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STUDIES OF ORGANOPHILIC CLAYS: THE DISTRIBUTION OF QUATERNARY AMMONIUM COMPOUNDS ON CLAY SURFACES AND THE ROLE OF IMPURITIES

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Abstract—Wyoming bentonite (predominantly Na^+ form) was shown to contain quartz as a major impurity, together with a number of minor impurities. Air refinement of the clay gave some separation by particle size, but impurity phases persisted in both the coarse (7.3–188 μm) and fine (1.9–9.8 μm) fractions. Exchange of the clay with a long-chain alkylquaternary ammonium salt, $R_2NMe_2 \cdot Cl$ ($R = C_{18}$, 64%; C_{16}, 31%; C_{14}, 4%; C_{12}, 1%), by a "dry" process gave a partially exchanged material (68–78%) with surface-sorbed quaternary ammonium ion pairs as demonstrated using X-ray photoelectron spectroscopy. The surface-sorbed material was somewhat labile to washing. Despite a relatively high paramagnetic gram susceptibility, good quality ^{29}Si MAS NMR spectra were obtained from the materials. The origin of the paramagnetism is iron present in a small amount as structural Fe^{II} and to a larger extent as Fe^{III}, the distribution of which is more ambiguous. The surface-sorbed quaternary ammonium species induces a measurable shielding of the ^{29}Si nuclei of both clay and quartz particles which is considered to arise from an anisotopic magnetic susceptibility effect

The interaction of smectite clays with surfactants is well documented[1] and cationic surfactants will exchange for inorganic interlayer cations from aqueous solution in the pH range 5–7. Such materials, sometimes termed "organoclays" enjoy a wide range of application in a variety of areas such as ink technology,[2] foundry moulding sands,[3] paint technology[4,5] and drilling muds.[6,7] In addition, applications in environmental science as sorbants for toxic organics have been considered.[8–10] Within the laboratory, the uses of organoclays as phase-transfer catalysts[11–13] and as stationary phases in g.l.c. columns[14] have been documented.

The alkylammonium compounds may be sorbed in excess of the cation exchange capacity (c.e.c.) of the clay implying the intercalation of ion pairs, although the extent to which this happens depends on factors such as alkyl-chain length, layer charge and pH. Usually the ion pairs are labile to washing, although some material may be more tenaciously held. For technical purposes the organophilic bentonites (montmorillonites) may be prepared by a "wet" method involving the contact of a dilute aqueous dispersion of sodium bentonite with, usually, a dialkyl dimethyl ammonium salt. Alternatively, a "dry" method may be employed which involves the reaction of the clay and the surfactant at 60°C in a high shear mixer. The "wet" process can aid the removal of non-clay impurities from the natural bentonites, but the product of the "dry" process will retain such material. It is the purpose

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of this paper to examine in more detail the nature of the material from a laboratory simulation of the "dry" process and to examine the role, if any, of the impurities in determining the bulk properties of the product.

EXPERIMENTAL AND RESULTS

Characterization of clay

A sample of Wyoming bentonite showing a dehydroxylation weight loss of *ca* 6% (TGA) with a cation exchange capacity[15] of 70 meq 100 g^{-1} was obtained from Steetley Minerals Limited* and subjected to grinding and air refinement to produce "coarse" (70%) and "fine" (30%) fractions. X-ray powder traces (XRD) of both fractions were very similar, implying that air refinement is based on particular size and that chemical separation was at best partial. A low-angle reflection gave a basal spacing of 14 Å, in good agreement with accepted values for such materials.[16]

