Crystalline swelling of organo-modified clays in ethanol–water solutions

Will P. Gates[*]

Adelaide Laboratory, CSIRO Land and Water, Private Mail Bag No. 2, Glen Osmond SA 5064, Australia

Abstract

The swelling of organo-modified clays in organic solvents may have important consequences on bulk properties of materials based on this technology. X-ray powder diffraction was used to study the swelling of orientated films of dioctahedral smectites exchanged with benzyloctadecyldimethylammonium (BODMA) cations, when equilibrated in ethanol–water solutions. The influence of total layer charge and the location of the layer charge on swelling of two organo-modified bentonites and three organo-modified reference smectites in ethanol–water solutions were evaluated. The measured interlayer spaces of BODMA smectites equilibrated in water increased with total layer charge and with the relative amount of tetrahedral charge. At intermediate ethanol concentrations, a distinct plateau was observed in the swelling profiles of BODMA smectites having layer charges >0.8 e$^-$ per $O_{20}(OH)_4$. When equilibrated in ethanol, all BODMA smectites expanded to similar values ($34-36$ Å). The magnitude of the change in crystalline swelling of organo-smectites in ethanol compared to that in water was found to be inversely proportional to total layer charge density but proportional to the ratio of octahedral to tetrahedral layer charge. Calculations using NEWMOD showed that the d-spacings measured were unlikely to be due to interstratifications of fully water-solvated with fully ethanol-solvated BODMA smectite layers. Introduction of up to 2.0 M aqueous NaCl resulted in a slight (~ 0.5 Å) decrease in the interlayer spacing of BODMA montmorillonite. However, 0.02 and 0.2 M NaCl added to ethanol–water mixtures enhanced interlayer expansion in these miscible solvents. The results suggest that inorganic salt depressed the activity of water in ethanol–water mixtures and thereby increased the proportion of ethanol actually penetrating the interlayer spaces of BODMA smectites. A plausible mechanism is discussed to describe the observed interlayer expansion in ethanol–water solutions and how this might impact possible applications.

1. Introduction

Permeable reactive barriers offer an effective method for the control of hydrocarbon-contaminated groundwater, as they are capable of reacting physically or chemically with contaminants, thereby minimizing contaminant transport without significant reductions in the permeability of the barrier to the treated groundwater (Guerin et al., 2002). Often, the pollutants are organic solvents or organic species with limited solubilities in water but having high affinity to organo-clays as determined from sorption isotherms

* Tel.: +61-8-8303-8512; fax: +61-8-8303-8550.
E-mail address: will.gates@csiro.au (W.P. Gates).

(Jaynes and Boyd, 1991; Koh and Dixon, 2001; Bonczek et al., 2002). Alther (1995, 2002) showed that organo-clays are cost effective as pretreatments when used ahead of activated carbon sorbents in pump-and-treat technologies. Recently, Slade and Gates (2004) showed that, when exposed to neat toluene, hexadecyltrimethylammonium (HDTMA) smectites swell to ~ 33–39 Å from interstratified mono- and bimolecular interlayer arrangements (initially at ~ 15–17 Å) and to 42–45 Å from bimolecular (17.7 Å) and paraffinlike (>21 Å) interlayer arrangements. Xu and Boyd (1995) and Bonczek et al. (2002) found that these materials sorb increasing amounts of organics with increasing organic carbon content. Slade and Gates (2004) showed that the organic carbon in these organo-clay intercalates consisted of both charge balancing HDTMA cations and intercalated organic salt molecules.

Organically modified clays are commonly used as emulsifiers (thinners) of water–oil systems (e.g., drilling muds) but can also be dispersed in oils (thickeners) to form lubricating greases with lower susceptibilities to heating (Jordan, 1963; Van Olphen, 1963). The degree of dispersion is related to the ability of the organo-clay to sorb organic moieties and to swell to form long-range particle–particle interactions (Lagaly et al., 1983; Moraru, 2001). Jordan (1963) reported that the gel volumes of bentonites saturated with various alkylammonium cations increased by as much as 27 times when dispersed in *n*-alkanols of varying carbon tail lengths. Weiss (1963) observed that 2:1 layer silicates, intercalated with *n*-alkylammonium cations and solvated with *n*-alkanols or *n*-alkylamines of like carbon tail length, resulted in layer spacing increases consistent with the formation of bimolecular layers of *n*-alkyl moieties within the interlayers. Lagaly (1976) further observed that various *n*-alkanols were capable of expanding alkylammonium 2:1 layer silicate intercalates to layer spacings as great as 70 Å and postulated that the thickness of the bimolecular layer was dependent on the most frequent end-to-end arrangement of alkanol–alkylammonium pairs. Lagaly and Witter (1982) and Lagaly et al. (1983) found that alkylammonium-exchanged clays swelled in various binary (organic-water) mixtures, that the ratio of organic–inorganic solvent sorbed by the organo-clay was constant and inde-

pendent of the bathing solution mixture at intermediate composition. Furthermore, the presence of inorganic salts, the alkyl tail length (number of carbons) and the layer charge density all influenced the swelling of organo-modified clays. Moraru (2001) found that organic cation coverage up to the cation exchange capacity (CEC) of the clay enhanced gel formation in organic solvents (e.g., toluene) and observed that Bingham yield stress values of these dispersions were maximal at organic cation coverage equivalent to the CEC. Slade and Gates (2004) showed that the incorporation of HDTMA-Br above that amount required to satisfy the CEC increased the ability of HDTMA clays to absorb and disperse in toluene. The initiation of organo-clay dispersion in solvents is related to the ability of certain anions (e.g., Cl^-, ClO_4^-, I^-) to impede the formation of solvent clusters within the interlayer pore-space (Lagaly and Witter, 1982; Lagaly, 1984, 1987). Enhancing the expansive capacity of organo-modified clays in the presence of polar organic solvents forms the basis of various polymer–clay nanocomposite synthesis methods (e.g., Gilman et al., 2000; Moraru, 2001).

