Adsorptive Interaction Studies of Aqueous Carboxylic Acids with Smectites, Kaolin and their Li-Exchanged Forms

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Summary: Commercial smectites (montmorillonite, hectorite and bentonite) and kaolin clays were purified by fractionated sedimentation with fraction < 2 μm particle size and their Li-exchanged forms were prepared by cation exchange method and characterized by XRD and SEM techniques. The XRD Patterns confirmed the purity and crystalline nature and SEM images indicated the particle sizes and morphologies of the materials investigated. Gels of smectites are formed when concentrations are greater than ~ 2 % by weight in deionized water. The effects of adsorptive interactions of aqueous carboxylic acids (HCOOH, CH₃COOH and CH₃CH₂COOH) 20 % (V/V, 10mL) were examined refractometrically using 0.05g of each clay sample in 14mL vials at room temperature. The experimental results proved that hectorite *i.e.*, trioctahedral magnesium smectite showed preferential adsorption of water from aqueous phase of carboxylic acids. Smectites (0.5 %) expanded and changed into jelly-like forms and kaolin formed a swollen paste in the aqueous carboxylic acids in vials. The sizes of the cylindrical shaped jells of smectites formed depend on the layer charge density, location of charge, size of carboxylic acid and nature of the interlayer cation and its hydration properties, were in the following order.

Li-montmorillonite > Na, Ca-montmorillonite > Na-bentonite > Li-bentonite ≥ Na-hectorite ≈ Li-hectorite.

It was also observed that the cylindrical shaped jells of the clays formed were largest in the aqueous propionic acid. The 0.5 % by weight of commercial clays formed slurries while pure clays changed to suspensions in deionized water in vials under similar conditions. The interactions of the water and carboxylic acids with the interlayer cations and the exposed smectite clay surface are responsible for the swelling due to the expansions of the interlayers from its dry state.

Introduction

In general clay minerals are phyllosilcates (or sheet silicates) which consist of one (or two) sheets of polymerized silicon-oxygen tetrahedra (T_h) and one sheet of polymerized aluminium or magnesium oxygen-hydroxyl octahedra (O_h). There are about 24 common species of clay minerals [1,2].

Smectite belongs to the 2:1 dioctahedral clay minerals, a species characterized by an elemental block (unit cell) that consists of two tetrahedra sheets separated by one octahedral sheet. Thus, the thickness of the triple sheet ($T_hO_hT_h$) is 9.3 to 9.4 Å [3]. It has expanding crystal lattice. Its isomorphous substitution gives the various types of smectite and causes a net permanent charge per formula unit layer, O_{10} (OH)₂ that ranges between 0.25 and 0.6 electron charges. This negative charge is balanced by cations in such a manner that water may move between the sheets or the crystal lattice, giving a reversible cation exchange in inter-lamellar space and a high specific

surface area about 800 m^2g^{-1} on the cleavage planes [2-4].

We chose for our study three smectites, montmorillonite, bentonite (sodium form) and hectorite. They are dioctahedral in the case of Al-octahedra and trioctahedral for Mg-octahedra. In the former case two out of three octahedra sites are occupied and in the latter case all three are occupied [3]. Montmorillonite is the best known member of the smectite group. It is commonly used due to its relatively high surface area, cation exchange capacity, harmlessness to the environment and ease of operation [5]. Bentonite was named after Fort Berton (Wyoming, USA), the locality where it was first mined. Sodium bentonite, which contains Na-rich montmorillonite, is native, highly colloidal, hydrated, dioctahedral and is processed to remove grit and non-swellable ore components [6]. Hectorite received its name from the city where it is mined,

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Hector, San Bernadina County, California. It is a native, colloidal, mineral lithium silicate.It is processed to remove grit and impurities and hectorite clay products are characterized as having excellent rheological, thixotropic and suspension properties. It has almost no aluminum in the octahedral sheet [3].

We also selected fourth clay of a different structure. Kaolin, also known as china clay, is made predominately of the clay mineral kaolinite and has a non-expanding character. It is a dioctahedral with a 1:1 layer consisting of a tetrahedral silicate sheet alternating with an octahedral alumina sheet. The single composite sheets are electrically neutral. Bonding between the sheets is affected by the attractive forces between the O-ions of the base of the SiO_4-tetrahedral layer of one composite sheet and the OH-ions of the octahedral layer of the underlying sheet. The thickness of a two-layered sheet (T_h+O_h) amounts to 7 Å. The small cation exchange capacity sometimes found with kaolin inter alia with the termination of crystal faces [3]. 2:1 and 1:1 layers are strongly bonded internally but relatively weakly bonded to each other [6]. Subsurface kaolin deposits in the coastal plain of central and eastern Georgia in the southern United States are at the center of the world kaolin mining industry [7].

Clays are important industrial raw materials and their role in many important processes have been studied. It is estimated that about 8 million tons of bentonite were used in 1992 throughout the world [8]. In addition to many other applications, clays are used as adsorbents, decoloration agents, ion exchangers, supports and as catalysts. Recent work on these materials, particularly smectite clays, as catalysts as large pillars has received interest. Polynuclear inorganic cations have been used to hold the clay layers apart and allow entry of large molecules found in the heaviest fractions of petroleum residue. Because zeolite pores are too small to allow entry of these large petroleum residue fractions, clays are an intriguing alternative. Such modified clays exhibit a two dimensional porous structure with acidic properties comparable to that of zeolites and have attracted considerable attraction as acid catalysts for petroleum refining [9-12]. Cation doped pillard clays have attracted great interest in academics and industry [13].

The aim of this paper is to investigate the adsorptive interactions of aqueous carboxylic acids

($HCOOH$, CH_3COOH, CH_3CH_2COOH) with purified (< 2 μm particle size) smectites and kaolin clays and their homoionic, Li-exchanged forms, which were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. We want to find refractometrically the selectivity of adsorption of water or carboxylic acid and observe directly the influence on the expansion and formation of gels of the clays.

Results and Discussion

Clay minerals are usually extremely fine grained and commonly impure [4,14,15]. In order to eliminate any impurities, all parent samples of clays investigated were purified by size fractionation using a sedimentation procedure [16,17]. This also removed any phases that were coarsely crystalline and greater than 2 μm.