Other reflections observed could be attributed with confidence to α-quartz, which was the major impurity. Additional impurities suggested by the XRD data included corundum, feldspars (Na or K, or $Ca_{0.5}$; $AlSi_3O_8$), calcite, siderite, pyrite and haematite. All these minerals are found naturally within the Wyoming/Colorado region of the U.S.A. Optical microscopic examination confirmed the presence of impurity phases, the major component of which was a colourless material considered to be quartz. Simple determinations of the gram susceptibility, χ_g, were made on a Gouy apparatus: χ_g (coarse) $= 6.5 \times 10^{-6}$ c.g.s. units g^{-1} and χ_g (fines) $= 6.0 \times 10^{-6}$ c.g.s units g^{-1}. A Mössbauer spectrum of the "fines" revealed two resonances: (a) Fe^{III} $\delta = 1.34$, $\Delta = 0.57$, $\Gamma_{1/2} = 0.70$ mm s^{-1} (87%); (b) Fe^{II} $\delta = 1.29$, $\Delta = 2.59$, $\Gamma_{1/2} = 0.61$ mm s^{-1} (13%). A laser light-scattering technique was employed for the determination of particle size ranges (iodomethane was the non-swelling dispersion medium) with the following results:

Clay fraction	Particle size range (μm)
Fines	1.9–9.8
Coarse	7.3–188

Ion exchange of clay by a "dry" process

The quaternary ammonium salt used was a commercial material, Arquad 2HT-75, supplied by Akzo Chemicals Limited. This is a trade name for a 75% solution, in 60% propan-1-ol/water, of dehydrogenated tallow dimethylammonium chloride, $R_2N(CH_3)_2 \cdot Cl$, where R is predominantly stearic, i.e. $-C_{18}H_{37}$ 64%; $-C_{16}$ 31%, $-C_{14}$ 4%, $-C_{12}$ 1%. Wyoming bentonite (fines, 750 g) was placed in a high shear mixer operating at 60°C together with 1% w/w sodium carbonate as a fluid loss and viscosity improver.[17] Following dry blending (1 min) water (16.7% w/w) is blended in for 5 min, after which sufficient Arquad 2HT-75 to theoretically satisfy the cation exchange capacity of the clay is added. Blending was continued for 30 min, following which the mixture was extruded, dried in a fluid bed drier and milled. The process was repeated using a "coarse" fraction of the clay. Portions of each dried clay were washed with a solution of 75% propan-1-ol water until the washings were clear of chloride ion ($AgNO_3$). Washings were carefully conserved and analysed, by atomic absorption spectroscopy, for released Na^+ and Ca^{2+}. The washed clays were subjected to XRD examination, some relevant data are in Table 1.

Ion exchange of clay using a "wet" process

Bentonite (12 g) was added to distilled water (350 cm^3) and dispersed by agitation overnight on a mechanical shaker. The resulting suspension was set aside for 1 day to allow the more dense impurities to settle. The suspension was carefully decanted and the residue was separated, dried and weighed. The amount of montmorillonite in the suspension was then determined by difference.

The quantity of hexadecycltrimethylammonium chloride required to satisfy the c.e.c. of the remaining clay was weighed and placed, together with the clay suspension, in a 500 cm^3 conical flask and shaken for 1 week on a mechanical shaker. The product was filtered, washed (100 cm^3 distilled water per 2.5 g clay) and air-dried. Analysis of the filtrate (Na^+, atomic absorption) revealed 100% exchange.

The basal spacing [*d*(001), XRD] was determined to be 17.7 Å, a value consistent with complete exchange.

NMR investigations

Magic angle spinning NMR (MAS NMR) ^{29}Si spectra of the fine fraction of Wyoming bentonite, together with those for the dry product direct from

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*Elemental analysis: SiO_2, 55.6; TiO_2, 0.1; Al_2O_3, 16.5; Fe_2O_3, 5.1; CaO, 1.9; MgO, 2.0; Na_2O, 1.2; K_2O, 0.6; Mn_3O_4, 0.1%. Loss at 105°C, 11.5%; loss at 1000°C, 5.7%.

Table 1. Data for "dry" process quaternary ammonium exchanged Wyoming bentonite

Wyoming bentonite	Arquad 2HT M_{eq} per 100 g added	 % added cation ion exchanged	% Exchange sites ion exchanged	$d(001)$ (Å)
Coarse	84	62	70	12.4
Coarse	78	66	68	12.7
Fine	86	69	78	12.5
Fine	78	75	78	12.5

the "dry" process and of the same product following washing with 75% propan-1-ol/water (see above), were determined. Data are presented in Table 2.

