THE CATALYTIC AND MECHANISTIC PROPERTIES OF ORGANOCLAYS FOR TRIPHASE CATALYSIS

by

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ABSTRACT

The Catalytic and Mechanistic Properties of Organoclays for Triphase Catalysis

by

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Organoclays are smectites that are ion-exchanged by cationic organic compound such as tetraalkylammonium or -phosphonium ions. For the use in triphase catalysis, the onium ions are usually the cationic surfactants which have one long alkyl chain. Differences in layer charge density result in different orientation of surfactant cations in the clay interlayers. In laponite, the cationic surfactants adopts monolayer structures in which the alkyl chains lie parallel to the silicate surface whereas lateral bilayer structures are formed in hectorite and Wyoming montmorillonite interlayers. As the layer charge density of the clays increased as in organo montmorillonite and F-hectorite, a pseudo-trimolecular structure of the cationic surfactant in Arizona montmorillonite interlayer and a paraffin-like structure in F-hectorite gallery were observed.

Organo laponites with a monolayer structure do not stabilize emulsion mixtures of aqueous and organic solutions, causing them to be poor triphase catalysts. Organo hectorite with lateral bilayer structure do stabilize the water-in-oil emulsion and are good triphase catalysts. The mechanism for this organo hectorite triphase catalysis has been elucidated by studying the effect of solvent polarity on reactivity and by determining

the dependence of reaction rates on the reactant concentrations. The relative rates of the alkylation for benzyl bromide and naphthoxide also provide mechanistic information. The most plausible mechanism is one in which the organic reactant is first adsorbed at the boundary of the clay surface and organic solution. Subsequent nucleophilic substitution reaction occurs at the aqueous-catalyst interface.

Arizona montmorillonite organic derivatives with a pseudo -trimolecular structure and organo F-hectorite with a paraffin-like structure can also stabilize emulsion mixtures of aqueous and organic solution. However, for lipophilic surfactants, such as hexadecyltributyl phosphonium ion in the high layer charge density clay interlayer, the surfactants are sometimes ion-exchanged by metal cations and dissolved into organic solution, causing the organoclays to be poor catalysts for recycling. Surfactant desorption can be reduced by using non-polar organic solvents or a hydrophilic nucleophile in the triphase catalysis system. Hydrophilic surfactants such as hexadecyltrimethyl ammonium in these high layer charge density clay hosts do not desorb after triphase catalysis reaction. The desorption of hydrophilic surfactant occurs after triphase catalysis reaction when a co-surfactant, such as octanol, is present in the reaction system.

Organoclays exhibit mechanistic phase transfer properties different from those of polymer supported catalysts. Chemoselectivity and regioselectivity different from that of the typical triphase catalysts can be obtained by using organoclays for the triphase catalysis reaction.

To MY PARENTS

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CHAPTER I

INTRODUCTION

A. Structure and Properties of Layer Silicates

The layer silicates, hectorite and montmorillonite, described in this dissertation are smectite minerals which are a class of naturally occurring minerals. The term 'clay mineral' refers to specific silicates with particle size less than 2 μm and with definite stoichiometry and crystalline structure.

Smectites are composed of units made up of two silica tetrahedral sheets and a central octahedral sheet of magnesia or alumina[1,2]. The silicate tetrahedra are usually oriented so that the three basal oxygen atoms of each tetrahedron lie on the same plane, while the fourth oxygen atom defines a second common plane. The octahedral sheet contains a cation, usually Al or Mg, surrounded by six oxygens in an octahedral arrangement. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedrons of each silicate sheet and the oxygens of each octahedral sheet form a common layer. Smectite clays are 2:1 layer minerals which are divided into two structures: dioctahedral aluminum silicate minerals (Figure 1) and trioctahedral magnesium silicate minerals

charge arises predominantly from isomorphous substitution in the octahedral layer or from the substitution in the tetrahedral layer. Cations at particular locations of the silicate structure can be replaced by some other cation with similar ionic radius without changing the structure of the minerals. If the replacing cation has lower valence, a net negative charge will be developed. The negative charge is then balanced by the presence of hydrated metal cations in the interlayer region of the structure. These hydrated metal cations are usually located adjacent to the point of anion charge on the basal plane.

The trioctahedral silicate minerals used in the work are laponite, hectorite and F-hectorite. The idealized unit cell composition for laponite is

$$Li_{0.36}[Li_{0.36}Mg_{5.64}]^{VI}(Si_{8.00})^{IV}O_{20}(OH)_4$$

in which the superscripts (IV) and (VI) refer to the respective cation in the tetrahedral and octahedral sites. The first "$Li_{0.36}$" in the formula designates the exchangeable hydrated lithium in the interlayer region, and the second one represents the octahedral sheet lithium. Laponite is a synthetic low-charge smectite.

The idealized unit cell composition of hectorite is

$$M_{0.67}[Li_{0.67}Mg_{5.33}](Si_{8.00})O_{20}(OH, F)_4$$

Figure 1 The structure of a 2:1 dioctahedral alumina silicate mineral.

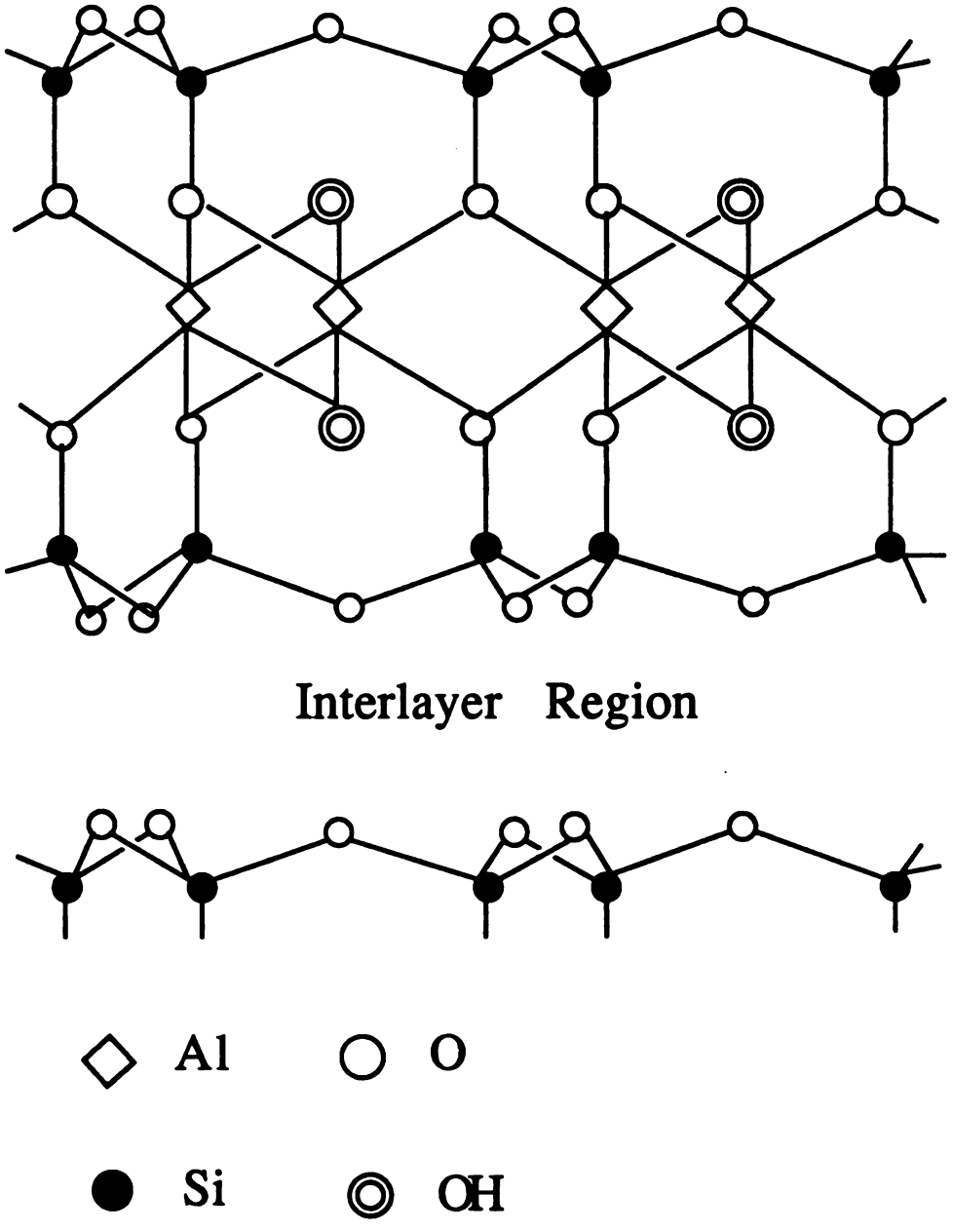
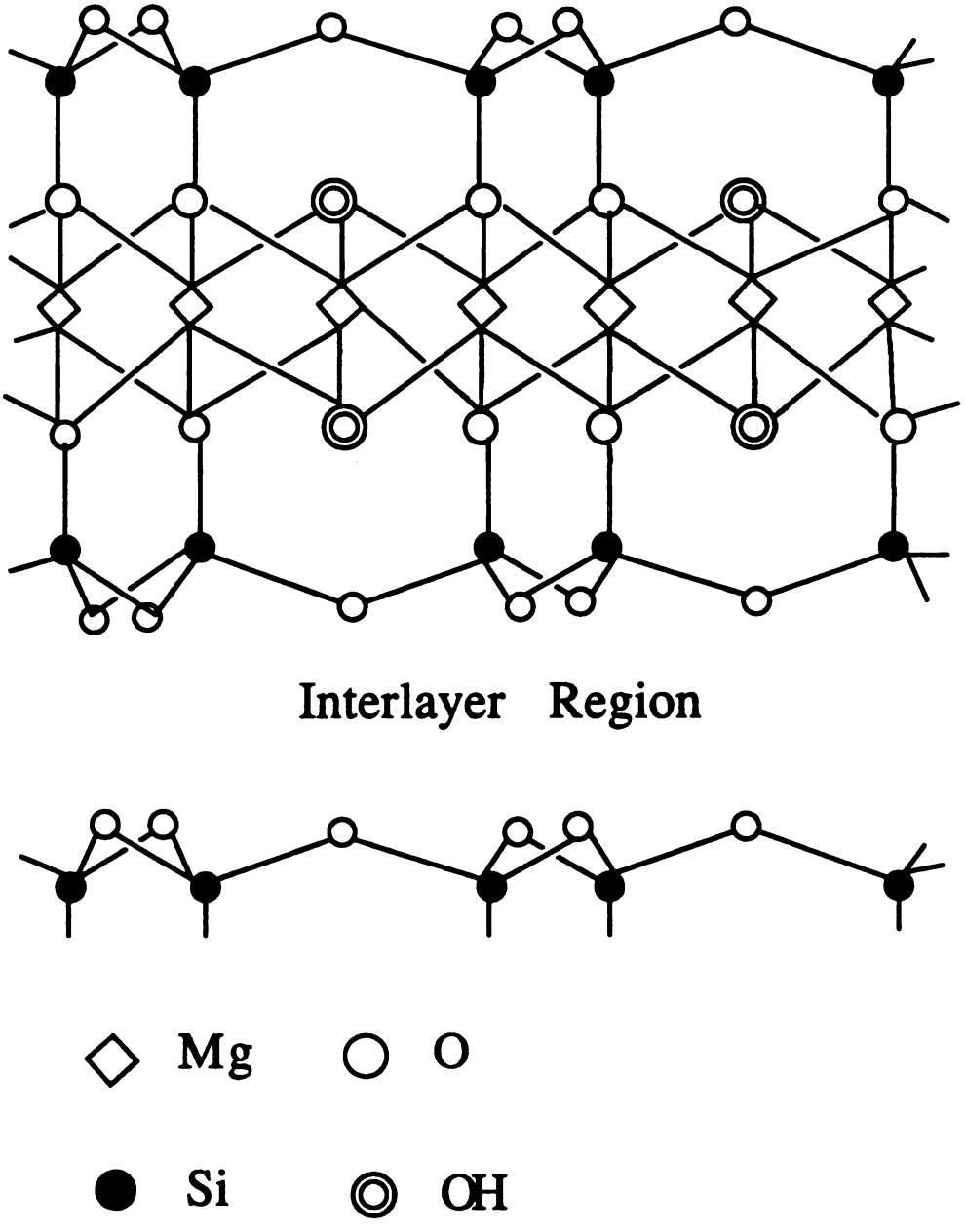