All wet samples of purified smectites clays were in the form of expanded, excellent gels. In smectites, swelling of clay minerals occurs because the parallel lamellae in these structures are bonded to each other not covalently but by van der Waals and electrostatic forces [3]. Electrostatic bonding arises because there is anionic charge on the sheets neutralized by interlayer cations. These cations provide a "cement" which helps to hold together the anionic sheets on either side of them. The crystals of smectites swell readily by hydration of exchangeable cations by penetration of water molecules between the sheets. The percentages of suspensions of clays in deionized water before centrifugation were 0.952, 0.753, 0.634 and 0.219 by weight of montmorillonite, hectorite, kaolin and bentonite respectively. The gelation phenomenon, which occurs at a concentration as low as 2 percent clay by weight, is believed to result from layer edge-to-face interactions which generate a "house – of – cards" structure [6] or a more "ribbon-like" arrangement. The strength of the gel is dependent upon the surface-charge density of the clays particles and their concentration in the suspension [15,18]. As the concentration of suspensions is increased, the dispersions thicken and eventually become gel-like masses with high impedance to fluid flow. The gels were so rigid and sticky that did not flow out on tilting from the centrifuge bottles. A spatula was used for removing and transferring gels of smectites from centrifuge bottles to porcelain evaporating dish for drying in the air. The dried samples of smectites shrank and the

volume decreased several times from its wet volume. As smectite clays are made of two layers, or sheets of crystal units loosely held together, when these clays get wet the sheets get farther apart when these clays dry, the sheets get closer together. The ability of clays to undergo this transformation is called their shrink-swell capacity. As the dried samples were sticky and gummy therefore could not be ground easily by using mortar and pestle. The small size of clay particles ($<$ 2 μm) make them tightly packed together. Additionally clay particles are normally flat and will stack like plates. The holes or voids between clay particles are quite small and the large surface area binds water to the particles.

Kaolin and its lithium form did not show any swell-shrink behavior. The interlayer bonding in kaolinite microcrystals arises from van der Waal's attraction between layers, from hydrogen bonding between octahedral OH groups on one layer and tetrahedral O atoms on the adjacent layer and from electrostatic interactions arising from the fact that each layer, although electrically neutral, bears a net fractional charge of opposite sign on each basal surface [19]. The clays carry a net negative charge due to the broken bonds around the edges of the silica-alumina units that would give rise to unsatisfied charges, which would be balanced by the adsorbed cations [20].The kaolinite layer is electrically neutral but in reality it carries a small negative charge due to a small amount of isomorphous replacement [21] and exhibits a minimal negative ($<$ 0.01) surface charge [22]. The presence of surface and broken edge-OH groups gives the kaolin particles their electroneutrality and their capacity to adsorb cations [23]. It has non-expanding character. The surface functional groups are aluminol (AlOH), silanols (SiOH) and Lewis acid sites (AlOH$^+_2$) and are chemically active [19]. The basal surfaces are thus largely neutral or in case of aluminum for Si permanently slightly negative, whereas the edge surfaces are charged [24,25]. Kaolin has only one layer and is not subject to the shrink-swell phenomenon. Further, as kaolin has no layer charge will not expand, because no additional

cations are needed to offset the lack of charge [26]. The wet samples of kaolin were paste-like material and dried ones were powder and non-sticky. The easiness of removal from the surface of the porcelain dish and grinding to powder form was found in the following order:

Kaolin $>$ Bentonite $>$ Montmorillonite $>$ Hectorite
(Powder) (Thin flakes and laths) (Flakes and laths) (Thin flakes and laths)

In the presence of water, the negative charge of smectites compensated cations on the clay layer surfaces were exchanged according to valence rule by 2 M of LiCl used contain hundreds of times of Li$^+$ ions in excess of exchangeable cations in clay suspension. As mentioned earlier the kaolin carries a small negative charge ($<$ 0.1) due to a small amount of isomorphous replacement. This negative charge is responsible for the small but measurable ($<$ 0.1 mol kg^{-1} monovalent cations) exchange capacity of kaolin under acid conditions. It has been proposed that the exchange sites are located on only the tetrahedral surface of the kaolin crystal [21]. Normally solid/liquid ratio after addition of LiCl solution was $\sim$ 1:80 at 50 °C for $\sim$ 24 hrs. As the external electrolyte concentration used for Li$^+$ ion exchange was low, therefore salt imbitions occurred to a negligible extent [27-29].

The percentage purity ($<$ 2 μm particle size) of the clay in the commercial clay, pH of the slurry (commercial), purified suspension, Li $-$ exchanging suspension and the colors of the purified and Li $-$ exchanged clays are listed in Table-1. The percentage purities of the commercial clays were determined from the quantities of the dried residue left in the beakers after decantation of the pure clay suspensions. The Table indicates that all forms of clays (parent, purified and Li-exchanging suspensions) were alkaline in nature, except Li $-$ exchanging suspension of kaolin which is slightly acidic i.e., 6.76 due to reduction of pH 7.2 of the kaolin suspension by the addition of LiCl (1 M) of which has pH 6.60. It is known that clays are very stable at higher pH. The crystal structure of kaolin

Table-1: Purity, pH of slurry, suspension, Li-exchange suspension and the colour of the purified Li-exchanged Clays.

Clay	Purity ($<$2 μm, size) (%)	1.2 % (w/v) slurry (parent clay) (pH)	Suspension (Purified clay) (pH)*	Li-exchanging suspension (pH)*	Purified and Li-exchanged clay, colour
Montmorillonite	63.45	9.97	9.35[a]	8.10[a]	Olive green
Bentonite	14.58	9.97	9.11[b]	7.64[b]	Light Olive-green
Hectorite	50.20	10.12	9.48[c]	8.35[c]	Tan
Kaolin	43.3	7.42	7.2[d]	6.76[d]	White