X-ray photoelectron spectroscopic investigations

For this purpose samples of Wyoming bentonite which had been totally exchanged with potassium ions or sodium ions were produced by the method of Posner and Quirk.[18] Also, a sample of distearyldimethyl ammonium bromide, $(C_{18}H_{37})_2N(CH_3)_2\cdot Br$, was produced using the Menschutkin reaction.[19] The Na^+ and K^+ bentonites were mixed with a 120 meq loading of $(C_{18}H_{37})_2N(CH_3)_2\cdot Br$ in a scaled down "dry" process experiment. The products were subjected to Br(3*d*) XPS examination, the results of which are given in Table 3.

Table 2. MAS NMR data for Wyoming bentonite

Wyoming bentonite sample	Chemical Shift ^{29}Si *vs* TMS[a] Q^3	 Q^4
Natural "fines"	−91.5	−105.7
Arquad dry-process exchanged	−94.9	−108.7
Arquad dry-process exchanged/washed	−92.3	−106.0
Arquad dry-process exchanged (new sample)	−94.4	−107.9
Arquad dry-process exchanged (washed/new sample)	−93.5	−107.8
HDTMA[b]wet-process exchanged (i)	−93.4	−107.6
HDTMA[b]wet-process exchanged/washed (i)	−93.5	−107.6
HDTMA wet-process exchanged (ii)	−93.5 −93.7[c]	−107.7 −107.8[c]
HDTMA wet-process exchanged/washed (ii)	−93.5	−107.6

[a] External.
[b] HDTMA ≡ hexadecyltrimethylammonium.
[c] Second sample from same batch.
N.B. Q^3—resonance from "SiO_4" sharing three vertices; Q^4—resonance from "SiO_4" sharing four vertices.

Instrumentation

A TGA trace for Wyoming bentonite was obtained with Stanton Redcroft TJ750 equipment. All XRD data were obtained with a Philips X-ray diffractometer using the Co-K_α line (1.79 Å). Magnetic susceptibilities were measured with standard Gouy equipment incorporating a Newport Instruments electromagnet and a Stanton SM12 balance. The ^{57}Fe Mössbauer measurement was kindly undertaken by Professor F. J. Berry (Open University) and particle sizing was achieved using an M 3.0 series laser particle sizer from Malvern Instruments. MAS NMR spectra (^{29}Si) were measured with a Bruker AC300 instrument operating at 59.628 MHz; rotor spinning rates were *ca* 5000 Hz. Analysis for Na^+ and Ca^{2+} was carried out with Perkin–Elmer AA equipment and XPS measurements were made on a VG scientific ESCALAB 200-D instrument using Mg-K_α (1.254 eV) radiation. $(C_{18}H_{37})N(CH_3)_2\cdot Br$ and KBr were employed as "standard" compounds for study of the Br(3*d*) spectra. Sample charging problems were

Table 3. XPS Br(3*d*) data for quaternary bentonites

Sample	Br(3*d*) Binding energy (eV, ±0.2)	
QBr[a]	67.1	
KBr		68.5
K bentonite/QBr	67.2	68.3
Na bentonite/QBr	67.2	68.3

[a] QBr = $(C_{18}H_{37})_2N(CH_3)_2\cdot Br$.

overcome by calibrating the spectra internally with reference to the C(1*s*) photopeak. Curve synthesis techniques were employed for analysis of the bromine XPS spectra; the process was terminated when the simplest fit consistent with a satisfactory reduced χ^2 value was obtained.

DISCUSSION

The systems discussed in this paper are based on both the clay and quaternary ammonium compounds used commercially. Clearly, the Wyoming bentonite used has a significant iron content, but given that the clay shows a fairly sharp Q^3 resonance in the ^{29}Si MAS NMR spectrum, albeit at a chemical shift that is doubtless an average for at least three "next nearest neighbour" environments, the decision was taken to work with the actual systems involved in manufacture rather than extrapolate from data obtained from more ideal systems. The spinning side band progression (see Fig. 1) doubtless reflects the presence of structural iron in the clay.