As part of an overall goal to develop clay-based reactive barriers for the remediation of hydrocarbon-contaminated groundwater, this paper aims to determine factors affecting swelling of two commercially available bentonites and three reference clay minerals, modified with the organic cation benzyloctadecyldimethylammonium (BODMA), in solutions of ethanol and water. BODMA was selected because steric effects were expected to yield greater interlayer porosities of BODMA intercalates than from di-alkyl-substituted quaternary ammonium cations. Ethanol–water solutions were used in the first instance because of the ease by which solvation reactions could be controlled. Inorganic salt (NaCl) was added to the solutions to mimic saline groundwater conditions.

2. Materials and methods

2.1. Purification and characterization of the smectites

The smectites studied were purified by sedimentation/centrifugation methods to remove the nonswelling components, and XRD and IR were used to check

their purity. The montmorillonitic fractions of two bentonites were studied. The Miles bentonite (United Minerals, Miles, Queensland) is composed of about 71% montmorillonite with the remaining materials being quartz, opal CT, feldspar and zeolite (Gates et al., 2002). Arumpo bentonite (Arumpo, Muldoora, New South Wales) is composed of randomly inter-stratified montmorillonite (∼ 85%) illite (∼ 15%) layers. No quartz or other minerals were observed in this material. These results for Arumpo bentonite are in agreement with the recent analysis by Churchman et al. (2002).

Reference materials included: Upton montmoril-lonite (CSIRO collection), SBCa-1 beidellite (Source Clays Repository, West Lafayette, IN) and De Lamar beidellite (CSIRO collection). All reference materials were purified to remove the nonswelling components by the usual means of Na-saturation, particle size separation and dialysis (e.g., Gates et al., 2002). Chemical analysis of each clay was obtained by X-ray fluorescence (XRF) on purified, Ca-saturated, ignited (1100 °C) specimens (Norrish and Hutton, 1969) and structural formulae of the Ca-saturated smectites were calculated from the oxides using the program CLAYFORM (Bodine, 1987).

2.2. Preparation and characterization of organo-clays

The Na-form of each clay, dispersed in 5 ml of water, was exchanged with 5 ml of 0.01 M solutions of the BODMA chloride salt at 40 °C for several days. The samples were then centrifuged and the solution was replaced with more 0.01 M solution. These steps were repeated for a total of three times over a period of about 2 weeks. Excess organic salts were removed by centrifugation and washing with several solutions of hot, deionised water until the $Ag(NO_3)_2$ test was negative for Cl^- and finally twice with warm ethanol. Analysis by X-ray fluorescence indicated that excess Cl^- in the complex was negligible. Total carbon and nitrogen analyses (by mass spectrometry) were conducted on oven-dried (4 h at 105 °C) samples.

Electrophoresis determinations were conducted on dilute aqueous suspensions using a Malvern Zeta-master fitted with a ZET5104 general purpose cell. The instrument was aligned with a suspension of carboxylated polystyrene latex in a 0.02 M phosphate buffer. An average of five measurements was recorded (with zero-field correction) in the potential range of − 100 to 50 mV; each measurement was of 20-s duration. Suspensions were diluted (generally < 0.1 mg ml^{-1}) such that the photon count rate was within the range of $1.5-2.0 \times 10^6$ counts s^{-1} and the result-ing potential width was < 3 mV. Zeta potentials were estimated from the electrophoretic mobility using the Smoluchowski approximation of the Henry equation (Malvern Instruments, 1991).

All measurements were referenced to the oven-dry state. Oven-dry mass was determined on duplicate weighed samples in titanium vessels that allowed for gas purge and sealing. The vessels were then placed within a heating manifold and heated at 105 °C for 4 h under dry N_2 purge. Vessels were sealed, allowed to cool and reweighed.

2.3. Determination of swelling in ethanol–water solutions

Orientated films of the organo-clays (∼ 60 mg) were deposited under suction onto ceramic tiles from suspensions in ethanol. The films were then washed with ethanol–water solutions containing successively less ethanol until 10 ml of deionized water was passed through. The samples were then rewashed with etha-nol–water mixtures containing successively more ethanol. For each diffraction measurement, 10 ml of a particular ethanol–water solution was vacuum-fil-tered through the orientated sample. Immediately after the solution had passed through the clay film, the tile supporting the orientated film was then immersed in 5 ml of the same ethanol–water mixture, was covered and allowed to equilibrate for 30 to 60 min. Samples thus treated were considered to be in equilibrium with the solution and wrapped in mylar film for further study.

Ethanol–water solutions were prepared with 0.02 and 0.2 M dissolved NaCl to determine the effect of salt concentration on organo-clay swelling. Solutions of 0.02 and 0.2 M NaCl were prepared to ethanol–water ratios (vol.%:vol.%) up to 90:10 and 70:30, respective-ly. Higher ethanol concentrations were not used due to the insolubility of NaCl in ethanol. Equilibrations with aqueous 2.0 M NaCl were also carried out.

X-ray powder diffraction measurements were col-lected using a Philips PW1710 diffractometer (Co Kα

radiation), fitted with 1° divergence slit, graphite monochromator and a proportional counter. Checks were made to ensure that evaporation had no significant effect on the measured $d(001)$ spacing by immediately rerunning some samples. XRD measurements were also conducted on air- and oven-dried (60 °C) samples.

3. Results and discussion

3.1. BODMA smectite properties

The structural formulae and layer charge characteristics are presented in Table 1. The octahedral cation occupancies provide a range in layer charge and, in general, the tetrahedral charge increases with increasing total layer charge. Upton montmorillonite has the lowest tetrahedral charge. Of the two beidellite samples, the SBCa-1, has a very low octahedral charge compared to the De Lamar beidellite.

The %C and %N in the BODMA smectite complexes (Table 2) indicate that, while some benzyl carbon may have been lost following heating, the layer charge of each material was essentially satisfied by the organic cation. This result is also substantiated by the zeta potential measurements (Table 2). The charge on external surfaces of particulates of the BODMA smectites remained negative when dispersed in water (compared to -50 to -35 mV for the Ca-saturated samples). A negative zeta potential would be expected unless sufficient excess organic cations were adsorbed by the external surfaces of particles to achieve particulate charge neu-

tralization or charge reversal (Moraru, 2001; Singh et al., 2003).