* pH of suspension (%, w/v): a: 0.952; b: 0.219; c: 0.753; d: 0.634.
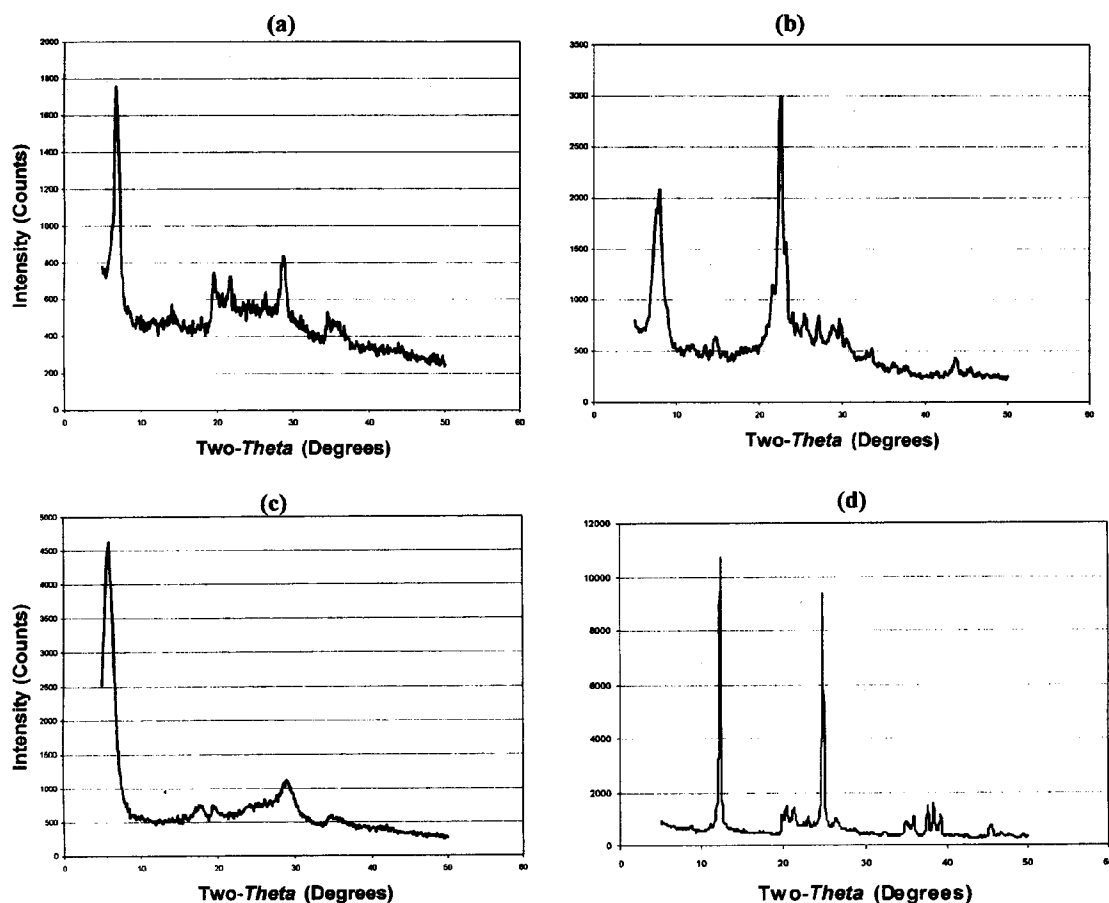
(a)

(b)

(c)

(d)

Fig. 1:   XRD patterns of purified dry clay powders of (a) Li-montmorillnoite; (b) Li-bentonite; (c) Li-hectorite; (d) Li-kaolin;

suggests that the octahedral basal surface of a platelet should be gibbsite-like and should present close packed hydroxyl groups; the tetrahedral basal surface of the platelet should be silica-like and present siloxane bonds. At the edges of a platelet, the lattice is disrupted and broken bond surface should be exposed [23]. Powder X-ray diffraction technique and the scanning electron microscope demonstrated that clays investigated had a crystalline structure. The great variations in properties can be accounted for only by assuming that the clay minerals are composed of comparatively simple building units and that the differences are primarily due to the way these units are put together. The XRD patterns indicated purity, the structural integrity and crystallinity of the clays investigated. The typical XRD patterns of Li-

exchanged clays are displayed in Fig. 1. The intensity of XRD peaks provides evidence of the retension of crystallinity of the clays structures after purification and lithium exchanged process. . The XRD patterns of Li-exchanged montmorillonite and kaolin agree very well with those reported by Colin *et al.* [30] and Kogel and Rule [31] respectively.

Fig. 2 shows the SEM images of the purified clays. These clays consist of small aggregates of platelets showing various morphologies. These samples are well crystallized and virtually pure shown by XRD. The SEM images of the Li-exchanged clays were almost same like their purified clay because the exchangeable cations are not part of the lamellae. Odom described [18] that smectite
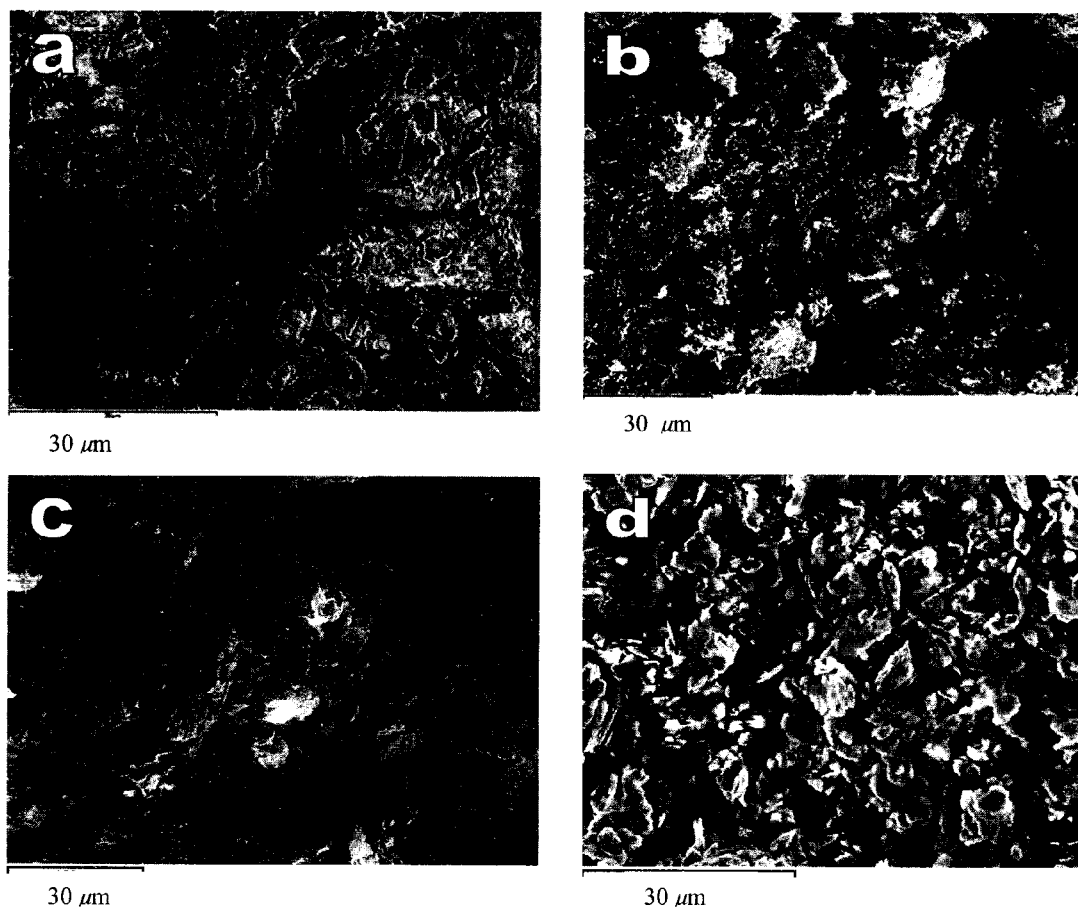
Fig. 2:   SEM images of dry powders of (a) PM ; (b) PB ; (c) PH ; (d) PK. (magnification 10,000 x). The scale bar in the SEM images is 30 μm.