Figure 2 The structure of a 2:1 trioctahedral magnesium silicate mineral.



in which the "M" designates a hydrated monovalent cation. Fluorohectorite is also a synthetic clay in which the hydroxyl groups are substituted by fluoride. The idealized unit cell composition of hectorite is

$$Li_{1.6}[Li_{1.6}Mg_{4.4}](Si_{8.00})O_{20}F_4.$$

The dioctahedral silicate minerals used in the dissertation are montmorillonites from Arizona and Wyoming. The idealized unit cell compositions for both montmorillonites are

$$M_{1.16}[Al_{2.84}Mg_{1.16}]Si_{8.00}O_{20}(OH)_4, \text{ and}$$

$$M_{0.67}[Al_{3.33}Mg_{0.67}](Si_{8.00})O_{20}(OH)_4, \text{ respectively}$$

Rectorite[3] as shown in Figure 3 consists of a regular alternation of a mica-like layer and an expandable layer having a smectite composition. Rectorite also belongs to the family of regularly interstratified clay minerals as well as to the family of smectite clays. Its basal spacing is greater than 19Å which is approximately double that of the smectite basal spacing. The formula of rectorite is

$$[Na_{0.72}K_{0.02}Ca_{0.05})(Ca_{0.24}Na_{0.07})](Al_{4.00}Mg_{0.02})[Si_{6.58}Al_{1.62})O_{22}]$$

The charge on the mineral arises from isomorphous substitution in the tetrahedral particle sheet of the 2:1 smectite clay layer. The cation exchange capacity (CEC) of rectorite is 60 milliequivalents per gram.

surface charge density of this material is approximately equal that of a smectite clay in which the CEC is 120 meq/100g.

Smectite clays can be swelled by adsorption of water or some organic solvents[4-7]. With multiple layers of solvent, the galleries become liquid-like and accessible for chemical reactions. As the solvent content increases, the basal spacing of smectite clays also increase. The swelling capacity of the clay can be reduced by introducing electrolyte to the solution. The electrolyte reduces of the electric double layer repulsion of two neighbor silicate layers. Generally, higher layer charge density clays are less swellable[4] than the lower layer charge clays.

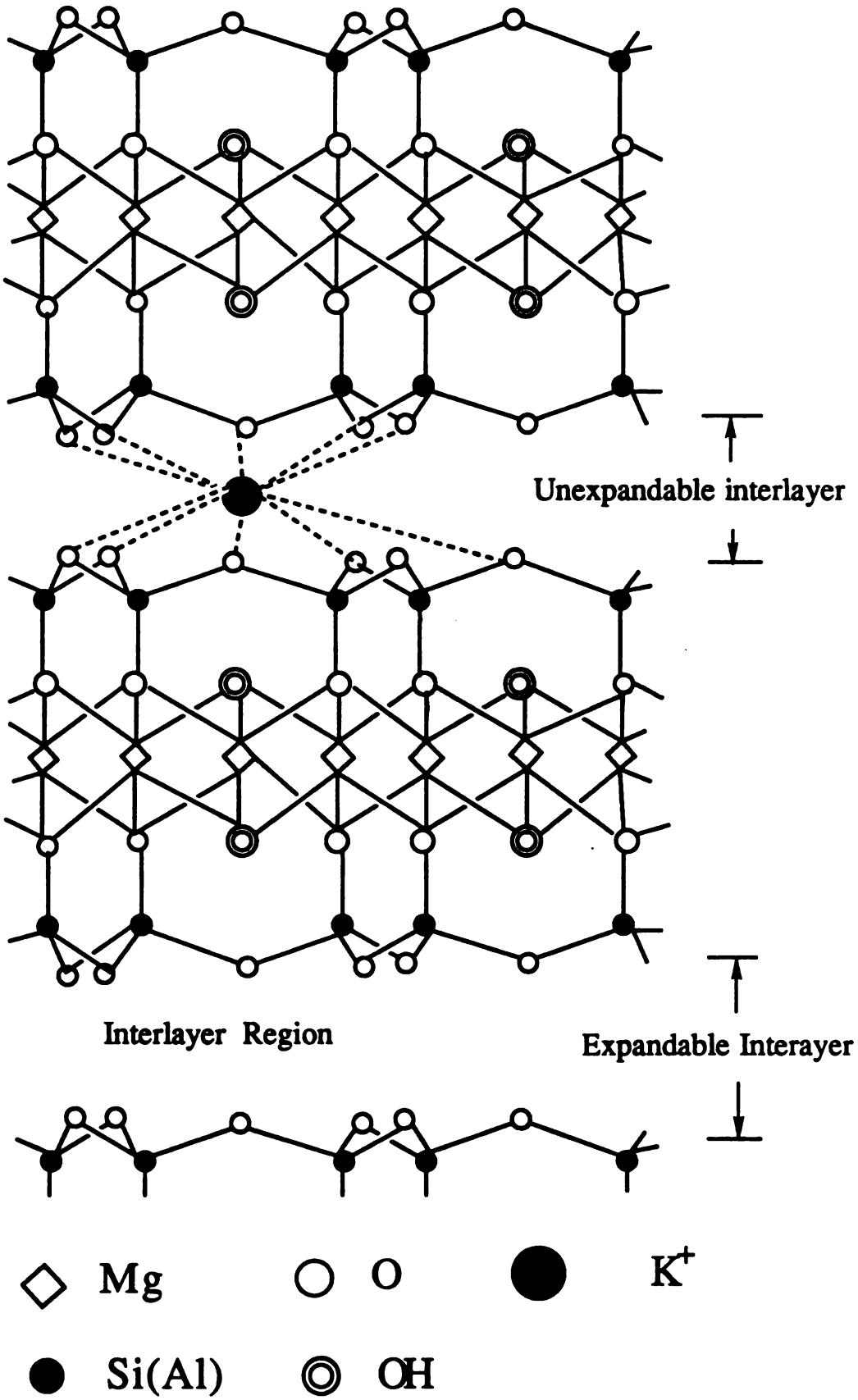
Smectite clays and their derivatives have shown catalytic properties for many reactions[8-11]. The acidic nature provides the source of the catalytic capacity. Both Lewis and Bronsted acidity have been noted, the former derived from aluminum or iron species located in the crystal. The Bronsted acidity resulys from dissociation of the interlayer water molecule coordinated to polarizing interlayer exchangeable cations[12].

B. Principles of Phase Transfer Catalysis

1. Biphase Catalysis

Chemists frequently encounter the problem of bringing the reactants in two mutually immiscible solutions into proximity to attain rapid reaction rates. The traditional procedure is to

Figure 3. The structure of rectorite.


Unexpandable interlayer
Interlayer Region
Expandable Interayer
Mg
O
K+
Si(Al)
OH

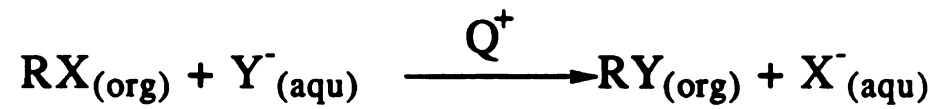
dissolve the reactants in a homogeneous medium. However, a suitable solvent is not always available and it is usually expensive and difficult to remove after reactions. Solvents such as THF or DMF sometimes present environmental problems in large scale operations.

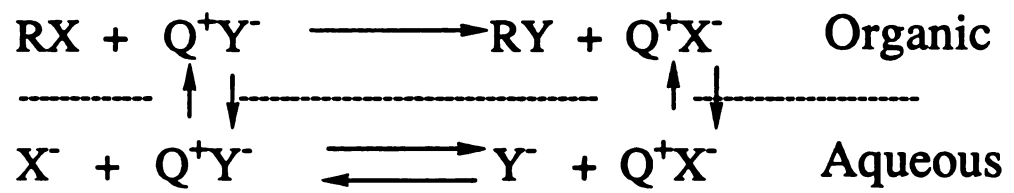
The technique of phase transfer catalysis can permit or accelerate reactions between ionic compounds and organic, water-insoluble substrates in solvents with low polarity. The concept of " phase transfer catalysis" is to transfer the ions, neutral molecules or free radicals from one phase to another where reaction can occur. It is clear that a phase transfer catalyst has considerable advantages over conventional procedures since it eliminates the requirement for expensive anhydrous or aprotic solvents, improves reaction rates, and lowers the reaction temperature[13-16].

The first type of phase transfer catalyst is the biphase catalyst[13,14]. Quaternary ammonium or phosphonium halide is typically used for typical biphase catalysis. The amphiphilic character of quaternary onium salts allows them to be wetted in both aqueous solution and organic solvents with low polarity. Stark and Owens[13] first developed the use of ternary ammonium and phosphonium salts for phase transfer catalysis in organic synthesis. The mechanism of biphase catalysis was studied by Stark and Owens[14] and Brandstorm[17].

A nucleophilic substitution reaction using onium salts as biphase catalysts[13] is represented in Figure 4. An onium cation pairs with an anionic nucleophile Y^- in the aqueous phase and the

Figure 4 Mechanism of biphase catalysis with a nucleophilic substitution reaction.





$Q^+ = NR_4^+; PR_4^+; Na^+$-Crown Ether

ion pair is extracted into the organic phase. Once the anion has been transfered into the organic phase, the anion and organic electrophile RX undergo nucleophilic substitution and form RY and a new salt, Q^+X^-. The new salt then returns to the aqueous phase, where Q^+ pairs with a new anion, Y^-, for the next cycle.