In work with natural clays it is important to have some understanding of the mineralogy of the material used. Investigations by TGA and XRD of the sample of Wyoming bentonite used in this work showed the bulk of the sample to be a smectite clay; however, the XRD gave clear evidence of the presence of impurity phases. The major impurity was silica but minor impurities were also present (see experimental section), the identities of which were established with less certainty but those tentatively identified are consistent with the geology of the Wyoming–Colorado clay deposits.[20] Air refining of the clay produced separation according to particle size ("coarse" and "fines"), but physical separation of impurity phases is less pronounced. Thus, even if the "fines" fraction is selected for ion-exchange by the "dry" process with quaternary ammonium compounds, readily detectable quantities of abrasive silica will be present in the product. It was assumed that the bulk of the sample was sodium bentonite. Analysis of inorganic ions released during the ion-exchange process revealed the presence of small (2.6%) quantities of released Ca^{2+}.

The purpose of this investigation was to examine the nature of the product obtained from a simulation of a so-called "dry" method of exchange. Quantities of the commercial quaternary compound Arquard 2HT-75 were added at ratios slightly in excess of the cation exchange capacity of the clay. Analysis of released Na^+ and Ca^{2+} ions revealed that, at best, a 78% level of ion exchange had been achieved (Table 1) for the "fines" and rather less (*ca* 69%) for the coarse fraction. Fully exchanged quaternary ammonium clays usually

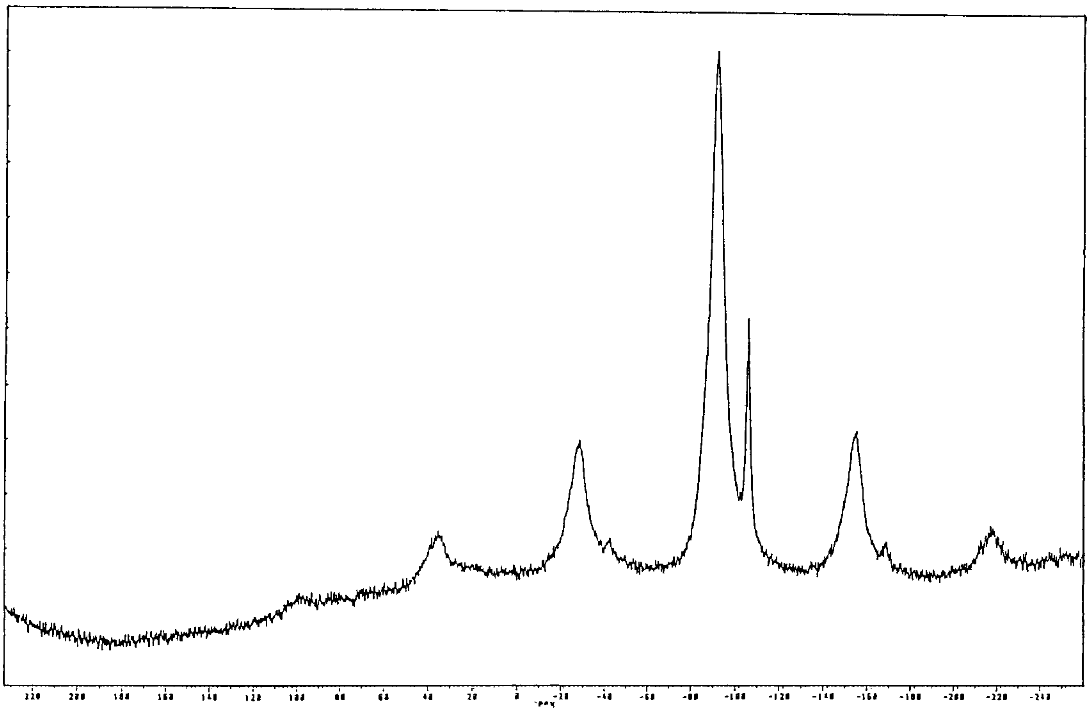

Fig. 1. ^{29}Si MAS NMR spectrum of the fine fraction of air classified Wyoming bentonite.