crystals may be as large as 2 μm and as small as 0.2 μm with an average size of about 0.5 μm. Individual crystal morphologies range from rhombic to hexagonal lamellar to lath and even to fiber shapes.. Kaolinite clays are six sided flat crystals and smectites are more complex, flat crystals. The SEM images of the kaolin and hectorite clays shown in Fig. 2 have the resemblance to those reported by Clausen *et al.* [19], Kogel and Rule [31] and Huve *et al.* [32] respectively.

The values of refractive indices in Table-2 indicate that most of the clays studied have nearly intermediate hydrophilic – hydrophobic character except PH and LiH of which refractive indices of supernatants have increased in all cases from blank

binary solution of carboxylic acids and water, demonstrating preferential selectivity for water; thus, some possibility in separation of carboxylic acids and water. The more hydrophilicity of PH and LiH is ascribed to the presence of strongly hydrated Li^+ cations in the octahedral layer (Table-4). It is possible, that a stable trihydrate configuration could exist on the silonane surfaces of $Li(H_2O)_3$ – hectorite [33]. Interlayer cations have a strong effect on adsorption depending largely on their hydration energies [34]. Weakly hydrated cations, e.g. K^+ and Cs^+, resulted in greater sorption compared to more strongly hydrated cations such as Na^+, Li^+ or Ca^{2+}. The cations Na^+, Li^+ and Ca^{2+} have greater hydration energies than those of Cs^+ and K^+. This results in larger hydration spheres [35]. The larger sizes of

Table-2: Refractive indices at 25 °C of 20 % (v/v) of aqueous carboxylic acids before and after interactions with purified and homoionic lithium clays.

Carboxylic Acids	PM	LiM	PB	LiB	PH	LiH	PK	LiK
HCOOH 1.3439	1.3438	1.3439	1.3438	1.3438	1.3441	1.3440	1.3438	1.3438
CH$_3$COOH 1.3465	1.3467	1.3465	1.3464	1.3466	1.3467	1.3467	1.3465	1.3465
CH$_3$CH$_2$COOH 1.3486	1.3486	1.3486	1.3486	1.3487	1.3488	1.3488	1.3487	1.3487

Abbreviations

PM: Purified montmorillonite, LiM: lithium exchanged montmorillonite, PB: Purified bentonite, LiB: lithium exchanged bentonite, PH: Purified hectorite, LiH: lithium exchanged hectorite, PK: Purified kaolin, LiK: lithium exchanged kaolin.

highly hydrated cations may obscure a greater portion of siloxane surfaces and shrink the size of the effective adsorption domains so that fewer sites are of sufficient size to accommodate adsorbate molecules. It is likely that carboxylic acids have firstly, weaker electrostatic interactions with more strongly hydrated interlayer cations (Ca^{2+}, Na$^+$ and Li$^+$) of smectites (Table-4) and secondly, the surface oxygen of the tetrahedral sheets which may act as proton acceptors for the formation of H-bonds with carboxylic acid molecules. The purified clays and Li-exchanged clays of smectite group all swelled and formed a nice cylindrical shape jells in 20 % (10 ml) aqueous solution of carboxylic acids in the vials (14 ml). It has been claimed [36] that intensive gel formation is always associated with the presence of traces of water, as the water molecules favour interlinkage of the smectite particles by hydrogen bridges to form wide-mesh frameworks (edge-to-edge association). Probably the most important attractive and repulsive forces involved in expansion are considered only the forces due to attraction of interlayer cations to the silicate layer and repulsion due to cation hydration [37].

The aqueous carboxylic acids used were HCOOH, CH$_3$COOH and CH$_3$CH$_2$COOH which are completely soluble in water due to the ability of the hydroxyl groups to form hydrogen bonds with water molecules. However, with the possible exception of formic acids, CH$_3$COOH and CH$_3$CH$_2$COOH show very limited dissociation in aqueous media and they exist for the most part in the uncharged state [21]. All the carboxylic acids used for adsorption can penetrate the pores of smectites, because the kinetic diameters of HCOOH, CH$_3$COOH and CH$_3$CH$_2$COOH in aqueous solution are ~ 3.5, ~ 4.5 and ~ 5.5 Å respectively [38] while the pore openings of Na Li-

smectites are > 40 Å in distilled water [21]. Bourg *et al.* [39] introduced a conceptual model in which pore space of water saturated Na-bentonite is divided into 'macropore' and 'interlayer nanopore' compartments; with 80 % of its pore water in interlayer nanopores. Tournassat *et al.* reported [16] total (basal, interlayer and edge) surface area of clay suspension to be 788 m^{2}g^{-1}. An exact calculation of surface area is possible, if the density and the size of a single sheet are known [4]. Hence, for 2 μm particles the surface area of the smectite is 800 m^{2}g^{-1} and for 50 nm particles it is 832 m^{2}g^{-1}, the difference is caused due to the difference in edge surface. Here the separation efficiency of water from carboxylic acids/ water feeds was found not dependent on the size, polarity or dielectric constant of carboxylic acid molecules.