3.2. Swelling in ethanol–water mixtures

Upon oven drying at 105 °C for 4 h, the BODMA smectites lost $2-2.5\%$ mass (Table 2). Table 3 shows the values of $d(001)$ spacings measured for the BODMA bentonites and reference clays at the oven- and air-dried states. In general, the $d(001)$ measured at the oven- and air-dried states increases with the total layer charge of the clay. The $d(001)$ spacings at the oven- and air-dry states are between $\sim 19-21$ Å for clays with total layer charge <0.8 e$^-$ per $O_{20}OH_4$, and between $\sim 24-26$ Å for clays with a total layer charge >0.8 e$^-$ per $O_{20}OH_4$. The location of layer charge also has a significant effect on $d(001)$ spacings at these solvation states as can be observed by comparing the $d(001)$ values observed for BODMA Miles bentonite and BODMA Upton montmorillonite (Table 3).

In general, the spacing measured for organo-smectites exposed to ethanol–water solutions were rational (Fig. 1). Rational spacings implied that interlayer solvation reactions were complete, and, given the length of time required for diffraction measurement, also indicated that the samples remained in equilibrium with the bathing solutions during analysis. Increased ethanol content in the miscible solvent increased the interlayer spaces of the organically modified clays as measured from the X-ray powder diffraction of orientated films equilibrated with the appropriate mixed solvent (Figs. 1 and 2). For BODMA Miles, the swelling profile was markedly

Table 1

Structural formulae and layer charges of the smectites studied calculated from their chemistry as obtained by X-ray fluorescence (Norrish and Hutton, 1969) on purified, Ca-saturated, ignited (1100 °C) specimens

	Per $O_{20}(OH)_4$								
	Layer charge			Interlayer	Tetrahedra		Octahedra		
Smectite	Total	Octahedral	Tetrahedral	Ca	Si	Al	Al	Fe	Mg
Miles	0.72	0.48	0.26	0.36	7.74	0.26	3.02	0.52	0.45
Upton	0.73	0.66	0.07	0.37	7.93	0.07	3.08	0.41	0.44
Arumpo	0.83	0.25	0.57	0.41	7.43	0.57	3.01	0.35	0.84
SBCa-1	0.88	0.02	0.86	0.44	7.14	0.86	3.81	0.18	0.02
De Lamar	0.94	0.23	0.71	0.47	7.29	0.71	3.73	0.05	0.23

The values for Arumpo bentonite were adjusted to account for 15% of interstratified illite. A small component of opaline material in the Miles bentonite (Gates et al., 2002) was discounted in the determination of its structural formulae.

Table 2
Calculated and measured carbon and nitrogen contents, water content (105 °C) and electrophoretic mobilities (Z.P.) of BODMA smectites

Smectite	%C		%N		%H$_2$O (105 °C)	Zeta potential (mV)
	Calculated	Measured	Calculated	Measured		
Miles	23.8		1.0		2.4	− 33.0
Upton	24.1	21.0	1.0	1.1	2.4	− 32.1
Arumpo	26.3		1.1		2.1	− 47.2
SBCa-1	29.6	27.3	1.2	1.1	2.0	− 42.8
De Lamar	29.0		1.3		1.9	

s-shaped, with substantial increases in d(001) values at ethanol–water mixtures from 30:70 to 70:30. While the profile for BODMA Upton lacked the s-shape, it showed only marked increases in d(001) values for >30–40% (vol.%) ethanol in the ethanol–water mixtures. The interlayer spacing of BODMA Miles bentonite was greater than that measured for BODMA Upton over ethanol concentration range up to 80%, where the interlayer for BODMA Upton continued to expand substantially. A different behavior was observed for the BODMA Arumpo bentonite and the two BODMA beidellites having layer charges >0.8 e$^-$ per O$_{20}$(OH)$_4$. For these materials, a substantial proportion of the increase in interlayer spacing occurred at lower ethanol contents (10–40 vol.%) of the ethanol–water mixture, resulting in a different swelling profile with ethanol content in the mixtures.

XRD measurements were made on one film of BODMA Upton montmorillonite (Fig. 2), starting at pure ethanol, to allow an estimation of the effect of hysteresis on organo-clay swelling in ethanol–water. The order in which the films of BODMA Upton montmorillonite were wetted with ethanol–water mixtures had insignificant effect on the d(001) values obtained for BODMA Upton.

The differences in the swelling behavior between BODMA montmorillonites and BODMA beidellites in ethanol–water solutions could be due to preferential or competitive sorption of ethanol over water in the case of the beidellites (Lagaly and Witter, 1982). Lagaly and Witter (1982) found that the interlayer composition *was relatively constant and independent of* the external or bulk composition for several alkylammonium clays bathed in binary mixtures of water and dimethyl sulfoxide (DMSO) when bulk solutions were of intermediate compositions. Materials with high-packing densities of the organic cation in the interlayer tended to produce interlayer spacings more similar to the fully DMSO-solvated state at much lower DMSO concentrations, thus producing swelling curves with plateaus in the intermediate DMSO concentrations much like that observed here for the BODMA beidellites. Lower alkyl tail packing densities of BODMA clays compared to mono-substituted alkyammonium-exchanged clays studied by Lagaly et al. (1983) probably allow for greater connectivity of the interlayer pores with the bulk ethanol–water solutions. As will be discussed in detail below, the affect of adding an inorganic salt, NaCl, to the ethanol–water solutions provides evidence that pref-

Table 3
Layer spacings determined by XRD on free swelling orientated films of BODMA smectites equilibrated with ethanol–water solutions containing 0.00, 0.02, 0.2 and 2.0 M NaCl

BSDMA smectite	Oven-dried [d(001) Å]	Air-dried [d(001) Å]	EtOH:H$_2$O [vol.%:vol.%]	NaCl			
				0.0 M [d(001) Å]	0.02 M [d(001) Å]	0.2 M [d(001) Å]	2.0 M [d(001) Å]
Miles	19.7	21.5	0:100	22.5	22.4	22.2	22.0
Upton	19.5	19.8	0:100	20.3	19.8	19.7	19.6
Arumpo	24.2	25.1					
SBCa-1	36.0	26.2					
De Lamar	24.7	26.1					