show basal spacings [i.e. $d(001)$] of *ca* 17 Å,[21] reflecting the presence of a double layer of ions in the interlamellar region; however, the samples investigated here show values of $d(001)$ in the range 12.4–12.7 Å. This is indicative of a single layer of quaternary ions in the interlamellar space, the decrease from the original clay value of 14 Å reflecting the lower solvation of the exchanged quaternary ammonium ions. The product of the "dry" process will contain quaternary ammonium-exchanged smectite clay, mineral impurities, unexchanged quaternary ammonium salt and released inorganic salts. It is supposed that the latter two components may be removed by washing, but it was decided to employ physical methods of analysis to determine the distribution of these materials in the bulk product.

Table 2 presents ^{29}Si MAS NMR data for the "fines" fraction of the clay both before and after exchange by the dry process. The influence of the effect of rigorous washing of the exchanged sample is also examined. Recent work from our laboratory[22] investigated the tolerance to paramagnetic impurity of the resolution of Q^n resonances in ^{29}Si MAS NMR spectra and the results of those studies of the thermolysis of hectorite doped with paramagnetic ions suggested that a simple determination of χ_g, the gram magnetic susceptibility of the sample, was a good predictor of the spectral quality to be expected. The observed value of χ_g for Wyoming bentonite used here was well into the range established to give poor spectral resolution ($\chi_g > 2.2 \times 10^{-6}$ c.g.s. units),[22] yet good quality MAS NMR spectra were obtained (see Fig. 1). It will be noted that the nature of the work with hectorite ensured that the paramagnetic was in close contact (next nearest neighbour) with the bulk ^{29}Si, also relaxation times in the two systems may be very different. However, the χ_g value determined for Wyoming bentonite demonstrates the presence of significant paramagnetism and the ease with which a ^{57}Fe Mössbauer spectrum was obtained suggested that the bulk of this paramagnetism is due to iron. A weak Fe^{II} component has parameters (experimental section) in close agreement with other examples of Fe^{II} in dioctahedral minerals.[23] The more intense Fe^{III} resonance also has parameters typical of Fe^{III} in clay mineral environments,[24] but unfortunately, given the large value of $\Gamma_{1/2}$ (0.7 mm s^{-1}) it is not possible to exclude the additional presence of very finely divided (super paramagnetic) Fe_2O_3 or Fe(O)(OH) which could contribute to the iron(III) quadrupole split spectrum and to the observed value of χ_g. If present, such material may contaminate the surface of major mineral components and enhance sorption capacity without necessarily exerting influence on the values of T_1 for the bulk ^{29}Si atoms.