The swelling (cm^{3}g^{-1}), relative to the dry weight of the smectite clays are summarized in Table-3. The Table shows that, in general, the basal spacing expansion between the clay plates increases with the kinetic diameter of carboxylic acids. It has been proposed [21] that the fatty acid molecules are attached by their active carboxyl groups to the oxygens of the silicate surface leaving the methyl terminations relatively free in a head-to-tail arrangement in pairs, with some lateral displacement due to the bulky carboxyl ends. Greathouse and Sposito [33] described that inner-sphere complexes were observed to form exclusively on Li-bedellite (tetrahedral charge site) and both types of surface complex formed on Li-montmorillonite, which also contains both types of charge sites. Here under the identical conditions commercial clays (0.05 g) formed slurry in 20 percent aqueous carboxylic acids and purified clays changed to suspension in 10 ml of H$_2$O in vials and did not form gel even after many days. The formation of gels of smectites depends on

Table-3: The volume of unidirectional swelling (cm^3g^{-1}) of cylindrical like jells of smectites and swollen paste of kaolin in vials in 20 % aqueous carboxylic acids at 25 °C.

Carboxylic Acids	PM	LiM	PB	LiB	PH	LiH	PK	LiK
HCOOH	112	117	112	61	51	66	15	15
CH₃COOH	178	203	94	56	61	61	15	15
CH₃CH₂COOH	188	209	112	107	107	97	15	15

the concentration of pure clay in water. A suspension of >2 % by weight of smectite in water after standing for a while set to gel [6, 18]. The water molecules are enclosed within the interstices of continuous framework of clays, so that they are no longer freely mobile. Under some conditions, the layers of smectites can be separated by tens of nanometers of water and the layers can be completely dispersed [4]. The percentage concentrations by weight in commercial montmorillonite, bentonite, hectorite and kaoline of pure clay (<2 μm particle size) were respectively 0.317, 0.073, 0.251 and 0.216 in 20 % aqueous carboxylic acids and of PM, PB, PH and PK were 0.5 g in deionzed water in the vials. As the concentration of pure clay in commercial clay was less than 2 %, therefore gels of smectites did not form [6]. Although the percentage concentration of PM, PB, PH, LiM, LiB and LiH was 0.5 i.e., less than 2 %, instead of that all three smectites changed to cylindrical shape jells in 20 % aqueous carboxylic acids in the vials. It is attributed to the reduction of the dielectric constant of water (C=80) due to the presence of HCOOH (Є=58), CH₃COOH (Є=6.2) and CH₃CH₂COOH (Є=3.3) [38], as the effect of dielectric constant makes solvents such as water much better solvent for ions than are low dielectric media, such as carboxylic acids in interlayer nanopores, then they are attached by their active carboxyl groups to the oxygens of the silicate surface and prevent the layers from getting completely dispersed and so formation of jell occurs. Furthermore, smectites having Ca^{2+}, Na^+ and Li^+ as interlayer cations which are highly hydrated and having larger hydration spheres may obscure a greater portion of siloxane surfaces and shrink the size of the effective adsorption domains so the fewer sites are of sufficient size to accommodate carboxylic acid

molecules, that is why the clays investigated here show intermediate hydrophilic – hydrophobic behavior [40].

The unidirectional expansions per gram of smectites in vials were in the following order: LiM > PM > PB > LiB ≥ PH ≈ LiH. The smectites have the unusual property of expanding several times its original volume when placed in water. Beyond the solvation of the exchanged cations, the water adsorbed by smectites can condense in micropores and on external surfaces [36]. Cases *et al.* [41] found by thermal analysis of sodium montmorillonite that it contained physically adsorbed water, water molecules directly bound to exchangeable cations and the weight loss at > 527 °C represents dehydroxylation of the structure. The extent of expansion of the layers depends on the nature of the swelling agent, the size and charge of the cation, the layer charger density and the location (tetrahedral or octahedral or both sheets) [41]. One reason of smaller sizes of cylindrical shape jells of PB, LiB, PH and LiH as compared to PM and LiM is different value of charge and location of layer charge (Table-4). The Table-4 indicates that structural formulae of bentonite and hectorite have charges in both tetrahedral and octahedral sheets due to isomorphic substitution of cation(s), the negative charge is distributed over the whole two dimensional structure. Therefore, strong electrostatic bonds are expected between the interlayer cations and the negatively charged interlamellar surfaces. Thus, less expansion of PB, LiB, PH and LiH occurs as compared to PM and LiM, where molecular structural formula (Table-4) has charge sites deep in the octahedral layer only, due to isomorphic substitution of Al by Mg, the resulting excess negative charge distributed over several surface oxygen ions, makes it possible to form weak electrostatic bonds between the interlamellae tetrahedral sheets and interlayer cations, consequently in PM and LiM more expansion of interlayers occurred. The Table-3 also indicates that expansion of PM is less than LiM which is due to mixed Na-Ca filling in PM, whereas in LiM there are only Li^+ cations in the interlayers. The hydration of

Table-4: Parent (Commercial) clays used for investigations.