Values for d(001) reported represent averages of at least two measurements.
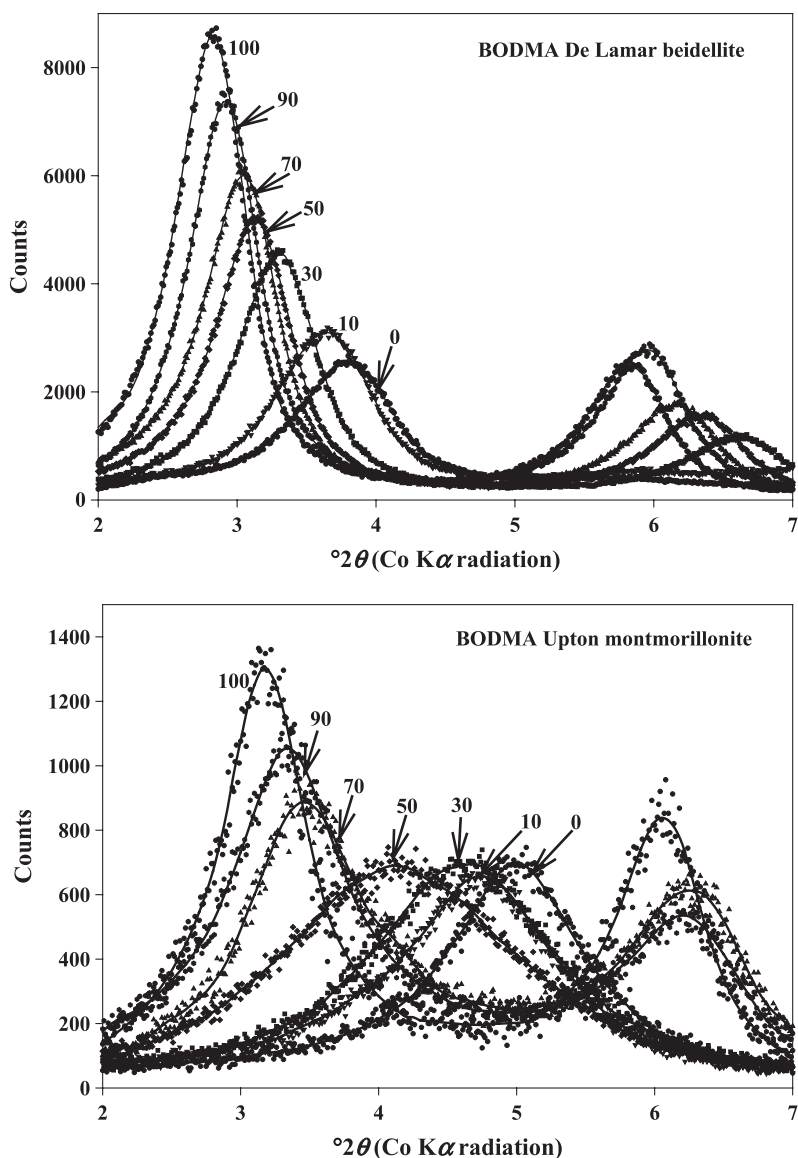
Fig. 1. X-ray powder diffraction patterns of oriented films of BODMA-saturated smectites. Numbers next to patterns indicate vol.% ethanol in ethanol–water solutions.

erential sorption of ethanol over water in BODMA montmorillonites is inconsequential.

A related phenomenon that could explain the swelling profiles observed here for the montmorillonites would be development of interstratifications of fully ethanol-solvated with fully water-solvated BODMA clays. To determine whether the swelling profiles might have been affected by such interstrati-

fications, X-ray powder diffraction patterns were calculated for random and regular interstratifications using NEWMOD (Reynolds, 1985). Calculated positions of the $001(d_{ETOH})/001(d_{H2O})$ and $002(d_{ETOH})/002(d_{H2O})$ peaks were compared to those determined experimentally. Calculated regular interstratifications of water- and ethanol-solvated organo-smectites resulted in s-shaped swelling profiles for the 001
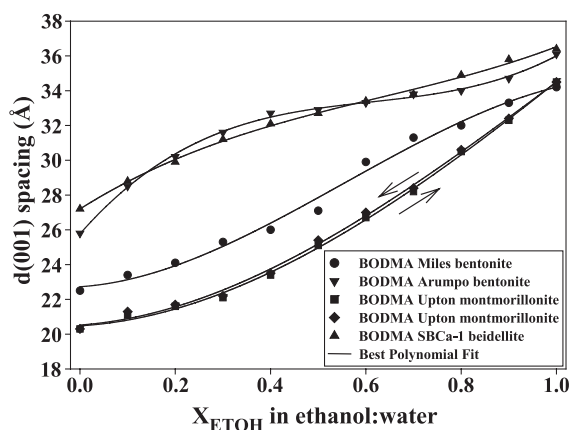
Fig. 2. Swelling profiles of some BODMA-saturated smectites as a function of ethanol concentration. Arrows indicate the progression of ether increasing (→) or decreasing (←) ethanol concentrations.

reflections (Fig. 3A) similar to that observed for the BODMA Miles bentonite. However, the differential 2θ ($\Delta 2\theta$), defined as the angular difference between the $001(d_{ETOH})/001(d_{H2O})$ and $002(d_{ETOH})/002(d_{H2O})$ reflections (Fig. 3B), indicates that the swelling of BODMA smectites in mixtures of ethanol and water are unlikely to be a result of such interstratifications of water- or ethanol-solvated layers. These results provide support to the conclusion that the interlayer region of BODMA montmorillonites contain solutions of similar composition to the bulk solution, and, therefore, the measured $d(001)$ spacings are unlikely to be influenced by competitive sorption effects.

3.3. Effect of NaCl concentration

Increasing the concentration of NaCl from nil to 0.02, 0.2 and 2.0 M in water slightly depressed the $d(001)$ values measured for BODMA Miles bentonite and BODMA Upton montmorillonite by ~ 0.5 Å (Table 3). However, equilibration of BODMA Miles bentonite in ethanol–water solutions containing 0.02 and 0.2M dissolved NaCl enhanced swelling at all ethanol concentrations (Table 3, Fig. 4). Swelling was enhanced such that the $d(001)$ value measured for samples equilibrated in 0.02 M NaCl 90:10 ethanol–water or 0.2 M NaCl 70:30 ethanol–water solutions were as expanded as a sample equilibrated in pure ethanol. Thus, the combined effects of dissolved salt in depressing the spacing measured for the water-

solvated samples, while increasing the spacing measured for the ethanol-solvated samples, resulted in greater total expansion of the BODMA Miles with increasing electrolyte concentration.