If there is one long alkyl chain in the onium ion, the biphase catalyst may also function as a surfactant. The surfactant molecules form small aggregates of 10 to 50 organic molecules dispersed in the aqueous phase. The small aggregations are called micelles, wherein the nonpolar organic parts of the molecules occupy the internal volume and the highly polar group of the surfactant occupy the outer surface[18]. For micelle-catalyzed reactions, the positively charged outer surface attracts and concentrates anions from the bulk aqueous solution into the so-called Gouy layer near the surface of the micelle. Reaction then occurs at the Gouy layer[19-24].

As comparable volumes of the organic solutions are added to the aqueous micellar solution, an emulsion mixture of aqueous and organic solution stabilized by surfactant is formed. If a co-surfactant, which is typically an alcohol with more than five carbon atoms, is added to the micellar solution, the emulsion is converted to a transparent microemulsion[25-27]. The microemulsion has a smaller droplet size and a lower surface tension than those of the emulsion[27-30]. Moreover, a microemulsion is thermodynamically stable, unlike an emulsion which is only kinetically stable[25,29]. As the microemulsion is utilized into the

biphase catalysis, a more efficient catalytic reaction can be obtained due to increased interfacial area between aqueous and organic phases.

Crown or macrocyclic ethers usually containing the basic unit $(-O-CH_2-CH_2)_n$ have also been met with interest for phase transfer catalysis[31-35]. These are exemplified by 18-crown-6 in which 18 indicates the number of atoms in the ring and 6 represents the number of oxygens. Other commercially available crown ethers are dibenzo-18-crown-6, dicyclohexano-18-crown-6 and 15-crown-5. A common feature of all crown and related compounds is a central hole or cavity which can chelate the substance. The cation complex of general interest for phase transfer catalysis are those formed with potassium, sodium cations, hydronium, ammonium, and diazonium.

Complex formation between a crown ether and an anionic nucleophile has two important characteristics. The first is the organic masking of the alkali metal providing an "onium ion" like entity that can be extracted into organic solvents with the accompanying anion. The second is that the anion part of the ion pair in the organic solvent is activated. In a dipolar aprotic solvent, this effect is most notable because the anion-solvent interactions are weak. Such a system has been described as involving the "reaction of naked anions".

Since the discovery of phase transfer catalysis, numerous applications have been described, not only in organic chemistry, but also in inorganic chemistry[36], analytical applications[37], electrochemistry[38],

photochemistry[39] and polymer chemistry[40] have utilized phase transfer catalysis. In organic synthesis , phase transfer catalysis has emerged as a broadly useful tool for: a) nucleophilic substitution reactions b) alkylation and condensation c) reaction of dihalocarbenes and other carbenes d) ylide mediated reactions e) oxidations and reductions. In those reactions, the technique of phase transfer catalysis provides a method which avoids the use of a polar aprotic solvent and also improves the reaction rate.

2. Triphase Catalyssis

a) Nature of Triphase Catalysis

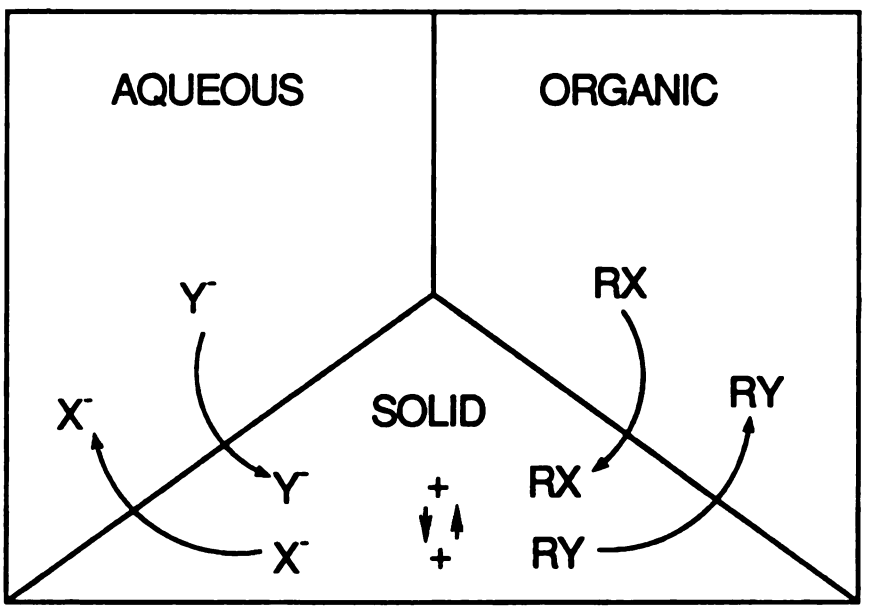
There is a new type of heterogeneous catalysis called " triphase catalysis" , in which the catalysts and each member of a pair of reactants are located in separate phases. Figure 5 illustrates the general features of a simple reaction of a triphase catalysis system[41].

Generally, the reactivity of triphase catalysis is lower than that of biphase catalysis based on the same equivalent of catalysts being used[42]. However, triphase catalysis exhibits the advantage of catalyst recovery and convenience of workup after catalytic reactions. Moreover, some triphase catalysts can provide regioselectivity due to the spatial constraint of the catalyst and the reactants.

Four major types of triphase catalysts have been developed. Three of these utilize onium ions as the catalytic center. These onium ions are supported on polymers[43-46], inorganic matrices[47-50], or layer

Figure 5 A general process of triphase catalysis for a a nucleophilic substitution reaction.

$$RX_{(org)} + Y^-_{(aqu)} \xrightarrow{\text{Catalyst}} RY_{(org)} + X^-_{(aqu)}$$



silicates[51-54]. Another type of the triphase catalysis uses polyethylene glycol as the catalyst[32,55-57].

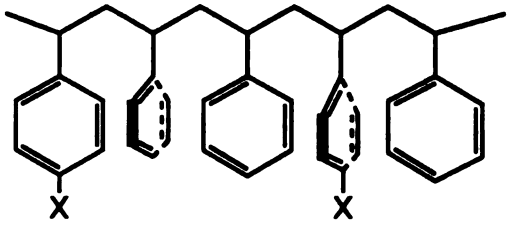
b)Polymer supported catalysts

Polymer supported catalysts are the first studied and best defined triphase catalysts. The backbone of the catalysts is polystyrene (Figure 6). Some of the phenyl rings are linked to onium salts. Also, the linear polymer can be expanded to a two-dimensional or three-dimensional network by cross linkage of two phenyl groups. In general, the higher the degree of cross linkage, the lower the diffusion of organic substance into the catalysts[58,59]. Tomoi and Ford[58,60], Regen and Beese[45], and Montanari et al.,[61] have reported extensively on the mechanism and properties of triphase catalysis. The fundamental mechanism of the polystyrene-supported catalysts for phase transfer catalysis is verified by solvent effects[46,61,62], O/C alkylation reactions of benzyl bromide and sodium naphthoxide[61,63-65], and the dependence of rate on bulk cyanide concentrations[66]. Also, NMR studies of the swellability of the triphase catalysts in two immiscible solvents[64], the rate dependence on cross-linking of the polystyrene backbone[58,59], and the rate dependence on percentage of onium salts attached to the phenyl groups provide information on the mechanistic process[67].

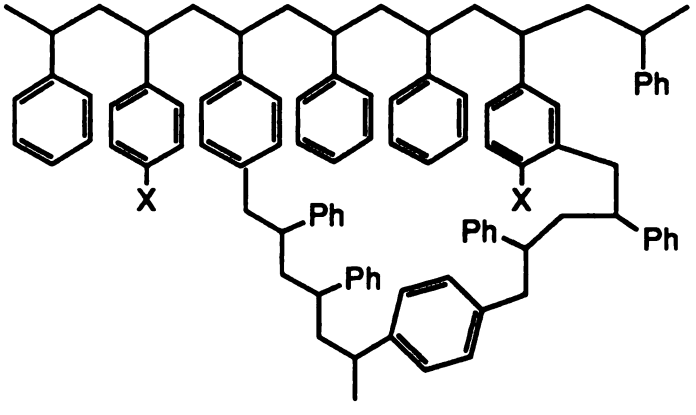
The location of the catalytic reactions in polymer supported catalysts is indicated by the following phenomena. a)The polymer-supported catalysts show higher catalytic capacity in the presence of polar organic solvents. The dependence of reactivity on the polarity of the organic solvent increases in the order decane

Figure 6 Linear and cross-linked structures of polystyrene-supported triphase catalyst.

Backbone



Crosslinking



$X = (CH_2)_nPR_3^+X^-$ or $(CH_2)_nNR_3^+X^-$

< toluene < o-dichlorobenzene[61,62]. This suggests that solvation of the ionic pair formed by the onium cation and nucleophile anion in the organic solution dominates the catalytic reaction. b) For the O/C alkylation reaction of naphthoxide by benzyl bromide (Figure 7)[68], the O-alkylation product is favored in aprotic solvent such as DMF, toluene etc., and the C-alkylation product is favored in protic solvents such as water, methanol etc. Polymer-supported catalysts afford mainly O-alkylation products (Figure 7)[61,63-65]. Therefore, the catalytic reaction for this triphase catalysis occurs mainly in an aprotic, polymer environment. c) The reactivity of a polymer supported catalyst is not sensitive to the bulk concentration of nucleophile[66], indicating that the catalytic reaction does not occur at the aqueous interface of polymer supported catalysts. Therefore, the nucleophilic substitution reactions occur at the organic phase, but the anion exchange at the onium cation site for the next cycle may occur at the aqueous interface.

The properties of polymer-based triphase catalysts suggest the fundamental kinetic processes[60] shown in Figure 8. The first step is the mass transfer of electrophilic reactant, RX, from bulk solution to the catalytic surface. The second step is diffusion of the reactant through the polymer matrix to the active nucleophilic site. Nucleophilic substitution occurs at the active site in the third step, followed by the diffusion of products to the surface of the catalyst and mass transfer of the products to the bulk solution as the fourth step. The ion pair may go back to the aqueous solution to exchange a new nucleophile for the next reaction cycle.

Figure 7 The O/C alkylation of benzyl bromide and naphthoxide in protic or aprotic solvents.