Clay	Sturctural Formula	Source	Lot. #
Montmorillonite	Na₀.₃, Ca₀.₃ [Al, Mg]₂ (Si₄) O₁₀ (OH)₂ mH₂O	WARD's U.S.A	46E0435
Bentonite (Sodium form)	Na₀.₆₂ [Al₃.₂₈ Fe³⁺₀.₃ Fe²⁺₀.₀₄ Mg₀.₃₈] (Si₇.₈₀Al₀.₂₀)O₂₀(OH)₄.mH₂O	Alfa Aesor U.S.A	H30K31
Hectorite	Na₀.₄₀ [Mg₂.₆₅ Li₀.₃₅] (Si₃.₉₅ Al₀.₀₅) O₁₀ (OH)₂ . mH₂O	WARD's U.S.A	49-5103
Kaolin	[Al₄] (Si₄) O₁₀ (OH)₈	EM Science U.S.A	45245545

Li^+ provides the driving force for more expansion of Li M. Paez. *et al.* [42] reported that CaM presented small basal spacing than NaM. They can differ by as much as 1 Å for given water content. They suggested that the valence of cations rather than their size has the larger impact on the behavior of clay-water system. Taking into account that Ca^{2+} ion (radius~0.99 Å) is only slightly larger than Na^+ ion (radius ~ 0.95 Å) but under similar conditions Na M has a more open structure than CaM. Ca-clays exhibit a tighter structure, thereby yielding more compact and stable clay particles at the macroscopic level. Montes has also reported [43] that swelling-shrinkage potential (%) of bentonite is governed by the relative humidity and by the nature of the interlayer cation. Thus, LiM has greater percentage volume expansion than PM (Table-3) due to homoionic Li^+ ion in the interlamellar space. The larger hydration radius (~ 3.82 Å) of Li^+ [44] causes larger interlayer spacings [25]. Lubetkin *et al.* [45] reported decreasing binding order for interlayer cations: $Cs^+ > K^+ > Na^+ > Li^+$ in montmorillonite. The least effective of these links *i.e.,* of holding the individual lamellas face to face is generally provided by the hydrated cations. Thus, due to loose electrostatic bonding between the Li^+ ions and tetrahedral sheets more expansion of the interlayer spacing occurs. Further, for ions of same charge, the cations with the smallest hydrated radius is strongly absorbed because it moves close to the site of charge. For example, K^+ with a hydrated radius of 3.31 Å will exchange for Na^+, hydrated radius of 3.41 Å on the exchange sites [44]. The smaller ions become more hydrated and their large radii reduce the rate of migration. Furthermore, the higher the charge density of the ion, the larger its hydration sphere and hence the greater the shielding of the charge. As radius of the hydrated Li^+ ion is maximum and accommodates more water between the interlamellars, so due to the least effective of these links forces the lamellae apart and this weakens the net forces of attraction compared to the situation in which a bare (small) cations balances the charges close to both surfaces. Hence, LiM has got maximum swelling as compared to other clays investigated.

Non-ionic organic compounds can be adsorbed and bonded to the surfaces of the clays' mineral particles by van der Waal's or hydrogen bonds [6]. The smectites have layer lattice structures in which two dimensional oxyanions are separated by layers of (hydrated) cations. Spaces between the layers are accessible even to large molecules, the incorporation being referred to as intercalation. Bayrak [5] has suggested from the values of Gibbs free energy (ΔG°_{ads}) that the process of adsorption is physisorption via hydrogen bonding of the carbonyl oxygen of the free fatty acid onto the silanol (SiOH) hydrogen at the montmorillonite silica/solvent interface. Hence, large swelling of PM and LiM in aqueous CH_3CH_2COOH may be attributed to larger diameter (~5.5 Å) of CH_3CH_2COOH molecule which penetrates between the interfaces of lamellae and exist in the form of cyclic dimer. It is likely that the cyclic dimer of CH_3CH_2COOH lies parallel with the silicate sheets and carbonyl of the dimer forms hydrogen bonds with the silanol (SiOH) of the framework of the clay and pull apart the interlamellar surfaces, consequently more expansion of PM and LiM occurred in aqueous CH_3CH_2COOH as compared to HCOOH (diameter 3.5 Å) and CH_3COOH (diameter 4.5 Å). Since uncharged polar organic molecules like carboxylic acids are adsorbed essentially by replacement of the interlayer water, the behavior of such molecules is likewise strongly influenced by the exchangeable cation. If the organic molecules are sufficiently large or form a sufficiently stable interlayer region, the clay will accommodate a large number of such molecules through expansion of the interlayers. Once an organic molecule is adsorbed in the interlayer region of the clay, the molecules reactivity may be modified by the new chemical and physical environment [36]. The lamellar surfaces of clays and the organic molecule can sometimes be linked through the formation of covalent bonds, or the interlayer and the organic molecule can become strongly associated through ion interactions, hydrogen bonding, dipole forces or dispersion forces.

Extensive hydrogen bonding between nonsolvating water molecules and the siloxane surface of the clay mineral also was observed [46], as were water molecules attracted into the ditrigonal cavities of the surface. Overall, cation-water interactions strongly influenced the interlayer water configuration. Nonsolvating water molecules form hydrogen bonds with surface O atoms and move freely on (x,y) planes above and below the midplane, but the presence of negative charge sites so close to the surface surely results in decreased water mobility. It is also suggested that association of carboxylic dimers via coordinated water of interlayer bridges in which one or both protons of each water molecule participate in H-bonding, so that if R represents the carboxylic acid then water bridges are of the types,

Clay - - M^{n+} - - O   or   Clay - - M^{n+} - - O
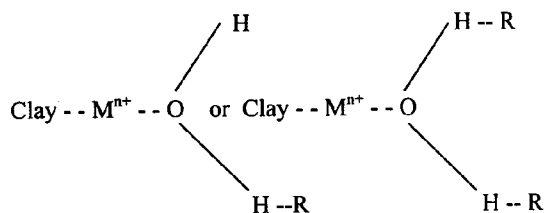
Where M^{n+} is interlayer cation [21,22].