The ^{29}Si shifts relative to a separate sample of TMS, which are presented in Table 2, clearly show that the dry exchange process results in screening of both Q^3 and Q^4 resonances. However, when the dry exchanged materials are washed the shifts return towards their natural values. The preparation of the clay-process exchanged material was repeated in a totally independent experiment and ^{29}Si MAS NMR data were obtained for unwashed and washed samples. For Q^3 resonance the trend in shift relationships is seen, although the absolute magnitude of the effect is smaller in this experiment; Q^4 on this occasion is invariant. The differences are believed to reflect the non-homogeneity of both clay and impurity particles at the microscopic level. The shift differences in the Q^3 resonance between washed and unwashed clay are well outside the limits of reproducibility expected for replicate measurements on the same sample (see below) and are therefore treated as real differences. Superficially, this behaviour may be associated with the removal of the surface-unexchanged quaternary ammonium ion. There is some evidence to support this from the data in Table 1. From these it can be seen that the percentage added cation–ion exchanged is greater for the fine Wyoming bentonite which must have a larger surface area than the coarse sample. The fact that the basal spacings are the same for both the coarse and fine samples after exchange suggests that the interlamellar composition in both samples may be similar, so that the difference in the percentage ion exchanged must be due to a surface area effect. If this is the case the ion-exchanged induced screening could be due to a surface effect. However, before this can be considered as certain an alternative explanation must be debated. Clay crystals are platelets and have a pronounced anisotropy of magnetic susceptibility and there is the possibility that the platelets will tend to align, particularly in the MAS NMR experiment with rotor spinning speeds in excess of 5000 Hz. Thus, the assumption of a perfect powder with complete orientational averaging may not be valid in this case, hence variations in bulk magnetic susceptibility screening may occur from sample to sample as a result of partial orientation and manifest themselves as differences in shielding of the ^{29}Si nuclei. A sample of bentonite was exchanged with hexadecyltrimethyl ammonium ions using a "wet" method (see experimental section), which should provide specimens with no surface-sorbed ion pair material. Independent samples of this clay were examined by ^{29}Si MAS NMR both before and after further washing. It will be noted (Table 2) that exchange with a quaternary ammonium ion does induce a shielding of the ^{29}Si nuclei compared with the natural clay value; however, the variation from measurement to measurement is slight and is certainly less than the variation between unwashed dry-exchange materials. Since platelet orientation effects should be similar for both "wet" and "dry" exchanged systems, it is concluded that the greater variation of δ (^{29}Si) for the unwashed and washed dry-exchanged clay is most probably due to the sorbed ion pair material which is absent for the wet process clay.

In solution NMR spectroscopy, intermolecular induced screening changes are well known to be associated with bulk susceptibility (σ_b), van der Waals (σ_w), electric field (σ_E), magnetic anisotropy (σ_a) and specific interaction screening effects (σ_s). Each of the last four screening effects are operative only over relatively short distances. Consequently, because the particles used were in the range 1.9–9.9 μm, and a factor of *ca* 1500 times larger than the absorbed species, it is evident that any of these four screening effects could only be operative in the first (few) surface layers of the bentonite particles. If such effects could be detected they must necessarily lead to resonance shift. The observed dry-exchanged and dry-exchanged/washed lines show no detectable difference in shape and a change in full width at half maxima (FWHM)) from 400 to 417 Hz. The implications are that the observed shift changes must be due to $\Delta\sigma_b$.

Based on the concepts originally developed by Dickinson,[25] Zimmerman and Foster[26] have shown that σ_b is controlled by the function $(1-3\cos^2\theta)$, where θ is the angle between the direction of the applied field and the axis of rotation. In the MAS NMR experiment $\theta = 54.7^\circ$, so that the controlling function should vanish and there should be no magnetic susceptibility screening effect. Of course, if the magic angle is mis-set there could be a residual susceptibility screening effect: for the present work the magic angle was carefully set by minimizing the bromine resonance linewidth for a sample of KBr, and it is unlikely that the shift changes presented in Table 2 can be explained on the basis of a mis-set magic angle.

Earl and Van der Hart[27] have pointed out that the notion that chemical shifts in MAS experiments involve no bulk susceptibility corrections hinges on the susceptibility being isotropic. Through elegant experiments on films of polyethylene-terephthalate (PET), they supported their contention that samples that exhibit macroscopic anisotropy in their bulk magnetic susceptibility may give rise to a bulk magnetic susceptibility screening effect. A film of highly crystalline PET (with aromatic rings parallel to the plane of the film) wound around a capillary of TMS along the rotation axis presented an effectively anisotropic susceptibility environment to the TMS, which was consequently screened by 1.5 ppm. When discs of PET were stacked with their planes normal to the capillary the TMS experienced an isotropic environment and no susceptibility shift.