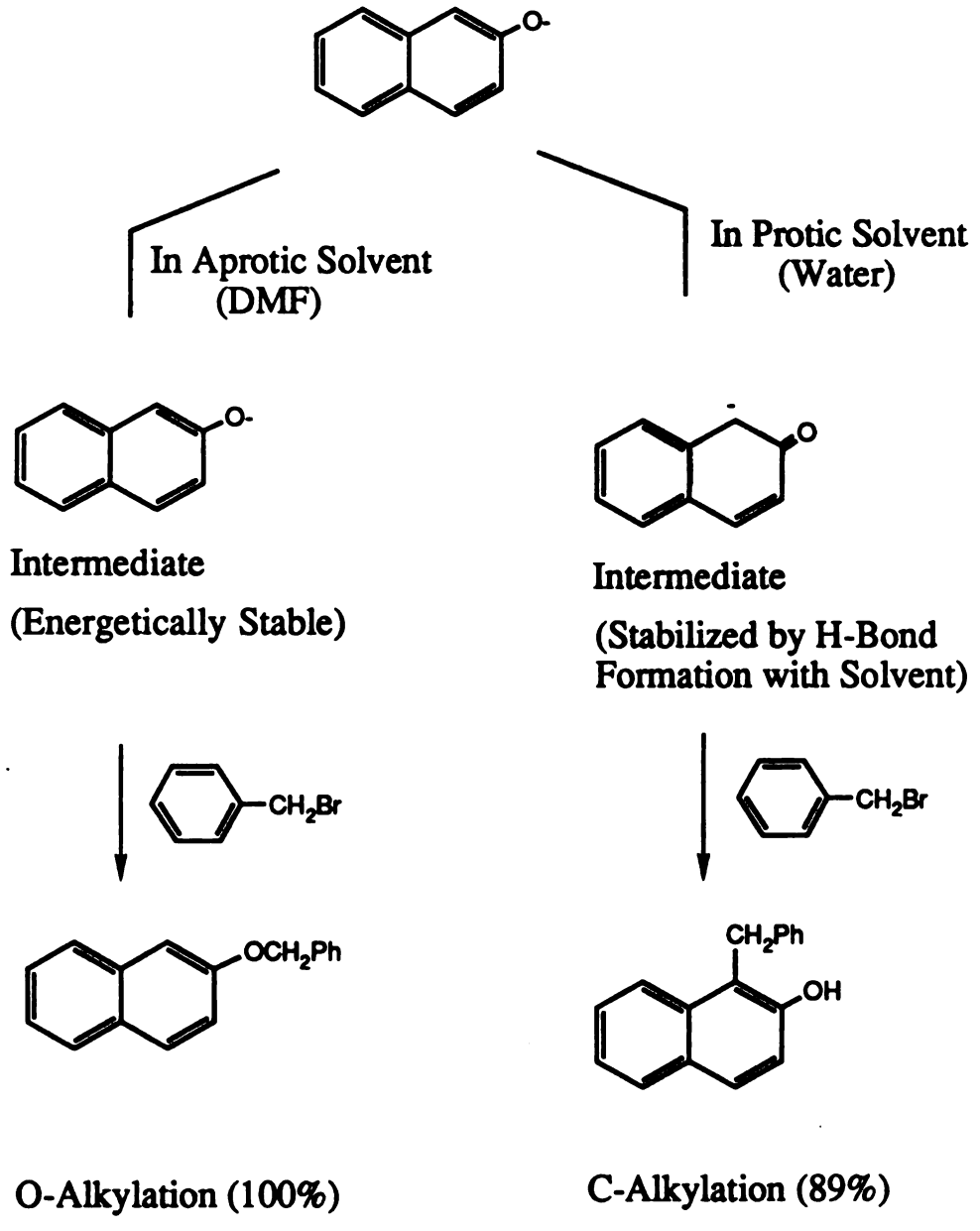
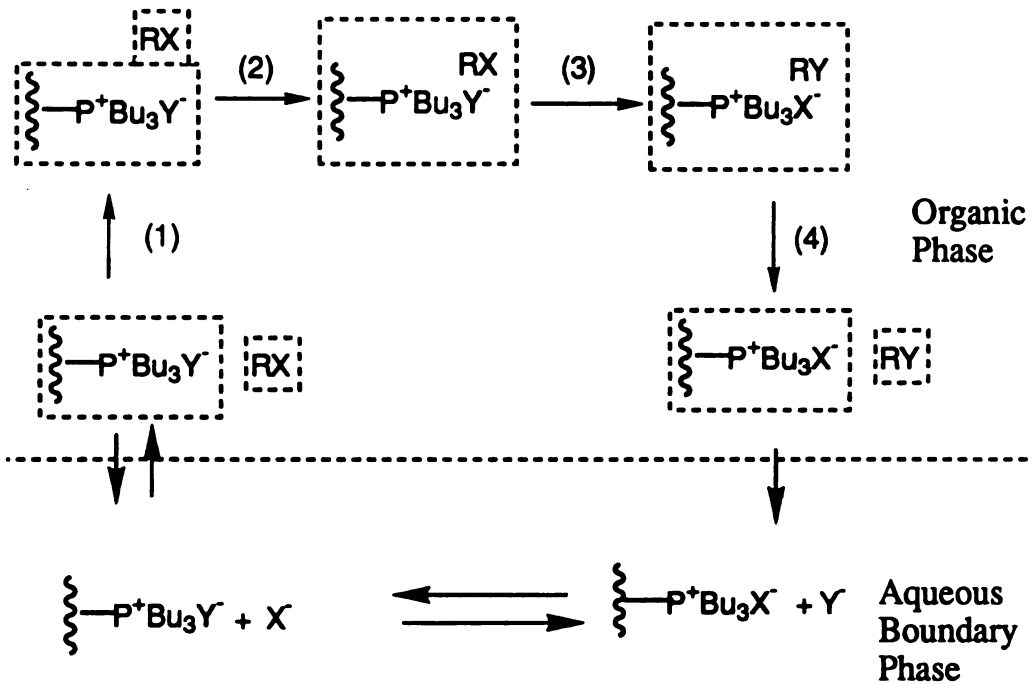


Figure 8 Mechanism of the polymer-supported triphase catalysis.



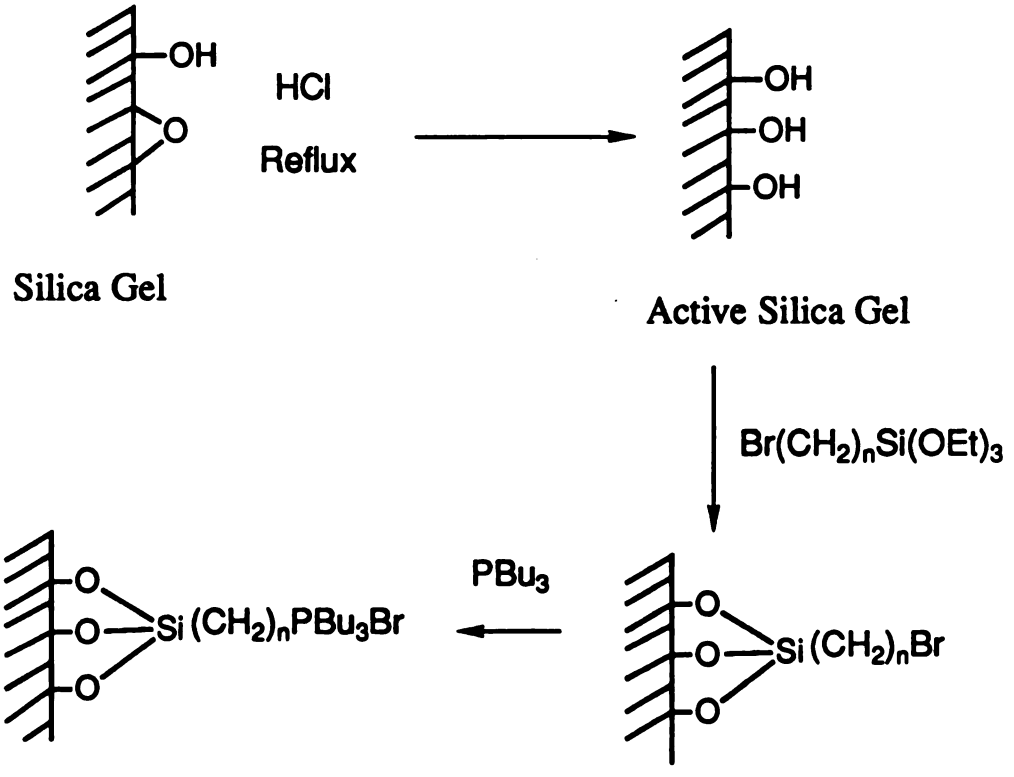
c) Inorganic-based triphase catalysts.

The synthesis of inorganic-based triphase catalysts involves the anchoring of an alkyltriakoxysilane (either a haloalkyl or aminoalkyltrialkyoxy silane) to the surface of silica gel or alumina to afford an alkyl functionalized inorganic matrix (Figure 9)[47]. Several types of onium salts can be immobilized by means of various hydrocarbon chain length containing different functionalization[57,48]. Important considerations for effective catalyst design are (i) the porosity and type of the inorganic support; (ii) the length of spacing of the alkyl chain; (iii) the chemical structure of the onium salt. Silica gel with a titer of 0.5 mmole Cl^-/g, is designated as 60SiC3PBu^+Cl^-(0.50), where 60Si indicates a silica gel support with a mean pore diameter of 60Å, C3 indicates the length of the alkyl chain supporting the phosphonium salts, and the value in parenthesis represents the loading in millimoles of the onium counterion per gram of catalytic support.

The main difference between inorganic solid and polymer supported catalysts is the influence of solvent polarity on the triphase catalysis reaction[49,69]. In the case of the silica gel triphase catalysis, the activity increases with decreasing solvent polarity. On the contrary, polystyrene supported catalysts show higher activity in more polar solvents. The catalytic reactions are carried out in different microenvironments.

The functionalized inorganic matrices are wettable both by the aqueous and the organic solution. This property allows these

Figure 9 The synthesis of silica gel supported catalysts.



systems to be active in liquid-liquid phase transfer catalysis even without stirring[69], since the inorganic matrix acts as a supply and a pump for the aqueous phase which contains the nucleophile anions. As the catalytic reactions proceed very close to the catalyst surface, the exhausted onium salt can be regenerated easily by means of exchange with the aqueous solution. The large surface of the support promotes the anion exchange process[70].

The exact structure of these systems during catalytic reactions remains unknown and not all the questions concerning the deposition of the aqueous and organic phases into the functionalized pores have been answered. The adsorption of the organic substrate on the catalyst pores or surface may play an important role in the mechanism. However, the diffusion of the organic reactants onto the catalyst surface or pore does not play an essential role for inorganic material-supported phase transfer catalysis.

Various applications concerning the use of silica gel or alumina based triphase catalysts in nucleophilic substitution reactions have been reported[48,49]: halogen exchange, synthesis of phenyl ethers and sulfides, reduction of carbonyl compounds with aqueous sodium borohydride, synthesis of nitrile, thiocyanate, nucleophilic, and N-alkylphthalimides. Depending on the reaction conditions, however, the functionalized inorganic matrices may lose some of their functionalization under the strong alkaline solution[69], and then reactions can actually be catalyzed both by the phase transfer catalyst and the silica gel or alumina-based triphase catalysts as well as the hydrolyzed catalytic groups free in solution.