The PK and LiK formed a slightly swollen paste as compared to dry sample in 20 % (10 ml) of aqueous carboxylic acids in the vials. As the superposition of oxygen and hydroxyl planes of successive layers within a single kaolin crystal gives rise to pairing of O and OH ions and interlayer O - - HO H-bond formation [21]. Clearly, the forces arising from H-bonding and those due to non-specific van der Waals interactions holding adjacent layers together must be overcome if interlayer sorption (intercalation) of extraneous species is to occur [21]. The water does not intercalate between 1: 1 sheets in kaolin, the lamellae of which ideally carry no negative charge so that there would be no interlamellar cations. Interlamellar sorption can be regarded as a type of solution, just as for sorption in zeolite or clathration [40]. In the minerals of silicates group with two layer sheets, there is no net anionic charge on the double sheets and so in the ideal structure there are no interlayer cations. The small cation exchange capacity sometimes found, for example with kaolinite is probably a result of lattice imperfections, associated inter alia with the termination of crystal faces [3]. Ion exchange can modify sorption often profoundly but kaolin has no interlayer exchange capacity. For this reason, penetration of the kaolin interlayers by carboxylic acids is difficult to achieve and adsorption is generally confined to the external crystal surface. In this connection the edges of the kaolin crystals are of particular importance. This is so because the edges containing unsatisfied valencies ('broken bonds') occupy an appreciable proportion (10 – 20 percent) of the total crystal area [21]. Kaolin shows no interlamellar expansion due to inability of water to penetrate between the sheets which have no interlayer cation(s) and bonding between the layers arises from van der Waal's attraction [36]. Kaolin has only one layer and is not subject to the shrink-swell phenomenon. Dry clays readily take up water on

wetting. It has been reported by Newman [47] that Li-saturated kaolinites have the smallest monolayer coverage. It was described that Li through its small size was able to fit into the structure so that no longer influenced hydration of the surface and subsequent work tended to confirm this. The water adsorbed by kaolin can condense in micropores and on external surfaces. Futhermore, the cations adsorbed on the surface of kaolin can serve essentially fixed hydrophilic sites. Therefore, the formation of slightly swollen paste of PK and LiK as compared to dry sample in the vials containing 20 % aqueous carboxylic acids is contributed to the condensations of water molecules in micro pores and on external surfaces and formation of electrostatic and hydrogen bonding on external surfaces of dissociated HCOOH and cylic dimers of CH_3COOH and CH_3CH_2COOH respectively. The values of refractive indices of supernatants (Table-2) have decreased from blank solutions of aqueous HCOOH indicating adsorption of the acid. Newman [48] described that kaolin has at the external surface H^+, OH and siloxane basal surfaces. The HCOOH is almost completely dissociated in water, then H^+ ions are attached electrostatically with OH ions at the edges of the crystal due to broken structure and HCOO ion is coordinated with the adsorbed cation or attached through H-bonding with the surface silanol (SiOH). HCOO may also bond electrostatically with the Lewis acid sites ($AlOH^+_2$) or H^+ ion at the edge of the kaoline surface [48]. In case of 20 % aqueous CH_3COOH the refractive indices of the supernatants and blank solutions are same indicating equal hydrophilic – hydrophobic behavior of PK and LiK. As CH_3COOH is partially ionized when dissolved in water and most of the molecules tend to cling together to form cyclic dimers through hydrogen bonding. It is suggested that dimers of CH_3COOH are attached through oxygens of carbonyl group to the surface functional groups *i.e.*, AlOH and SiOH of PK and LiK by H-bondings. In case of aqueous CH_3CH_2COOH the refractive indices of supernatants have increased from blank solution, indicating preferential selectivity for water as compared to CH_3CH_2COOH. There is only limited physical interaction between the carboxylic acids and the kaolin surface which is necessary for adsorption, but that hydrophobic interactions also contribute [5]. It is possible that the relatively hydrophobic silica faces of kaolin, which carry low density permanent negative surface charge, facilitate aggregation and adsorption of the carboxylic acids. [19, 49].

Experimental

All parent (commercial) clays used were in powder form, their idealized structural formulae [3,14,16,18,50,51] source and lot numbers are given in Table-4.

Cations enclosed in square brackets occupy octahedral sites and the cations in parentheses occupy tetrahedral sites. The exchangeable cations preceding the square brackets are attached to the surfaces of the clay particles and do not normally penetrate the structure. In each formula m denotes the number of water molecules per unit cell which vary with relative humidity and with the size and nature of the exchangeable cations present. Montmorillonite has octahedral charge substitution only, whereas bentonite and hectorite have both octahedral and tetrahedral charge substitution.

To eliminate impurities, parent materials of clays were first purified and treated to extract clay particles size < 2 μm by the following size-fractionation sedimentation procedure [16,17].

12 grams of clay was sprinkled slowly over 1L of deionized water in a beaker, with rapid stirring, to prevent clumping of the clay and to ensure rapid dispersion. Vigorous stirring was achieved with a magnetic stir bar (VWR brand, teflon-coated, octagonal with pivot rings, L x Dia; 2 inc x 5/16 inc) at room temperature on a magnetic stirrer / hot plate. The PH of the slurry was noted by using a digital PH-meter (JENCO, Model 608). The dispersion was left for 24 h to allow impurities and heavy minerals fractions to settle. The clear clay suspension was poured into a graduated beaker and the residual heavy mineral fractions were saved for drying for several days in the beaker. By measuring the weight of the heavy mineral fractions (impurities) the purity of particles less than 2 μm size contained in the parent clay was found. The PH of the suspension (800 ml) was recorded. The suspension was transferred to centrifuge bottles (250 ml) for centrifugation. It was centrifuged at 13000 RPM for 30 minutes at room temperature using refrigerated super speed centrifuge (Du Pont Instruments, Sorvall Rc-5B) and rotor GSA, radius 14.56 cm. The supernatant was discarded and the swelled jelly-like clay (except kaolin which was in the form of paste) was transferred to a porcelain evaporating dish (Dia; X Ht. 90 x 22 mm) for drying in air at room temperature for several days. The dried sample of smectites shrank considerably and stuck with the porcelain dish and formed thin flakes and laths. The smectites were scratched and removed from the porcelain dish and ground by using a mortar and pestle and stored in glass vials for further investigations.