The enhanced swelling of BODMA Miles bentonite in ethanol–water mixtures with NaCl is probably related to the lower relative activity of water when salt is present. The addition of NaCl "tied up" a significant proportion of water in the ethanol–water mixtures and increased the relative proportion of ethanol actually bathing the organo-clay. Because 0.2 M NaCl
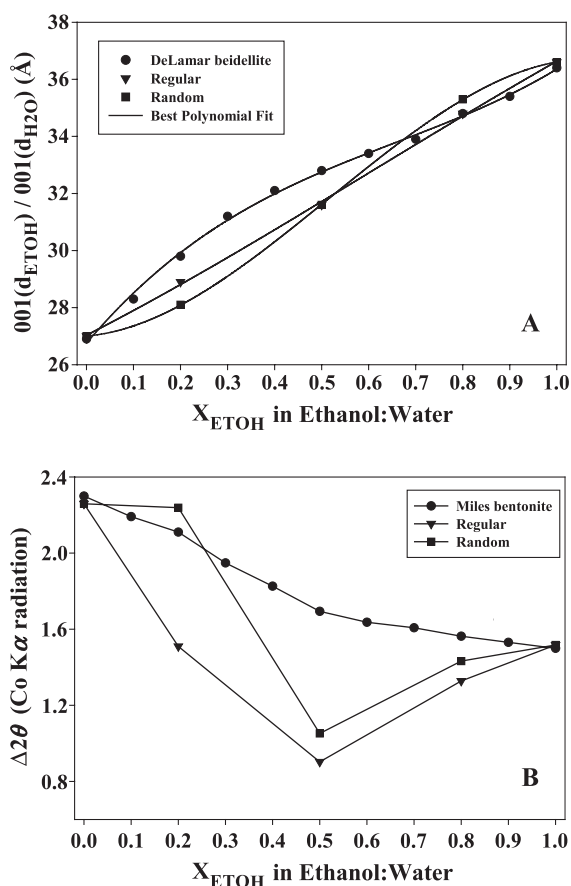

Fig. 3. (A) Calculated swelling profiles for regular and random interstratifications of fully ethanol- and fully water-solvated BODMA smectites compared to experimental data for BODMA beidellite. (B) Analysis of $\Delta 2\theta$, the angular difference between the $001(d_{ETOH})/001(d_{H2O})$ and $002(d_{ETOH})/002(d_{H2O})$ reflections for regular and random interstratifications of fully ethanol-solvated with fully water-solvated BODMA Miles bentonite compared with experimentally determined values.
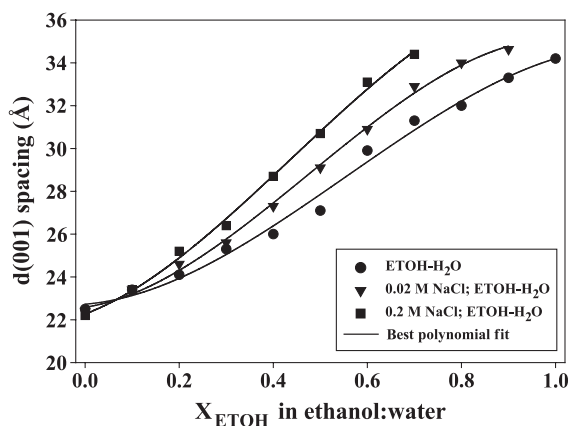
Fig. 4. The effect of dissolved NaCl concentrations on the d(001) values measured for BODMA Miles bentonite equilibrated in ethanol–water mixtures.

in ethanol–water mixtures containing >70% (vol.%) ethanol exceeded the solubility limit of NaCl, nearly all the water available in a 70:30 ethanol–water mixture reacts with the salt, and the interlayer space of the organo-modified clays are bathed in essentially pure ethanol. This salt-induced depression of the activity of water results in a relative increase in the proportion of ethanol penetrating the interlayer spaces of the organo-modified clays as compared to salt-free ethanol–water mixtures.

These results for BODMA montmorillonites contrast sharply with the results of Lagaly and Witter (1982) and Lagaly et al. (1983), who found that the presence of various sodium salts (e.g., NaCl) enhanced the swelling of tetradecylammonium (TDA) beidellites in water, but the same salts in ethanol resulted in interlayer collapse. Their interpretation was that greater alkyl tail packing densities enhanced the stability of liquid structures forming within the interlayer pores balanced with the relative "structure breaking" ability of introduced inorganic anions such as Cl^-, I^- or ClO_4^-. The alkyl tail packing density or the connectivity of the interlayer pores with the bulk solution influences the structure breaking ability of salts. The results reported here show an opposite effect: NaCl in water causes (slight) shrinkage, but NaCl in ethanol causes swelling. A general equilibrium exists between the ethanol concentrations of the bulk mixed solutions and those of the sorbed interlayer solutions at any ethanol concentration.

The differing results discussed above might plausibly be explained in the following way. The bulky size of the BODMA cation used here imparts a lower alkyl tail packing density with greater average distances between alkyl tails, and thus would influence less strongly any interlayer pore liquid structures formed compared to the TDA-clays studied by Lagaly and Witter (1982). The gallery pores of the BODMA clays are larger compared to clays saturated with simple mono-substituted alkylammonium cations because the benzyl group will limit the packing arrangement such that larger pores spaces occur, and the gallery pore size will be inversely related to layer charge. In their proposed model, greater distances between alkyl tails not only decreases the affinity of the surface for organic solvents but also improves the connectivity of the interlayer to the external solutions. Thus, the influence of salt on the bulk solutions is extended to the interlayer solutions in BODMA clays due to this greater connectivity. This interpretation substantially reconciles the above-mentioned disparities.

3.4. Effect of layer charge and location of charge on swelling

The layer charge that separates the two types of swelling profiles observed in Fig. 2 is ~ 0.8 e^-. Because the initial interlayer space (in water) was greater for BODMA clays of higher charge densities, the absorption of ethanol–water mixtures resulted in less subsequent swelling.