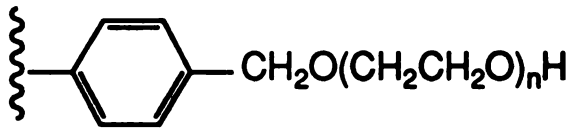
d). Poly(ethylene glycol)derivatives as phase transfer catalysts

The polyethers, specifically poly(ethylene glycol)'s (PEG), are widely used in phase transfer catalysis. The function of this reagent in phase transfer catalysis reactions is similar to that of crown ether. PEG's openly chelate the metal cation (Figure 10)[42] and carry the nucleophile to the organic phase to undergo the nucleophilic substitution reaction. Therefore, PEG may be used in most applications where crown ethers are currently used. While it is true that the reactivity of PEG's is often less than that of crown ethers, this may be compensated for by increasing the concentration of PEG.

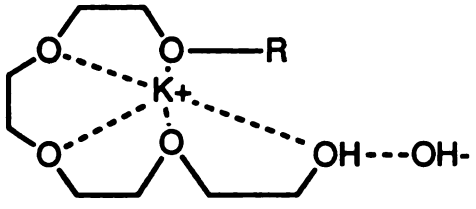
Many applications of organic reactions using PEG's as catalysts have been reviewed by Totten and Clinton[42]: the Biltz synthesis of phenyltoin; the synthesis of triaryl phosphate; the N-alkylation of nitrogen heterocycles; alkyloxymethyl and formation of alkoxypolyethoxymethyl derivatives of acylanilines; dehydrohalogenation of 2-bromoethylbenzene by hydroxide; carbonyl reduction; synthesis of phenyl ethers and sulfides; Williamson ether synthesis; polyether synthesis; aryldiazonium salt reactions; and oxidation chemistry. However, there is no report about the recyclability of these catalysts.

Figure 10 (a) The structure of polymer-supported poly(ethylene glycol) (b) The function of the PEG atoms as oxygen chelating sites for the metal cation.

(a)



(b)



e) Organoclay as triphase catalyst

Organoclays, which are the smectite clays intercalated by ternary ammonium or other organic cations, have been used as triphase catalysts. Kadahodayan and Pinnavaia used clay derivatives with metal complexes such as $M(phen)_3^{2+}/XO_4^{2-}$ ion pairs in the interlayer to facilitate the liquid-liquid phase transfer reactions[51]. Cornelius, Laszlo and P. Pennetreau utilized montmorillonite derivatives as triphase catalysts for alkylation of dihalomethane[54]. More recently, Choudary, et al. used the acidified clays linked with onium salts to accelerate cyanation reactions[52]. Lin, Lee and Pinnavaia contributed extensively to understanding of the nature and the application of the phase transfer catalysis by using organoclays as the triphase catalysts[53]. This work is continued by focusing on the mechanism, colloidal properties and longevity of organoclays as triphase catalysts.

C. Research Rationale and Objectives

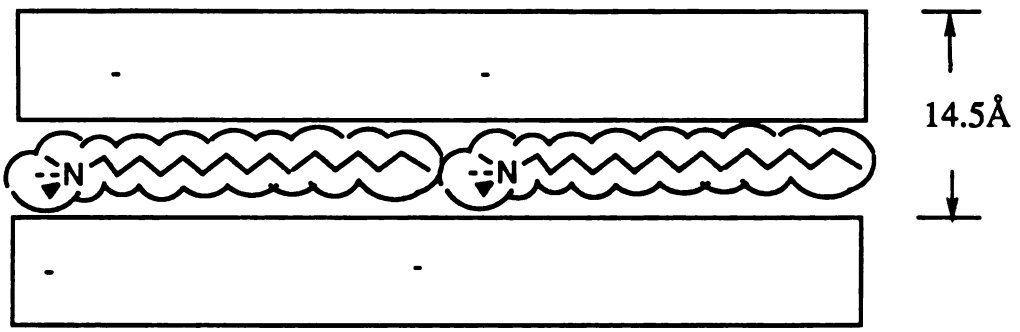
1. Nature of Organoclays as Triphase Catalysts

a) The structure of organoclays

The orientation of the cations in smectite clay interlayers depends on the onium structure and the layer charge density of the layered silicate[71-73]. Generally, a good organoclay for triphase catalysis should have an onium cation with more than one long alkyl chain. This onium ion can also be used as a surfactant. Lagaly summarized the surfactant orientations in the galleries of various layer charge density clays (Figure 11)[71]. For layered silicates with an extremely low layer charge density,

Figure 11 The surfactant orientation in the interlayers of various layer charge density clay.

(a) Monolayer: $[C_{16}H_{33}NMe_3]^+$ Laponite
(Cation exchange capacity, 55meq/100g)



(a) Lateral Bilayer, $[C_{16}H_{33}NMe_3]^+$Hectorite
(Cation exchange capacity, 73meq/100g)

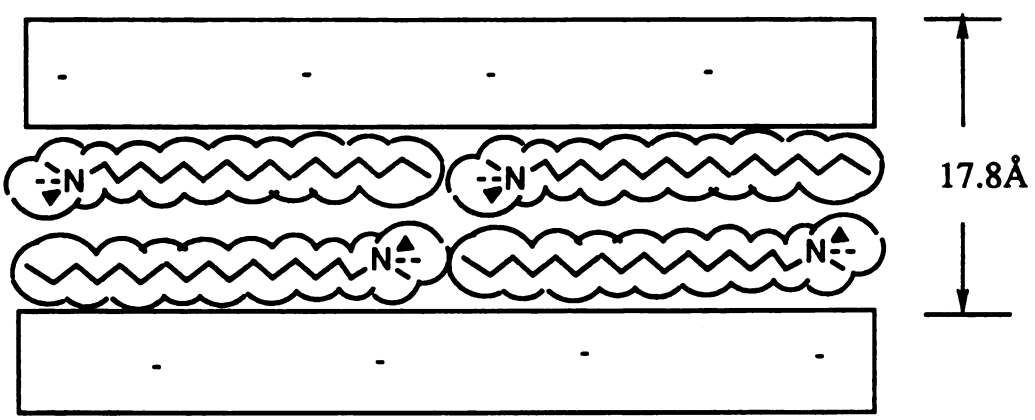
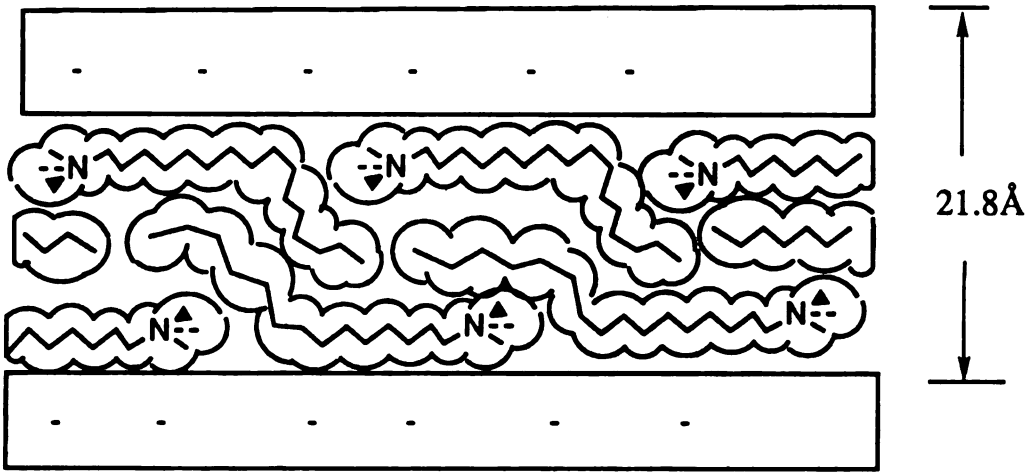


Figure 11(Continued)

(c) Pseudo Trimolecular Structure:
$[C_{16}H_{33}NMe_3]^+$ Montmorillonite(Arizona)
(Cation exchange capacity, 118meq/100g)



(d) Paraffin Structure, $[C_{16}H_{33}NMe_3]^+$ F-hectorite
(Cation exchange capacity, 140meq/100g)

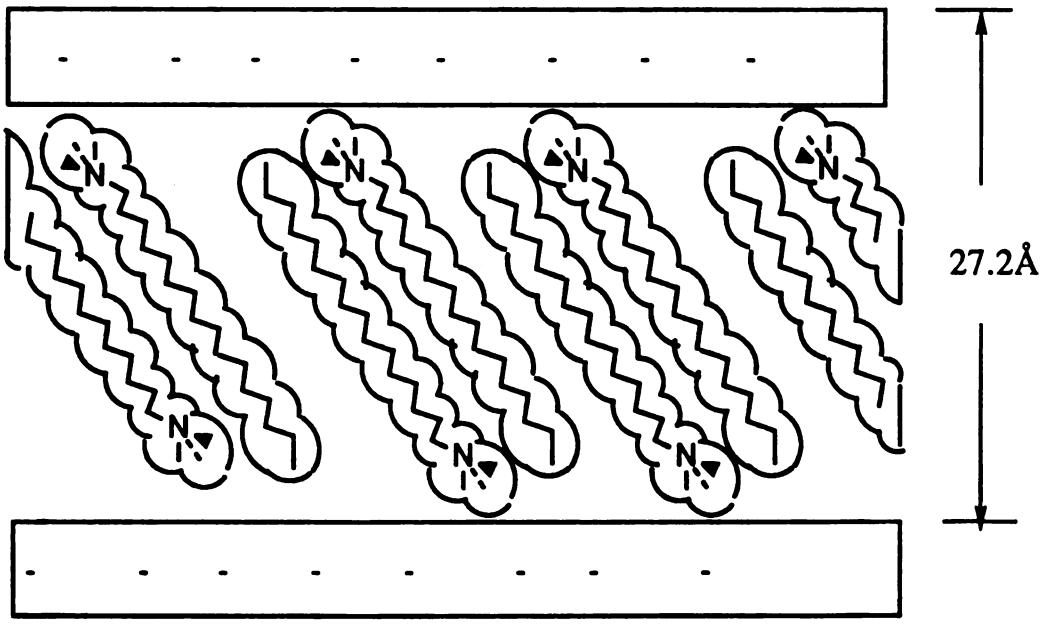
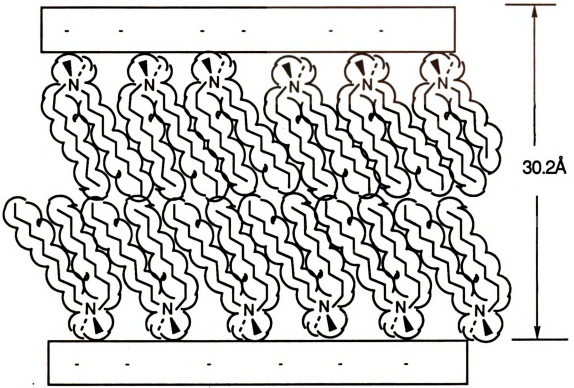
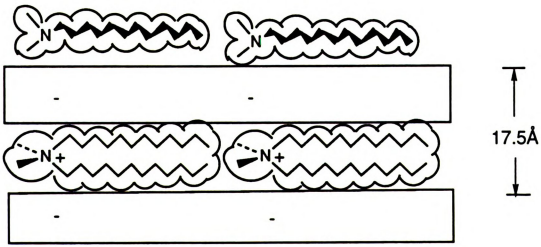