In principle, the phenomenon described above might be responsible for the shift differences seen in Table 2. However, for this to be the case the question immediately arises as to what constitutes a *bulk* environment. Little attention appears to have been paid to the effect of the thickness of a material on the susceptibility screening of an enveloped substance. In his work on susceptibility screening involving samples containing disperse phase globules, Homer[28] has shown that the susceptibility screening is independent of the number of globules present. As his samples were essentially emulsions with a range of globular sizes, and no unusual line broadening of asymmetry were observed, it may be reasonable to speculate that any molecular assembly that presents a homogeneous medium for the applied field may be deemed to be bulk. From a different viewpoint, evidence that the so-called anisotropic bulk susceptibility shifts may actually stem from molecular magnetic effects is inherent in Earl and Van der Hart's explanation of the PET-induced shifts.[27] They attribute these shifts to the anisotropy in susceptibility resulting from aromatic ring current effects. It is not unreasonable to assume that induced bulk susceptibility shifts are dominated by molecular magnetic anisotropy effects. It may be that the lengthy and mobile, though directionally averaged, steric chains in the quaternary ammonium ion adsorbed on the bentonite surface may be considered to offer an anisotropic magnetically susceptible environment to the bentonite particles.

It is probable that the quaternary ammonium ions are adsorbed on the surface of the bentonite particles in such a way that, on average, the stearic chains are aligned pseudo-radially from the particles. In this case there must be an analogy with the Earl Van der Hart PET wound film situation. Consequently, even during the eccentric rotation of the bentonite particles, they will continually have a magnetic anisotropic environment relative to the direction of the applied field. The volume magnetic susceptibility for the quaternary ammonium salt has been determined to be 2.04×10^{-6} c.g.s. units and although the anisotropy in χ_v is unknown, it is almost certain that $\chi_\perp - \chi_\parallel$ will be positive and cause a positive screening of the ^{29}Si nuclei in the bentonite, as observed.

If the above explanation of the shift changes recorded in Table 2 is correct, it is possible that the adsorption of quaternary ammonium ions on to the surface of solid particles may offer a method of manipulating chemical shifts for materials studied by MAS NMR spectroscopy. The particular effects observed by Earl and Van der Hart[27] are dependent on their use of an iron magnet, whereas results in this paper have been obtained with a super conducting magnet. However, since each long alkyl chain of surface-sorbed quaternary ammonium ion will have a different orientation to B_o, the spectrometer field, the isotropic surface binding to pseudo-spherical particles renders the susceptibility screening anisotropic irrespective of the specific direction of B_o.

Further evidence for the presence of quaternary ammonium ion pairs on the surface of the product from the dry process comes from studies of X-ray photoelectron spectra (XPS). In principle it should be possible to differentiate Q^+X^- and M^+X^- on the clay surface where Q^+ is the quaternary ammonium ion, X^- the counter-ion (halide) and M^+ the inorganic ion released in the ion exchange process. A convenient approach is to examine the X^- spectra where differences in binding energies for X^- between Q^+X^- and M^+X^- are maximized if $X = Br$[29] and $M = K$ (or Na). Accordingly, a potassium exchanged bentonite was prepared (experimental section) and exchanged by the "dry" process with $(C_{18}H_{37})_2N(CH_3)_2 \cdot Br$; the experiment was repeated using sodium bentonite. Examination of the Br (3*d*) binding energy data (Table 3) of the exchanged clays gave photopeaks whose FWHM were significantly greater than those for Q^+Br^- and K^+Br^-. Deconvolution techniques were employed and, we believe, afford good evidence for the sorbed Q^+Br^- ion pairs on the clay surface (Table 3).

CONCLUSIONS

Air refinement of a natural Wyoming bentonite gave some separation by particle size but impurity phases were significant in both coarse and fine fractions. Exchange of the clay with a long-chain alkyl-quaternary ammonium salt using a "dry" process afforded a partially exchanged bentonite with extra surface-sorbed quaternary ammonium salt. The surface-sorbed material was somewhat labile to washing and it produced a measurable shielding of the ^{29}Si nuclei in both clay and impurity (quartz) particles. It is proposed that such sorption of long-chain alkyl-quaternary ammonium species might be usefully employed to manipulate chemical shifts of materials studied by MAS NMR spectroscopy.

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