Total layer charge influenced the initial d-spacings measured in water-solvated samples and the degree to which the BODMA clays swelled in intermediate ethanol–water mixtures but had little effect on the final d-space measured for ethanol-solvated samples. The interaction of the tetrahedral layer charge of the smectite (Table 1) with this relationship can be seen if the ratio of octahedral to tetrahedral layer charge is plotted against the difference in interlayer expansion measured for BODMA smectites solvated in water compared with that in ethanol. Such an effect is plotted in Fig. 5. Comparison of Upton and Miles montmorillonite reveals that, while both have essentially the same total layer charge (Table 1), the difference in d-space for ethanol- and water-solvated states is nearly 3 Å. The main cause of this difference is presumably due to the effect of layer charge
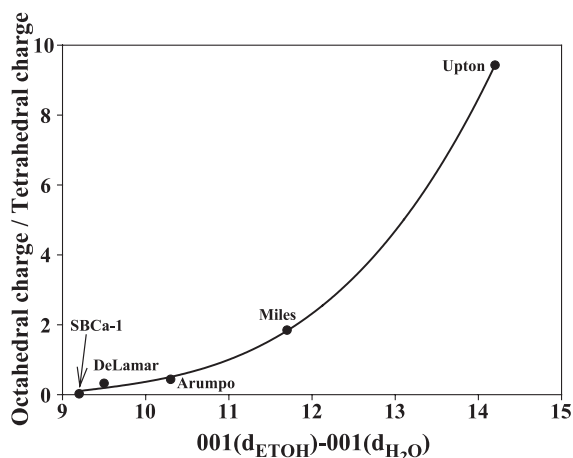
Fig. 5. Relationship between the difference in measured $d(001)$ of BODMA smectites in the ethanol-solvated ($001d_{ETOH}$) and the water-solvated ($001d_{H_2O}$) states, and the octahedral to tetrahedral layer charge ratio.

location on the interlayer structures in the water-solvated states. Miles bentonite has nearly 50% of its layer charge located in tetrahedral sheets, whereas Upton has nearly all of its layer charge located in octahedral sheets. Layer charges residing predominantly within tetrahedral sheets result in less total swelling between the ethanol and water solvation states for these organo-clays (Fig. 2). These results indicate that the relative degree of swelling of organo-modified clays in ethanol relative to water is substantially greater for those dioctahedral clays with low total layer charge and high octahedral to tetrahedral charge ratio.

3.5. The interlayer arrangement of BODMA

The total layer charge of the clay, and how it controls interlayer packing density of the organic cations, is of obvious overall importance in determining the resultant swelling behavior of BODMA smectites. The greater interlayer spacings measured for the BODMA Arumpo bentonite and the BODMA beidellites at the air- and oven-dried states are a direct measure of this effect.

A BODMA cation occupies an interlayer surface of ~ 152 Å^2; thus, any layer charge density greater than ~ 0.3 e$^-$ per $O_{20}(OH)_4$ requires that the aliphatic tails and benzyl functional groups of adjacent BODMA

cations begin to overlap. For clays with charges <0.8 e$^-$, BODMA molecules likely lie with their alkyl tails flat and with the benzyl side groups projecting outward from the clay surface at an angle of $\sim 30°$ (Fig. 6A). This configuration would allow the flat-lying aliphatic tails to overlap to form a bimolecular layer arrangement (Lagaly and Weiss, 1969). Thus, at low charge densities, sufficient space is available for more water and ethanol molecules, and, hence, the water loss at 105 °C is greater than for samples with higher charge densities (Table 2). Clays with charges <0.8 e$^-$ per unit cell would also require the sorption of more solvent molecules to expand in comparison to those which have charges >0.8 e$^-$ per unit cell as is also observed by the swelling curves depicted in Fig. 2. In contrast, at layer charge densities of 0.8 e$^-$, interlayer packing densities would require substantial overlap of the aliphatic tails, causing them to become inclined ($\sim 30°$) with respect to the interlayer surfaces (Fig. 6B). An inclined orientation of the aliphatic tails of the BODMA cations effectively reduces the area of the interlayer surfaces occupied by individual molecules and thus allows a higher packing density.

3.6. Mechanism of swelling of organo-clays in ethanol–water mixtures

Solvation by ethanol (and ethanol–water mixtures) interrupts van der Walls forces operating between the hydrocarbon tails of the BODMA cations. The lower dielectric constant, dipole moment and surface tension of ethanol compared to water (Table 4) enable it to penetrate the interlayer space of the organo-modified clays more easily than water. The ability of ethanol to disrupt these hydrophobic forces can be observed by the fact that washing with ethanol or other organic solvent removes intercalated organo-salt molecules from organo-clays, whereas washing with water is only partially effective (Lee and Kim, 2002; Slade and Gates, 2004). Presolvation and crystalline swelling of the organo-modified clay with polar organic solvents is an important first step in the preparation of fully dispersed gels or sols (Moraru, 2001) because it enhances the further penetration of the interlayer space by polymeric moieties.

