous, 1987). Propylene carbonate (PC) forms intercalation complexes with montmorillonite (Mt) that have been found to enhance the swelling of Mt in brines (Onikata and Kamon, 1996; Onikata, 1999), a phenomenon exploited in the 'multiswellable' bentonite products (Onikata et al., 1999; Katsumi et al., 2008). Unlike sodium bentonite, PC-modified bentonite retains good swelling in up to 0.3 M $CaCl_2$ (Onikata, 2002) and is currently proposed as an alternative material for liner systems (Katsumi et al., 2008).

Glycerol carbonate (GC) and several of its COC derivatives, were catalytically synthesized from urea and 1,2-diols employing zinc monoglycerolate as a catalyst (Turney et al., 2013). Preparations of cyclic carbonate intercalates of Na^+-Mt were made (see Supplementary information) to study the mechanisms by which the composite materials maintained a swollen state in high ionic strength leachates, with the aim to develop new materials for application in clay barriers against high levels of salinity. This study details the results from X-ray diffraction and infrared spectroscopic study of the structures and properties of the intercalates.

2. Materials & methods

Sodium-bentonite, supplied from Sibelco Pty. Ltd. (Melbourne) is mined near Miles, Queensland and has well known and consistent

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mineralogy. The <0.2 μm fraction of 25 g of bentonite (containing >98% smectite, Table 1) was separated by sedimentation and centrifugation following general procedures (Gates et al., 2002). The fine fraction was rinsed three times with ~2 M NaCl, washed and dialyzed to remove excess salts and freeze-dried to a powder. Approximately 13 g of <0.2 μm Na^+-Mt was prepared from 25 g starting material.

Reagent grade glycerol, 1,2,4-butanetriol, 1,2,6-hexanetriol, *meso*-erythritol, and propylene carbonate were purchased from Sigma Aldrich. Reagent grade urea, methanol, chloroform, and dichloromethane were purchased from Merck, while diglycerol was purchased from Tokyo Chemical Industry Co., Ltd. *cis*-1,2-Cyclohexandiol was supplied from Alfa Aesar and zinc monoglycerolate from Micronisers Pty Ltd, Dandenong, Australia.

2.1. Cyclic organic carbonates (COC)

The following COC derivatives (Table 2) were synthesized for this study using zinc monoglycerolate as a catalyst: glycerol carbonate (GC), 4-(2-hydroxyethyl)-1,3-dioxolan-2-one (HED), 4-(4-hydroxybutyl)-1,3-dioxolan-2-one (HBD), 4-((benzyloxy)methyl)-1,3-dioxolan-2-one (BMD), and 4′-(oxybis(methylene))bis(1,3-dioxolan-2-one) (OBD). See Turney et al. (2013) and the Supplementary information for specific details of synthesis, substrate conversion and product yield.

2.2. Preparation of COC intercalates of Na^+-Mt

Accurately weighed amounts (10–90 mg) of Na^+-Mt were dispersed in 3 mL deionized water and deposited onto a ceramic tile under suction to form an oriented film. Accurately weighed amounts, ranging from 10 to 90 mg, depending on coverage rate desired by the specific COC, were dissolved in 1 mL deionized water and then filtered through the still-wet Na^+-Mt film. After air-drying under ambient conditions for 3 h the samples were studied by powder X-ray diffraction (XRD). XRD traces were collected on a Philips PW 1140 diffractometer from 2 to 22° 2θ at 1°/min with a step size of 0.02° using a Cu Kα source ($\lambda = 1.5406$ nm) at a power of 40 kV and 25 mA. A 1° divergence slit, 1° receiving slit and 0.2° scatter aperture were used. The centre of gravity of the 001 reflection was used to determine *d*-values.

Fourier transform infrared (FTIR) spectra were obtained using a Perkin Elmer Spectrum RX1 spectrometer having a diamond attenuated total reflectance (ATR) crystal. Samples were presented as either a liquid film or as a powder directly pressed onto the upper surface of the ATR. Mid-IR (400–4000 cm^{-1}) spectra at a resolution of 2 cm^{-1} were co-added from 80 scans and converted to percent transmittance using Spectrum™ FT-IR software. All spectra were background and base-line corrected to the clean ATR (diamond) crystal reference.

Table 1
Properties of the Mt.