Figure 11(Continued)

(e) Lipid Structure, $[(C_{12}H_{25})_2NMe_2]^+$ F-hectorite
(Cation exchange capacity, 140meq/100g)



(f) $[(C_{12}H_{25})_2NMe_2^+]$Laponite
(Cation exchange capacity, 55meq/100g)



the surfactant adopts a monolayer structure with the chain parallel to the silicate surface (Figure 11a). As the layer charge density of the layer silicate increases, the ion will form a two layer structure with the chain parallel to the silicate layer, the so-called bilayer or lateral bilayer structure (Figure 11b). When the layer charge density of the layered silicate increases further, a pseudo trimolecular (Figure 11c) or paraffin structure (Figure 11d) of the surfactant will be adopted in the interlayer of the smectite clay. If a high layer charge density organoclay contains surfactants with two long alkyl chains, a lipid-like structure of the clay can be found (Figure 11e). The orientation of the surfactants in the interlayer can influence the wettability of the organoclay on the aqueous and organic phase. Also, the efficiency and longevity of the organoclay as triphase catalyst are affected by the surfactant orientations, as will be discussed in the later chapter.

b) Colloidal properties of the organoclays

The amphiphilic character of the organoclays is a potentially important property for efficient triphase catalysis. Sodium clays are only wettable in aqueous solution or polar aprotic solvents such as methanol. The purpose of intercalating an onium ion surfactant into the clay interlayers and external surface is to increase the hydrophobicity of the material. The hydrophilicity or hydrophobicity of the organoclay are easily judged by observing the wettability of the material. Also, BET surface area measurements can provide information on the hydrophilic portion. The surfactant alkyl group will fill the interlayer gallery leaving no empty space accessible for the nitrogen adsorption.

An amphiphilic organoclay can stabilize an emulsion of water and aprotic organic solution. Therefore, the nucleophile and the organic electrophile from two immiscible phases can be brought together on the phase boundary to undergo nucleophilic substitution reaction. Generally, an organoclay with a monolayer structure is a poor emulsifier for the water and oil mixture. However, the surfactants adopted in pseudo trimolecular and paraffin-like structure sometimes desorb from the reaction condition, making the high charge density organoclays poor catalysts.

The amphiphilic nature of organoclay surfaces has been applied already in photochemistry[74-77] and as absorbents for environmental pollutants[78,79]. Some organoclay surfaces may adsorb neutral chromophores, such as pyrene dissolved in aqueous solution. The adsorbed surfactants in clay hosts provide a hydrophobic site for the adsorption of luminescent organic molecules such as pyrene. In these colloids a large amount of pyrene excimer, in the form of dimerized pyrene, is generated at a pyrene concentration of $5x10^{-6}M$, significantly below that needed to form an excimer in homogeneous solution. Hence, pyrene excimer formation is a result of localization of pyrene on the surface of a clay particle, which has the effect of dramatically increasing the local concentration. The pyrene excimer has an emission spectrum different from that of the pyrene momomer. Also, the probe molecule (pyrenylbutyl)trimethylammonium bromide (PN^+) fluoresces well on the clay surface containing hexadecyltrimethyl ammonium bromide (CTAB).

However, PN^+ fluorescence is quenched by dimethylaniline, nitrobenzene and nitromethane in the CTAB-Clay system. The hydrophobic clay surface adsorbs the organic quencher and reduces the life time and the intensity of PN^+. This hydrophobic property of the organoclay has also been utilized for environmental applications. Boyd and co-workers have used amphiphilic organoclays to eliminate organic contaminants, such as phenyl derivatives from aqueous solution[78,79]. The sorption isotherms of benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, naphthalene and biphenyl on the CTAB-clays indicate that sorption occurrs by partitioning interaction with the $C_{16}H_{33}NMe_3^+$-derived phase. In general, increasing the $C_{16}H_{33}NMe_3^+$ content and basal spacings with increasing clay charge density increased the non-ionic organic compound sorption on CTAB-Clays. Increased sorption of alkylbenzenes by high charge density organoclays can be attributed to the ability of large basal spacing to accommodate larger solute molecules.

c) Mechanism of organoclay triphase catalysis

The mechanism of organoclay triphase catalysis are investigated by (i) observing the influence of organic solvent polarity on catalytic reactivity (ii) observing the relative O/C alkylation reaction of naphthoxide and benzyl bromide by using organoclays as catalysts (iii) studying the dependence of catalytic reactivity on the concentration of both anionic nucleophiles and organic reactants, and (iv) studying dependence of catalytic reactivity on the volume ratio of the two immiscible phases.

For polymer supported catalysts the nucleophilic substitution reaction proceeds in the organic phase. Since polar solvents have good polymer swelling ability, the catalytic reactivity for the ionic polymer catalysts increases with solvent polarity. If the swellability of organoclays by organic solvents plays an important role for triphase catalysis, the features of organoclay triphase catalysis should be similar to the catalytic reaction using polymer supported catalysts[61]. Otherwise, the nucleophilic substitution reactions may occur in the aqueous phase or at the boundary of clay-liquid phases.

O/C alkylation (Figure 5) can provide information about whether nucleophilic substitution proceeds in either aprotic or protic media[65,68]. An O-alkylation product results from reactions in an aprotic organic solution, and a C-alkylation product is favored from protic media such as aqueous solution. The O/C alkylation has been well studied for triphase catalysis using polymer supported catalysts[68]. Basically, the reaction products are predominately O-alkylation when using polymer supported catalysts, indicating that the nucleophilic substitution reaction occurs in the aprotic solvent. The organoclay triphase catalysis will be studied by the same reaction to determine the reaction microenvironment.

The reaction location can also be elucidated by the dependence of catalytic reactivity of cyanation (Equation 1) on the

$$C_5H_{11}Br + CN^- \text{------>} C_5H_{11}CN + Br^- \qquad (1)$$

bulk concentration of liquid phases. Since the nucleophiles and

substrates are not in the same phase, there should be one or two of the reactants adsorbed on the organoclay where the nucleophilic substitution reaction may occur. Three different plausible mechanisms can be described by the three following

$$\text{Rate} = k[\text{organoclay. RX}][CN^-]_{(aq)} \quad (2)$$

$$\text{Rate} = k[\text{organoclay. } CN^-][RX]_{(org)}, \text{ or} \quad (3)$$

$$\text{Rate} = k[\text{organoclay. } CN^- \text{ RX}] \quad (4)$$

equations. Equation 2 can be applied when the organic electrophile is adsorbed on the organoclay catalyst before reacting with the nucleophile located in the bulk aqueous solution. Equation 3 is appropriate only when the nucleophile is adsorbed on the organoclay catalyst and then contacted with the organic electrophile in bulk organic solution. If neither Equation 2 nor Equation 3 applies, the mechanism may be interpreted by Equation 4. If the mechanism for Equation 2 is favored, the pseudo first order rate constant, k_{obs}, can be determined from Equation 5. The k_{obs} will be equal to $k[CN^-]$. That is, the observed

$$-d[RBr]/dt = k_{obs}[RBr] \quad (5)$$

rate constant should be proportional to the bulk nucleophile concentration, $[CN^-]$, when the $[CN^-]$ is much larger than the [RX]. However, if the mechanism discussed by Equation 3 is true, another

pseudo first order rate constant, k_{obs}', can be determined from Equation 6. This k_{obs}' will be proportional to the bulk

$$-d[CN^-]/dt = k_{obs}'[CN^-] \qquad (6)$$

concentration of organic electrophile, [RX], because k_{obs}' is assumed to be equal to k[RBr]. The dependence of the pseudo first order rate constant on the bulk concentration of potassium cyanide (Equation 5) has been studied by Lin[95]. There is a linear relationship between the k_{obs} and $[CN^-]$, indicating the nucleophilic substitution reaction occurs at the catalyst-aqueous boundary. We further investigate the relation between the reaction rate, k_{obs}', and [RBr]. A non-linaer relationship between k_{obs}', and [RBr] can prove the the reaction is not occuring in organic phase.

The rate dependence on the volume ratio of organic and aqueous phase also provides information about the emulsion structure and the wettability of organoclays in the two liquid solutions. If the three phases, organoclay, aqueous and organic solution, adopt oil-in-water emulsion, a milky emulsion and excess of organic solution will be observed. Likewise, an water-in-oil emulsion will perform a milky emulsion and excess aqueous phase when the volume of the aqueous solution is more than the maximum content of aqueous droplets in the emulsion phase. This emulsion structure can be observed by changing the volume ratio of the two liquid phases. In a water-in-oil emulsion system, organoclays are mainly suspended in organic solution and aqueous droplets are immersed in the aqueous solution. As the volume of the aqueous solution increases,

a redundant aqueous solution appears and does not participate in the catalytic nucleophilic substitution reaction. That is, the reaction rate will not be influenced by the volume of bulk aqueous phase if the an excess quantity of aqueous solution appears. However, increasing the volume of organic solution will decrease the organoclay concentration in the organic suspension for the water-in-oil emulsion. This will result in low efficiency for the adsorption of organic electrolyte and catalytic reactivity in this water-in-oil emulsion system.

2. Longevity of the Clay Derivatives for Phase Transfer Catalysis.

a) Desorption of interlayer organic compounds

The most advantageous property of triphase catalysts is their potential recyclability. Polymer and inorganic matrices covalently link the onium salts so the catalyst structure will be maintained after the catalytic reactions. However, the polymer supported catalysts have yet to find industrial applications because of their diffusion limitations of mechanism and chemical instability[80,81]. Several inorganic supports suffer the same general disadvantage, namely, low reactivity on structural instability under reaction conditions. For example, silica gel as a support is destroyed by alkaline solution[69]. The decrease in organoclay recyclability for triphase catalysis is potentially limited by the ion exchange of the surfactants in the clay hosts with the counter cations of the nucleophile. The dissociated surfactants may dissolve into the organic phase, so the surfactant desorption may be dependent on the polarity of the organic solvent, the surfactant hydrophobicity and the affinity of the layered silicate for the surfactant.

Generally, polar organic solvents exhibit higher solubility for surfactants. Consequently, the surfactant may dissociate from the clay hosts to join the organic phase. To reduce the surfactant desorption, non-polar organic solvents are suggested for use in triphase catalysis. We expect organoclays suspended in non-polar organic solvents to exhibit good recyclability. Also, the organoclay triphase catalysis reactivity should be greater in non-polar solvents than polar solvents.