Interestingly, these interactions appear to be important for the penetration of any polar organic solvent. Moraru (2001) reported that the presence of
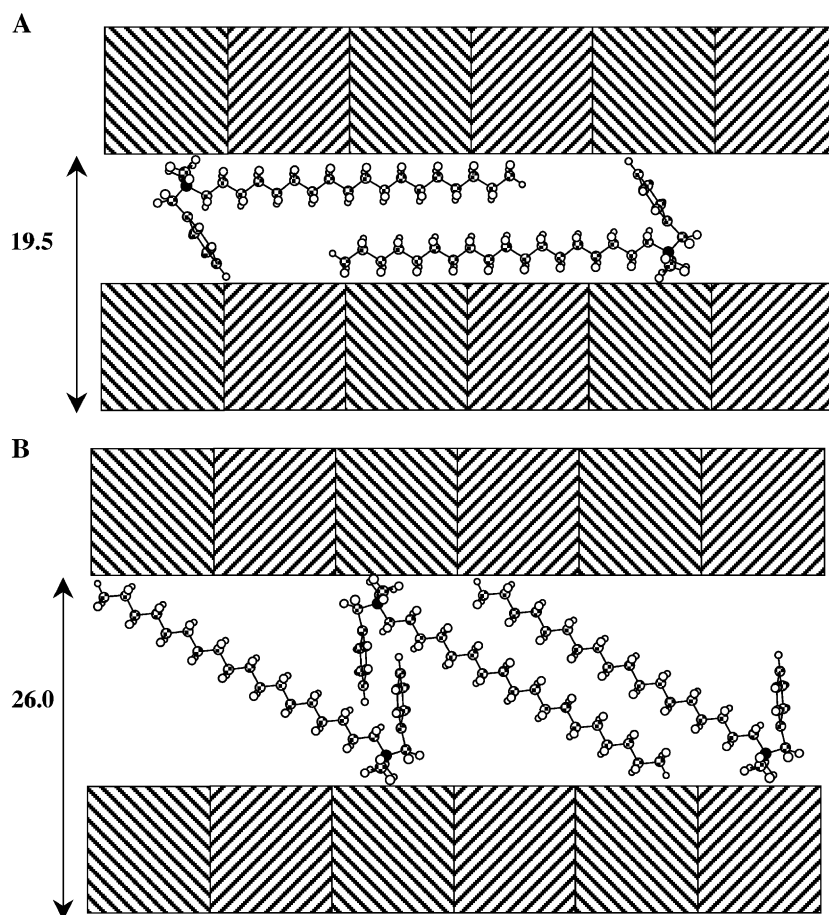
Fig. 6. Scaled representation of plausible interlayer arrangements of air- or oven-dried and BODMA smectites with layer charge densities of (A) <0.8 e$^-$ and (B) >0.8 e$^-$ per $O_{20}(OH)_4$. The lateral distances between alkylammonium units inversely related to layer charge density.

a small but significant amount of water in the inter-layer space of organo-modified clays was necessary to initiate crystalline swelling in polar organic solvents as well. Water can cause limited crystalline swelling of the BODMA smectites, and some water is probably important in initiating the penetration and sorption of larger organic molecules. BODMA smectites solvated

with ethanol–water mixtures of intermediate ethanol concentration expanded to the extent allowed by the balancing of forces of repulsion (electric double layer extending from the clay surface) and forces of attrac-tion (van der Waals and H-bonding) operating in the interlayer space of the BODMA smectites. Changes in solvent properties, e.g., dielectric constant and surface tension, influence these interactions. Changes in the orientation of the organic cation on the interlayer surface (i.e., with layer charge of ~ 0.8 e$^-$) might also impact these interactions by affecting the degree to which the surface charge is screened from the interlayer solutes or by imparting a change in the relative interlayer porosity (Fig. 6B).

When fully ethanol solvated, all BODMA smectites studied expanded to 34–36 Å which is consistent with

Table 4
Physical–chemical constants of water and ethanol at 298 K

	ε	μ [debye]	τ [Pa]	ρ [kg m^3]	η [Pa s (10^{-3})]	V_{mol} [nm^3]
EtOH	24.3	1.69	0.0228	0.7893	1.204	0.0352
H$_2$O	78.5	1.85	0.0729	0.9973	1.002	0.0109

Dielectric constant: ε; dipole moment: μ; surface tension: τ; density: ρ; viscosity: η; molecular volume: V_{mol}.

the development of bimolecular layers of BODMA cations with their hydrocarbon tails inclined ∼ 60° to the interlayer surface (Fig. 7). Thus, solvation of the interlayer with ethanol probably allows the BODMA cations to rotate about dimethyl functional groups so that ethanol molecules surround, and support, the aliphatic tails because, by rotation, the intercation pore space increases. For smectites with low-charge densities, the hydrocarbon tails of the BODMA cations lie flat to the interlayer surface and may only partially overlap. When fully ethanol-solvated, it is probable that the BODMA montmorillonites also develop a bimolecular layer structure similar to that proposed for the BODMA beidellites although with larger ethanol-filled pores between adjacent BODMA cations.

A similar intercalate structure has been implied for HDTMA smectites upon sorption of toluene (Slade and Gates, 2004) and for other alkylammonium–clay–alkanol systems (Weiss, 1963; Lagaly and Weiss, 1969; Lagaly, 1976). While the swelling due to ethanol or toluene (Slade and Gates, 2004) solvation is reversible, swelling induced by the sorption of organics with low-vapor pressures, or low-water solubilities (Singh et al., 2003), is expected to be less reversible due to a stronger interaction of these organics with the organo-clay. Thus, swelling induced by the sorption of low concentrations of contaminants over long periods of time may adversely impact properties such as the permeability of organo-modified clays to solutions (Gates et al., in press) and should be considered in the design of permeable reactive barriers.

4. Conclusions

Equilibration of BODMA smectites with increasing amounts of ethanol in ethanol–water solutions resulted in expansion of the interlayer spaces consistent with changes in interlayer configuration from bimolecular layers of BODMA cations, with their aliphatic carbon tails parallel to the layer plane, to bimolecular layers of BODMA cations whose aliphatic tails reside at a low angle (∼ 30°) with respect to the layer plane. Organo-modified clays have the capacity to swell more in organic solvents with lower dielectric constants than is known to occur for Na- or Ca-smectites in water. Even for bentonites containing an appreciable amount of nonswelling components (i.e., Miles and Arumpo), the absorption of mixed ethanol–water solvents resulted in expansion. Thus, it is expected that similar, extensive swelling of organo-clays may occur during the uptake of hydrocarbons. The solvent-induced swelling may be of particular

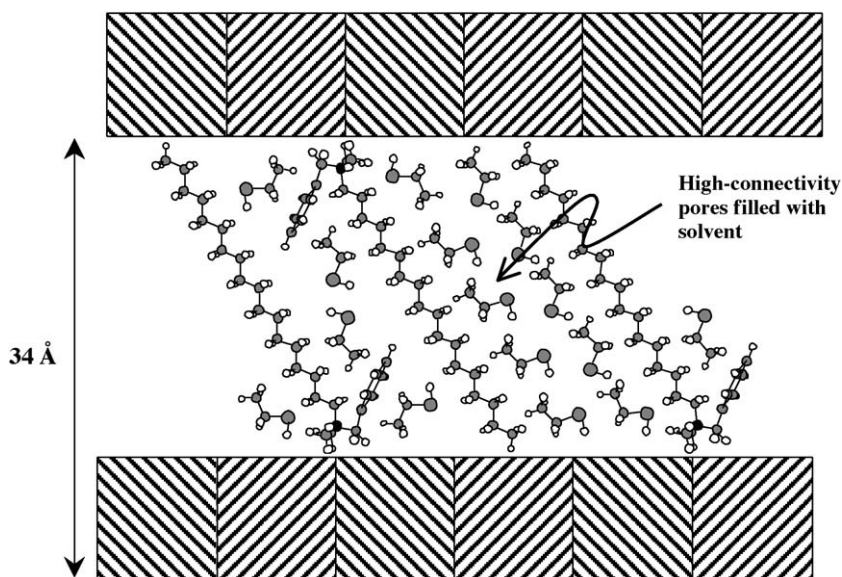High-connectivity pores filled with solvent