For comparison reasons, it is useful to obtain only one type of interlayer cations and, for purposes of identification, the interlayer cation of choice was Li^+. The following procedure represents an exchange reaction, where Li is exchanged for whatever inorganic cations(s) happens to be present in the interlayer. Exchange is achieved by producing a concentration gradient where a high Li^+ concentration is established outside the material under study in an aqueous Li-salt solution so that exchange occurs simultaneously. The reactions involve: 2 $Li^+ \rightarrow Ca^{2+}$ or $Li^+ \rightarrow Na^+$. To ensure complete saturation of the cations exchange capacity positions of the clay with Li^+ cations, the suspensions of particles < 2 μm were saturated with Li^+ cations by adding sufficient LiCl (EMD chemicals Inc. Lot # 1034B45) to achieve 1 M solution by adding to the stirred suspension at 50 °C on magnetic stirrer / hot plate in intervals of time in order to avoid the salt imbibent [27-29]. After adding 1 M LiCl solution to the stirring purified suspension of the clays then it was left for overnight stirring at 50 °C. The Li-exchanging suspension was centrifuged, the supernatant was discarded and the sediment (swelled jelly-like in case of smectites) was washed several times with deionized water in a graduated beaker. Again added 1 M LiCl (this provided Li^+ ions in over many times excess of amount required to completely exchange all available cations exchange sites) solution slowly to the stirring partially exchanged lithium exchanging suspension of clay at 50 °C and left for stirring for about 3h to allow for complete replacement of exchangeable cations by Li^+ ions and then it was centrifuged to separate the Li-exchanged clay from the supernatant containing the excess ions (Cl^-, Li^+, Na^+ etc). The Li-exchanged clay was washed several times with deionized water and resuspended in the deionized water and stirred for about 1 h and was recentrifuged to recover the Li – exchanged clay. The Cl^- ions of the supernatant tested by $AgNO_3$ solution and the clay was repeatedly washed, centrifuged and separated till the supernatant showed no further Cl^- ions indicating removal of all Cl^- ions from the Clay [29,52,53]. The Li-exchanged clays, expanded

fine gels (except kaolin which formed paste) were transferred to a porcelain evaporating dish for drying in air at ambient temperature for several days. The dried Li-exchanged samples of smectites shrank several times and stuck with the porcelain dish, they were removed by scratching with a spatula. They were in the form of flakes and laths were sticky and gummy and very hard. They were finely ground by using mortar and pestle. The dried lithium kaolin did not stick on the surface of the dish and was in the form of powder. Finally, the ground samples were stored in glass vials for further experiments.

The integrity of the framework structures of the purified and lithium exchanged clays were examined by powder X-ray diffraction (XRD) technique by using Rigaku Dmax-A diffractometer with a Ni-filtered Cu Kά radiation and the detector NaI scintillation with a photo-multiplier tube inside of a tight light capsule. The crystal size and morphology were determined by scanning electron micrograph (SEM) using Hitachi S-4500 cFEG SEM instrument operated at 5 kV and 10 μA, condenser lens 1-5mm, working distance 10 mm and aperture 2.

The interaction of aqueous carboxylic acids onto clays was investigated by adsorptive study using the following procedure. The adsorption experiments of aqueous solutions of formic (EMD chemicals Inc. Lot 44162613), acetic (VWR, Int. CAT. No. VW 3536-4) and propionic (Mallin Krodt Baker, Inc.) acids were carried out on parent, purified and lithium exchanged montmorillonite, bentonite, hectorite and kaolin clays in screw cap septum vials, 14 ml (L x Dia; 72 x 18 mm) at room temperature (25 $\pm$ 0.5 °C). A 10 ml (20 % v/v) of binary mixture of aqueous carboxylic acids were introduced into vials containing 0.05g of the clay samples and an egg-shaped stir bar (L x Dia; 19 x 9.5 mm) teflon coated. The volume covered by the dried clay was very small, it did not even completely cover the flat round bottom of the vial and stirred on magnetic stirrer/ hot plate at room temperature for about 1 h. The blank solutions were also stirred similarly but without clay samples. Then left for 24 h for settling the suspension and appearing of the transparent supernatant. Below the transparent supernatant of smectites, cylindrical shaped fine gels appeared in the vials. For kaolin samples thick pastes were formed at the bottom of the vials. The adsorption of aqueous carboxylic acids was also carried out on parent clays but they remained in the form of slurry and no fine jelly

appeared. 100 μL of the transparent solution was withdrawn by a micro liter syringe and dropped on the prism of a refractometer (Reichert AR 200 Digital Refractometer, Germany). Recorded the refractive indices of the binary mixture solutions. Similarly the refractive indices of blank solutions were measured. Under the same conditions the samples of commercial and purified clays were stirred with 10 ml deionized water for 1 h and then left 24 h for settling the slurry and suspension respectively. Even after several days no transparent supernatant appeared and the clays remained in the form of slurry and suspension. In general, the refractive indices of aqueous carboxylic acids showed a small change from blank solution after interaction with clays.

The lengths of the swelled jelly-like cylindrical shaped smectites in vials were measured directly by using a plane scale and then the swelling per gram of dry clay powder to cylindrical shape jelly was estimated by $\pi r^2 h/w$, where r is radius of vial (cylindrical shape jell), h is the height of the jelly, w is the weight (0.05 g) of dry sample of clay in the vial.

Conclusions

The main conclusions which may be deduced from this study, therefore, are that (a) purified (< 2 μm particle size) smectites (montmorillonite, bentonite, hectorite) are expansive clays and have swelling-shrinkage potential. The Kaolin is non-expansive clay. (b) The clays investigated in dilute aqueous suspensions are completely dispersed (delaminated). As the concentration of the dispersion is increased >2 % gelation occurred. In aqueous carboxylic acids even 0.5 % by weight of smectites turned to jells, perhaps due to less dielectric constant and polarity of aqueous carboxylic acids as compare to deionized water. Furthermore, intercalation of carboxylic acids through H-bonding to the interlamellar faces may prevent delamination of smectites. (c) The purified and Li-exchanged clays retained their crystallinity and morphology. (d) All the clays investigated, showed nearly intermediate hydrophilic-hydrophobic behavior due to strongly hydrated interlayer cations (Ca^{2+}, Na^+ and Li^+) and hydrophobic interfaces. An increase in the molecular size of carboxylic acids does not diminish adsorption due to steric constraints. (e) The extent of swelling is dependent on the size of carboxylic acid molecule, the layer charge density,

location of layer charge and the nature of the interlayer cation(s). (f) Li-montmorillonite showed maximum swelling in aqueous CH_3CH_2COOH solution due to less layer charge, octahedrally charged sheet, strongly hydrated interlayer Li^+ ion and greater molecular diameter of solvated / intercalated CH_3CH_2COOH molecule tending toward the higher interlayer spacings.

Acknowledgments

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