The desorption or ion exchange properties of an organoclay under triphase reactions should depend on the nature of the onium ion itself. For example, the carbon-rich surfactant, hexadecyltributyl phosphonium, may desorb from F-hectorite but hexadecyltrimethyl ammonium may not desorb from the clay host during the triphase catalysis reactions. The three bulky butyl groups shield the positively charged phosphonium leading to a surfactant with more organic than ionic character. Therefore, the ion pair of the carbon-rich surfactant and nucleophile should have good solubility in organic solvents, and this should favor desorption of the surfactant into the organic phase. Since the charge radius ratio of the positively charged nitrogen in hexadecyltrimethyl ammonium is large and this cation is only shielded by three methyl and one long chain alkyl groups, leaving the surfactant more ionic than organic in nature. The solubility of the surfactant derivative should be poor in organic solvents.

The attraction between the layered silicate and the surfactant should also depend on the layer charge density of the silicate host. The charge density of the host will determine the orientation of the organic cation in the gallery. Higher layer charge density clays should give paraffin structures and this should result in more surfactant desorption from the

layer sheet. However, surfactant desorption is not expected on organoclays with low layer charge densities causing these materials to be good triphase catalysts in terms of recyclability.

Behaving differently from intercalated surfactants, cationic crown ether complexes can also pillar the clay interlayer[82]. However, crown ether complex are poor candidates for triphase catalyst. The X-ray diffractogram diffraction data suggest thst a crown ether clay complex after a triphase catalysis reaction undergoes complex desorption by ion exchange. However, the recycled clay derivatives show IR absorptions of characteristic of the crown ether and reactivity for the catalytic reaction. Thus crown ethers may remain partially bonded to the external surface of the layered silicate instead of being intercalated in the gallery.

b) Thermal and chemical instability of the organoclay

Natural layered silicates are sometimes destroyed by strongly acidic or alkaline solutions, a potential limitation for their use in catalytic reactions which involve acidic or basic reagents. Surfactants based on the silicate surface can change the chemical reactivity of the smectite clay hosts. Structure changes due an acid or base reaction can easily be observed from the X-Ray diffraction measurement. It is very surprising that some of the organoclay derivatives with medium layer charge density such as organo hectorite are not affected by alkaline solution. This resistance to strong base is important and valuable since many nucleophilic substitution reactions employ strong bases such as cyanide or hydroxide as nucleophiles. In contrast, high layer charge density clay

derivatives do not seem to tolerate strong alkaline solutions since surfactant desorption produces an unprotected layered silicate surface. For triphase catalysis systems in strongly acidic environments all of the clays and their organoclays are expected to decompose at elevated temperature. However, typical phase transfer catalysis condition seldom utilizes strong acid reactants.

The layer charge density of dioctahedral smectite clays (Figure 1) with small metal cations in the interlayer causes them to be thermally unstable at temperature above 250°C. An interlayer small cation such as lithium or sodium may migrate into the empty octahedral site at elevated temperature, resulting in lower layer charge density. Since there is no octahedral empty site in trioctahedral smectite clays (Figure 2), the layer charge density of the layered silicate is not influenced by the thermal treatment. Under triphase catalysis conditions, the aqueous phase typically contains metal cations which may affect the layer charge density of the dioctahedral smectite clays[83,84] and cause surfactant desorption from the clay host. Thus, clay layer charge density reduction is a potential mechanism for surfactant desorption and the influence of thermal treatment on the the reduction of layer charge density is a potential disadvantage for dioctahedral organoclays as phase transfer catalysts. However, almost all phase transfer catalysis reactions proceed at temperatures below 250°C so this effect should not be significant in organoclay triphase catalysis.

Alkyl ammonium surfactants in clay interlayers may be thermally unstable under alkaline solution reaction conditions Quaternary hydroxides, for instance, are known to undergo Hofmann degration[85-87]. Thermal decomposition of the ammonium surfactants occurs at elevated temperatures. βH-elimination of the alkyl ammonium is the major cause for decomposition to olefin and amine compounds. The alkyl ammonium surfactants in the clay interlayer may be decomposed under reaction condition. The Hoffman degration reaction could be reduced if the alkyl ammoniums do not contain β-hydrogen. Fisk at Dow Chemical Company employs N-alkylarylpyridinium salts as the surfactant adsorbed on the metal surface for corrosion inhibition, since the surfactants can tolerate higher temperature treatment due to the absence of a β-hydrogen.

c) Co-surfactant influence on surfactant desorption

Hexadecyltrimethyl ammonium bromide (CTAB) is a typical cationic surfactant that forms an emulsion of two immiscible liquid phases. Adding an alcohol co-surfactant causes microemulsion formation. When this same surfactant is intercalated in layered silicate hosts for a triphase catalysis reaction, it is not expected to desorb even in the presence of concentrated electrolyte owing to the low solubility of the surfactant-anion pair in organic and aqueous solutions. Dobias found that adsorption of hexadecyl pyridinium chloride on minerals such as quartz decreases dramatically when the surfactant concentration is higher than the critical micelle concentration (CMC)[88]. It was suggested that surfactant in the form of a three dimensional micelle is more stable than a two-dimensional film adsorbed on the mineral surface. It is of interest to characterize the stability of an organo smectite clay when a

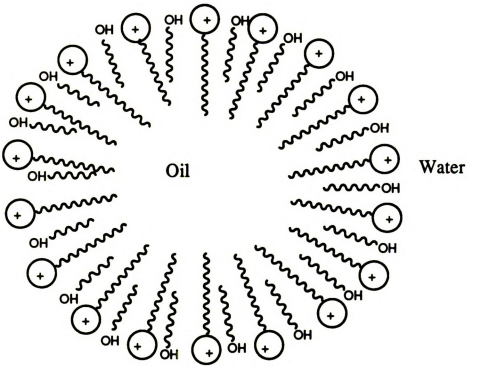
thermodynamically stable microemulsion is formed in the presence of a co-surfactant such as an alcohol with more than five carbon atoms.

Microemulsions are dispersions of oil and water made with surfactant and co-surfactant molecules[25,26]. Either type of dispersion, oil-in-water or water-in-oil (Figure 12) is possible. The droplet size are very small, typically 100Å, about 100 times smaller than typical emulsion droplet sizes[27,28]. Also, the interfacial tension of the fluid is lower[27-29,89], leading to larger contact surface between two immiscible liquids[90]. Moreover, microemulsions are thermodynamically stable, compared to emulsions[25,26]. Because the smaller surface tension results in smaller particle dispersion and an entropy increase. The negative entropy may compensate the surface energy to minimize the free energy. The co-surfactant plays an important role in partitioning between two neighboring polar groups of cationic surfactants to reduce the surface charge density on the surfactant-aqueous boundary[90,91].

Microemulsions are very useful in industry. Microemulsions have been used to improve oil recovery when oil prices reached levels where tertiary recovery methods became profitable[92].

Nowadays, microemulsion application is focused on solar energy conversion, liquid-liquid extraction, detergency and lubrication. Besides these applications, microemulsions can enhance the catalytic reactivity for micelle catalysis or biphase transfer catalysis. Introducing the co-surfactant to the oil\surfactant\water reaction mixture improves the catalytic reactivity of the biphase catalysis, because the smaller dispersion droplet leads to greater interfacial area for the catalytic reactions.

Figure 12 A droplet dispersion of oil-in-water microemulsion.



On the other hand, co-surfactant may facilitate desorption of a cationic surfactant such as hexadecyltrimethyl ammonium from some layered silicate surfaces by forming a more thermodynamically stable microemulsion containing the co-surfactant, the two immiscible liquids and the ammonium surfactant. The recyclability of the organo clays would then be reduced if the reaction mixture contains the co-surfactant. Alternatively the co-surfactant could improve dispersion of the clay particles in the triphase reaction and thus enhance reactivity.

CHAPTER II

EXPERIMENTAL

A. Material.

1. Sodium Hectorite

Naturally occurring California sodium hectorite (B1-26) with a particle size of <2 μm was obtained from Source Clay Mineral Depository, University of Missouri, in the pre-centrifuged and spray dried form. The mineral was purified by removing carbonates using pH5 acetate buffer solution and eliminating iron oxides by employing sodium hydrosulfate[93,94].

The idealized anhydrous unit-cell formula of hectorite is $Na_{0.67}[Li_{0.67}Mg_{5.33}(Si_{8.00})O_{20}(OH,F)_4]$, and the experimentally determined cation exchange capacity is about 73 meq/100g[95] of the air dried clay.

2. Sodium montmorillonites

Two naturally occurring sodium montmorillonites from Wyoming and Arizona with a particle size of <2 μm were also obtained from Source Clay Mineral Depository, University of Missouri, in the pre-centrifuged and spray dried form. The purification method for the montmorillonite is the same as that stated above for hectorite.

The idealized anhydrous unit-cell formula of montmorillonite (Wyoming) is $Na_{0.70}[Mg_{0.70}Al_{5.30}(Si_{8.00})O_{20}(OH)_4]$, and the experimentally determined cation exchange capacity is about 75 meq/100g of air dried clay[96]. The unit-cell of montmorillonite (Arizona) is $Na_{1.16}[Mg_{1.16}Al_{2.84}(Si_{8.00})O_{20}(OH)_4]$, with a cation exchange capacity of 118 meq/100g of air dried clay.

3. Laponite R

Synthetic laponite was obtained from Laporte Company, in England and was used without further purification. The unit-cell of this material is $Li_{0.36}[Li_{0.36}Mg_{5.64}(Si_{8.00})O_{20}(OH)_4]$, with the cation exchange capacity of 55 meq./100g[95] of air dried clay.

4. Fluorohectorite (F-hectorite)

In this synthetic hectorite the octahedral lattice hydroxyl groups have been replaced by fluoride ions. The unit-cell formula of F-hectorite is $Li_{1.60}[Li_{1.60}Mg_{4.40}(Si_{8.00})O_{20}F_4]$. The particle size of the material is larger than 2μm and the cation exchange capacity is approximately 140meq./100g[96] of air dried clay.

5. Rectorite

This mineral was from Ba-Tou, China[3]. The particles larger than 2μm were removed by suspending the mineral in an aqueous solution for 8 hours. Rectorite consists of a regular alternation of mica-like layers and expandable layers having the smectite composition. The chemical composition formula of the material is $\{(Na_{0.72}K_{0.02}Ca_{0.05})(Ca_{0.24}Na_{0.07})\}(Al_{4.00}Mg_{0.02})[Si_{6.58}Al_{1.12}]O_{22}$. The negative charge on the layer arises from isomorphous substitution on the tetrahedral silica oxygen sheet. The cation exchange capacity is 60 meq./100g of air dried clay[3].

6. Organic Reagents

All reagents were obtained commercially and used without further purification. Hexadecyltributhyl phosphonium bromide; hexadecyltrimethyl ammonium bromide; tetrabutyl ammonium bromide; and didodecyldimethyl ammonium bromide were obtained from Chemical Dynamics Company.