34 Å

Fig. 7. Scaled representation of plausible interlayer arrangements and gallery formation of fully ethanol-solvated BODMA smectites.

importance in the design of barriers for sites in which the disposal of concentrated organic solvents are planned. A companion paper will report the results of the permeability of BODMA smectites to miscible binary liquid mixtures (Gates et al., in press).

Acknowledgements

References

Alther, G.R., 1995. Organically modified clay removes oil from water. Waste Management 15, 623–628.

Alther, G.R., 2002. Using organoclays to enhance carbon filtration. Waste Management 22, 507–513.

Bodine Jr., M.W., 1987. CLAYFORM: a FORTRAN 77 computer program apportioning the constituents in the chemical analysis of a clay or other silicate mineral in a structural formula. Computers & Geosciences 13, 77–88.

Bonczek, J.L., Harris, W.G., Nkeda-Kizza, P., 2002. Monolayer to bilayer transitional arrangement of hexadecyltrimethylammonium cations on Na-montmorillonite. Clays and Clay Minerals 50, 11–17.

Churchman, G.J., Askary, M., Peter, P., Wright, M., Raven, M.D., Self, P.G., 2002. Geotechnical properties indicating environmental uses for an unusual Australian bentonite. Applied Clay Science 20, 199–209.

Gates, W.P., Anderson, J.S., Raven, M.D., Churchman, G.J., 2002. Mineralogy of a bentonite from Miles, Queensland, Australia and characterisation of its acid activation products. Applied Clay Science 20, 189–197.

Gates, W.P., Nefiodovas, A., Peter, P. Permeability of an organo-modified bentonite to ethanol–water solutions. Clays and Clay Minerals (in press).

Gilman, J.W., Jackson, C.L., Morgan, A.B., Harris, R., Manias, E., Giannelis, E.P., Whuehnow, M., Hilton, D., Phillips, S.H., 2000. Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites. Chemistry of Materials 12, 1866–1873.

Guerin, T.F., Horner, S., McGovern, T., Davey, B., 2002. An application of permeable reactive barrier technology to petroleum hydrocarbon contaminated groundwater. Water Research 36, 15–24.

Jaynes, W.F., Boyd, S.A., 1991. Clay minerals type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays. Soil Science Society of America Journal 55, 43–48.

Jordan, J.W., 1963. Organophilic clay-based thickeners. In: Swineford, A. (Ed.), Proceedings of the 10th National Conference on Clays and Clay Minerals. Pergamon, Austin, pp. 299–308.

Koh, S.M., Dixon, J.B., 2001. Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene. Applied Clay Science 18, 111–122.

Lagaly, G., 1976. Kink-block and gauche-block structures of bimolecular films. Angewandte Chemie. International Edition 15, 575–586.

Lagaly, G., 1984. Clay–organic interactions. Philosophical Transactions of the Royal Society of London. A 311, 315–332.

Lagaly, G., 1987. Water and solvents on surfaces bristling with alkyl tails. In: Kleeberg, H. (Ed.), Interactions of Water in Inoic and Nonionic Hydrates. Springer-Verlag, Berlin, pp. 229–240.

Lagaly, G., Weiss, A., 1969. Determination of the layer charge in mica-type layer silicates. In: Heller, L. (Ed.), Proceedings of the International Clay Conference, Tokyo, vol. 1. Israel Univ. Press, Jerusalem, pp. 61–80.

Lagaly, G., Witter, R., 1982. Clustering of liquid molecules on solid surfaces. Berichte der Bunsengesellschaft für Physikalische Chemie 86, 74–80.

Lagaly, G., Witter, R., Sander, H., 1983. Water on hydrophobic surfaces. In: Ottwill, R.H., Rochester, C.H., Smith, A.L. (Eds.), Adsorption from Solution. Academic Press, London, pp. 65–77.

Lee, S.Y., Kim, S.J., 2002. Expansion of smectite by hexadecyltrimethylammonium. Clays and Clay Minerals 50, 435–445.

Malvern Instruments, 1991. Zeta potential measurement applications manual. Malvern Instruments Applications Report. AN Z3-5. Malvern Instruments. 19 pp.

Moraru, V.N., 2001. Structure of alkylammonium montmorillonites in organic media. Applied Clay Science 19, 11–26.

Norrish, K., Hutton, J.T., 1969. An accurate X-ray spectroscopic method for the analysis of a wide range of geologic samples. Geochimica et Cosmochimica Acta 33, 431–453.

Reynolds, R.C., 1985. NEWMOD a computer protrgram for the calculation of one-dimensional diffraction patterns of mixed-layered clays R.C. Reynolds, 8 Brooks Rd., Hanover, NH.

Singh, N., Megharaj, M., Gates, W.P., Churchman, G.J., Anderson, J., Kookana, R.S., Naidu, R., Chen, Z., Slade, P.G., Sethunathan, N., 2003. Bioavailability of an organophosphorus pesticide, fenamiphos, sorbed on an organo-clay. Journal of Agricultural and Food Science 51, 2653–2658.

Slade, P.G., Gates, W.P., 2004. The swelling of HDTMA smectites as influenced by their preparation and layer charges. Applied Clay Science 25, 93–101.

Van Olphen, H., 1963. An Introduction to Clay Colloid Chemistry. Wiley-Interscience, New York. 301 pp.

Weiss, A., 1963. Organic derivatives of mica-type layer-silicates. Angewandte Chemie. International Edition 2, 134–144.

Xu, S., Boyd, S.A., 1995. Cationic surfactant adsorption by swelling and nonswelling layer silicates. Langmuir 11, 2508–2514.