Property	Value
<0.2 μm[a] (% of fraction)	
Mt[b]	98 ± 1
Opal/cristobalite-tridymite	2 ± 1
CEC[c] (meq/100 g)	
<0.2 μm	104
Unit cell ($O_{20}(OH)_4$)[d]	
Structural formula	$Na_{0.8}(Si_{7.77}Al_{0.23})(Al_{3.1}Fe_{0.30}Mg_{0.61})$
Total layer charge	0.80
Octahedral charge	0.57
Tetrahedral charge	0.23

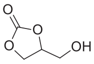
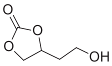
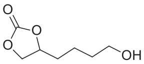
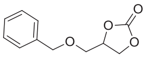
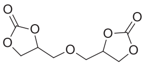
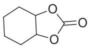
[a] The <0.2 μm fraction was separated by centrifugation following Gates et al. (2002).

[b] X-ray diffraction and Reitfeld analysis (performed by Mark D. Raven & Peter Self, CSIRO Land and Water).

[c] The Ba^{2+} CEC tests were conducted using X-ray fluorescence on oriented films of the <0.2 μm fractions by CSIRO Land and Water following in-house methods.

[d] Layer charge and structural formula determined from the chemical analysis of the <0.2 μm fractions.

Table 2
Names and structures of cyclic organic carbonates studied. Refer to Supplementary information of synthesis procedures, substrate conversion and product yield.[a]

Name	Structure	Molecular volume[a] (nm^3)
Glycerol carbonate (GC)		0.086
4-(2-hydroxyethyl)-1,3-dioxolan-2-one (HED)		0.106
4-(4-hydroxybutyl)-1,3-dioxolan-2-one (HBD)		0.160
4-((benzyloxy)methyl)-1,3-dioxolan-2-one (BMD)		0.204
4′-(oxybis(methylene))bis(1,3-dioxolan-2-one) (OMD)		0.132
Hexahydrobenzo[d][1,3]dioxol-2-one (HDD)		0.063

[a] Molecular volume estimated following the group summation method of Fedors (1974).

3. Results & discussion

3.1. Interaction of GC with Na^+-Mt

To determine the appropriate load rates of GC and its derivatives for modifying Na^+-smectite, the XRD traces of GC/Na^+-Mt intercalates were measured as a function of percent mass coverage (Fig. 1A). A d_{001} value of 1.29 nm was observed for the 001 reflection of the air-dried Na^+-Mt, indicating mostly a 1-layer hydrate. On loading with GC, the d_{001} value generally increased from ≈1.40 nm (9% coverage) to 3.7 nm (900% coverage). For the coverage from 35 to 67%, two d_{001} values were apparent, one near 1.4 nm and the other ranging from 1.78 to 1.85 nm. At a coverage of 100% (1:1 loadings of GC to Na^+-Mt) the d_{001} value was 1.99 nm, but increased to 2.47 nm (150%) and 2.83 (233%). A large excess of 400% and 900% mass coverage of GC resulted in a poorly developed 001 reflection centered, respectively, near 2.89 nm and 3.7 nm (Fig. 1A).

To better visualize the extent of intercalation of the Na^+-Mt by GC, the interlayer space was determined from the observed basal spacing and plotted in Fig. 2B (Deeds and Van Olphen, 1963; Seki and Ogawa, 2010). Disordered stacking or imperfect alignment of Mt platelets within the film resulted in broadening of the 001 reflection, as measured by the full width at half maximum (FWHM) (Fig. 2B). However, this was also influenced by the presence of two reflections for the intermediate coverage (10–67%), probably representing two distinct intercalate structures.

Similar to propylene carbonate (PC) (Onikata, 1999), GC presumably intercalates Na^+-Mt by replacing some or most of the interlayer water surrounding exchangeable sodium ions via a direct solvation of the interlayer cations. Thus, the distinct 001 reflections of the intermediate GC coverage (>25, but <100%) interpreted as being related to GC progressively replacing interlayer H-bonded water (i.e., that water associated with either the interlayer surface or H-bonded to other water molecules). Based on mass determinations, the eventual d_{001} value of 1.99 nm (trace e in Fig. 1A) represents an interlayer with ~6 GC molecules surrounding each Na^+ ion.

Analysis of the mid infrared (IR) spectrum of the 100 wt% GC/Na^+-Mt intercalate was conducted to better assess possible mechanisms of interaction between the GC molecules, Na^+ ions and the interlayer surfaces of Mt (Fig. 2). Compared to neat GC, a significant red shift (21 cm^{-1}) was observed for the characteristic GC carbonyl (C=O) stretch, and a larger