Pentyl bromide, pentyl cyanide, decane, dodecane, benzyl bromide, 1,2-dibromo-1-phenylethane, trans-stilbene, n-octanol, n-decanol, n-tetradecanol, 1,8-octandiol, 1,10-decandiol, 6-bromohexanol, 8-bromooctanol, benzaldehyde, 1-chloro-2,4-dinitrobenzene, 18-crown-6, dicyclohexa-18crown-6, and 2-bromoethylbenzene were obtained from Aldrich Chemical Corp. Toluene, methylene chloride, and dibromomethane were purchased from Mallinckrodt. Chloroform, methylene chloride, o-dichlorobenzene, butanol and naphthol were obtained from J. T. Baker Chemical company. Methyl orange, benzyl alcohol and isopentyl alcohol were purchased from Ficher-Scientific Company.

7. Inorganic Reagents

Sodium hydroxide, sodium bromide, sodium bicarbonate, hydrobromic acid and sodium acetate were purchased from EM Science company. Potassium cyanide was obtained from Fisher Scientific company. Hydrochloric acid, magnesium sulfate and sodium chloride were available from Columbus Chemical Industries Inc. Acetic acid, sulfuric acid and sodium hydrosulfate were purchased from Mallinckrodt. Sodium citrate was obtained from J. T. Baker Chemical company.

8. Synthesis of organic precursors

$BrC_{10}H_{20}OH$[97] was prepared by refluxing the mixture of 30 mmole of $HOC_{10}H_{20}OH$ and 20 mL of 48% HBr at 115°C in an oil bath for 5.5 hours followed by chromatographic separation using first hexane and then 1:1 hexane:ether as eluent. The purity of the $BrC_{10}H_{20}OH$ was 45%. The remaining 55% of the products consisted of $HOC_{10}H_{20}OH$ and $BrC_{10}H_{20}Br$.

Sodium naphthoxide was prepared by mixing 0.20 mole of NaOH in 20 mL aqueous solution and 0.21 mole of 2-naphthol in 100 mL methanolic solution and allowing the solvent to evaporate under reduced pressure at room temperature. The yield of pure sodium naphthoxide was 75.2%.

B. Preparation of Organic Clay Derivatives

1. Organoclays

An aliquot of 1 % aqueous suspension of the sodium clay was added to an aliquot of aqueous solution of known amount of tetraalkyl ammonium or phosphonium at the room temperature. The amount of the onium salts was twice on the clay cation exchange capacity (CEC). For example, for sodium hectorite with a CEC of 73 meq/100g, an aliquot of aqueous solution containing 146 mmole of onium salt was added to the suspension solution with 100 g clay to ensure that all the interalyer sodium cations were replaced by onium ions. After 24 hours of stirring, the products were purified by repetitively washing with ethanol to remove excess onium salt and then, resuspended in water until free of halide ion as tested by $AgNO_3$. The pure products were collected by centrifugation and air dried at room temperature.

2. Crown Ether Clay Complex

To sodium clay suspensions in methanol was added 2 CEC equivalent of 18-crown-6 or cis-dicyclohexa18-crown-6. These mixtures were stirred for 24 hours at room temperature. The excess crown ethers were removed by continuously washing with methanol.

C. Organoclay Triphase Catalysis

1. Determination of Cyanation k_{obs} (Equation 5)

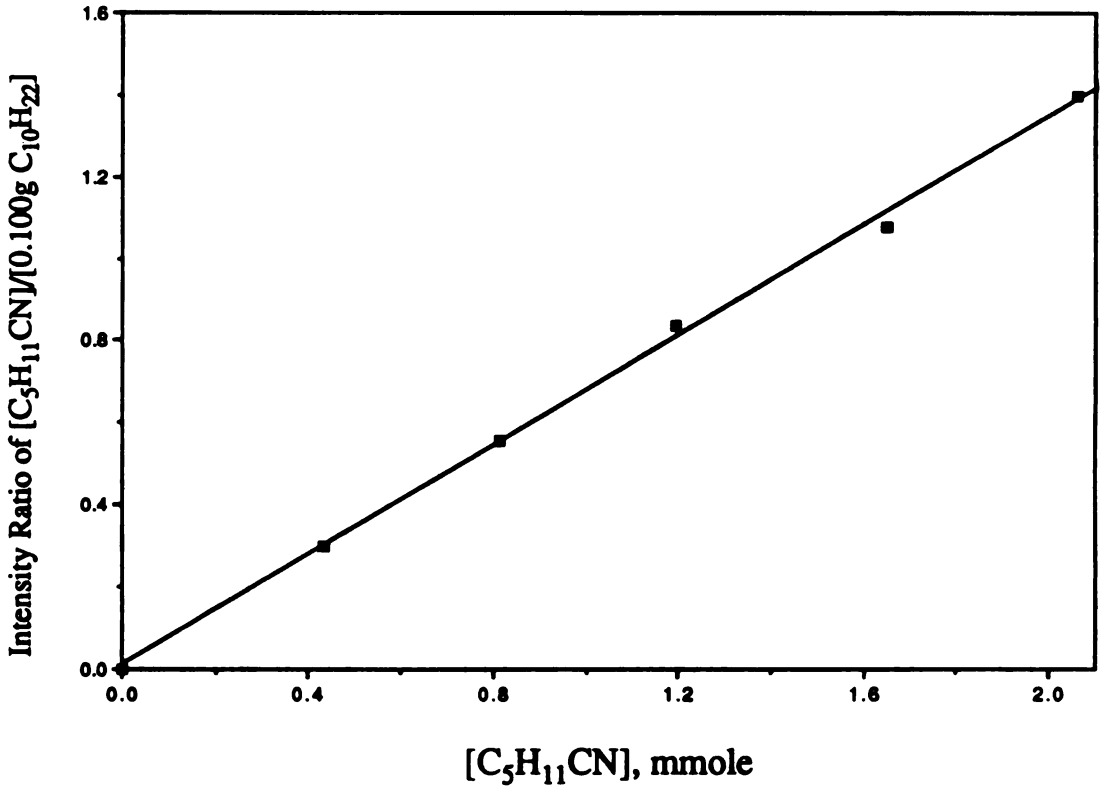
To a Corning culture tube was added 0.100 g of organoclay catalyst containing 0.06 mmole of onium ion, an aliquot of 3 mL 6.67 M potassium cyanide aqueous solution, 6 mL toluene solution containing 2 mmole of pentyl bromideand the internal standard, 0.15 g decane, the tube was sealed and stirred vigorously in a 90°C oil bath. Aliquots of 5 to 10

microliter of the organic solutions were withdrawn at 20 to 30 minutes interval and diluted in 0.5 ml of ether for GLC analysis. The conversion of pentyl bromide to pentyl cyanide was calculated from the ratio changes of pentyl bromide to decane. Pseudo first order rate constants were calculated with a least square program. Generally, the total reaction time was 1.5 to 3.5 hours.

2. Determination of Cyanation k'_{obs} (Equation 6) when the Amount of Pentyl Bromide Is Much Larger than Potassium Cyanide

To a Corning culture tube, was added to a solution of 0.130g of potassium cyanide in 3 mL of water, 0.100 g of organoclay, and 5 mmole of pentyl bromide in 6 mL toluene solution containing exactly 0.100 g decane. The same procedure for determining different k'_{obs} was applied to pentyl bromide concentrations in toluene equal to 0.83M, 1.67 M, 2.50 M, and 3.33 M. Reactions carried out in a 90°C oil bath were monitored by withdrawing 5 to 10 microliter samples from the organic phase at 20 to 30 minute intervals. It was assumed that the loss of cyanide ion was equal to the formation of pentyl cyanide. A standard GLC curve was made by area integration of a standard solution containing 0.2 to 2 mmole versus 0.100 g decane. The plot of mmole of pentyl cyanide against the ratio of pentyl cyanide to decane is shown in Figure 13. The chemical yields of pentyl cyanide were determined by calculating the integration ratio of pentyl cyanide to decane from the GLC data and interpolating the ratio value in Fig 13 to find the pentyl cyanide concentration in the reaction mixture.

Figure 13 The standard curve of the intensity area ratio of $[C_5H_{11}CN]/[0.100\ g\ C_{10}H_{22}]$ in GLC analysis versus $[C_5H_{11}CN]$ in 6 mL toluene as the organic solvent.



3. Solvent Effect on Iodination

To a Corning culture tube, 0.100 g of hexadecyltributyl phosphonium hectorite (H26AA) (equivalent of 0.06 mmole of hexadecyltrimethyl phosphonium) was added, then 8 mmole of potassium iodide in 3 mL water followed by 6 mL of desired organic solvent containing 2 mmole of pentyl bromide. The deserved organic solvents could be decane, toluene, or o-dichlorobenzene. An internal standard, 0.15 g decane or dodecane, was added to the mixture, and the tube was sealed and stirred vigorously at 90°C in an oil bath. Aliquots of 5 to 10 microliter of the organic solution were withdrawn at intervals of 20 to 30 minutes and diluted in 0.5 mL of ether for quantitative GLC analysis. The conversion of pentyl bromide to pentyl cyanide was calculated from the ratio of pentyl bromide to internal standard. Pseudo first order rate constants were calculated with a least square program.

4. O/C Alkylation of Benzyl Bromide and Sodium Naphthoxide.

A deserved amount of catalyst was added to a mixture of 0.5g (3 mmole) of sodium naphthoxide in 5 mL water and 0.34 g (2 mmole) of benzyl bromide in 5 mL of organic solution. The mixture was stirred at room temperature for 4 hours, then the organic phase was separated and the organic solvent was evaporated under reduced pressure. The ratio of O-alkylation and C-alkylation product (Figure 7) was determined by integration of the methylene proton absorption resonances in the ^1H NMR spectra. The methylene proton resonances in the ^1H NMR spectrum for C-alkylation and O-alkylation products occur at 4.48 ppm and 5.12 ppm, respectively.

5. Dependence of k_{obs} on the Volume Ratio.

Aliquots of 6.25 M potassium cyanide aqueous solution, 0.33M pentyl bromide in toluene, and 0.100 g catalyst were stirred in a 90°C oil bath. The conversion of pentyl bromide to pentyl cyanide was calculated from the chromatographic ratio of pentyl bromide to the internal standard decane in GLC analysis.

6. Catalytic Cyanation in the Absence of Water

A 6 mL quantity of toluene solution containing 2 mmole of pentyl bromide, 20 mmole potassium cyanide and 0.100 catalyst H26AA were stirred at 90°C in an oil bath. The conversion of pentyl bromide to pentyl cyanide was calculated from the chromatographic ratio of pentyl bromide to decane in the GLC analysis. The total reaction time was generally 1.5 to 3.5 hours.

D. Longevities of Organoclay Derivatives

1. Recyclabilities of Organoclays for Cyanation

Aliquots containing 20 mmole of potassium cyanide in 3 mL water and 2 mmole of pentyl bromide in 6 mL organic solution were added to 0.100 g of the organoclay catalyst. The organic solvent was either toluene or decane. The mixture was sealed in a Corning tube and stirred at 90°C in an oil bath. After the catalytic reaction was finished and the observed rate constant (k_{obs}) was determined, the organoclay catalyst was filtered and then washed with 10 ml of water and ethanol. The catalytic reaction was then repeated using the recycled catalyst.

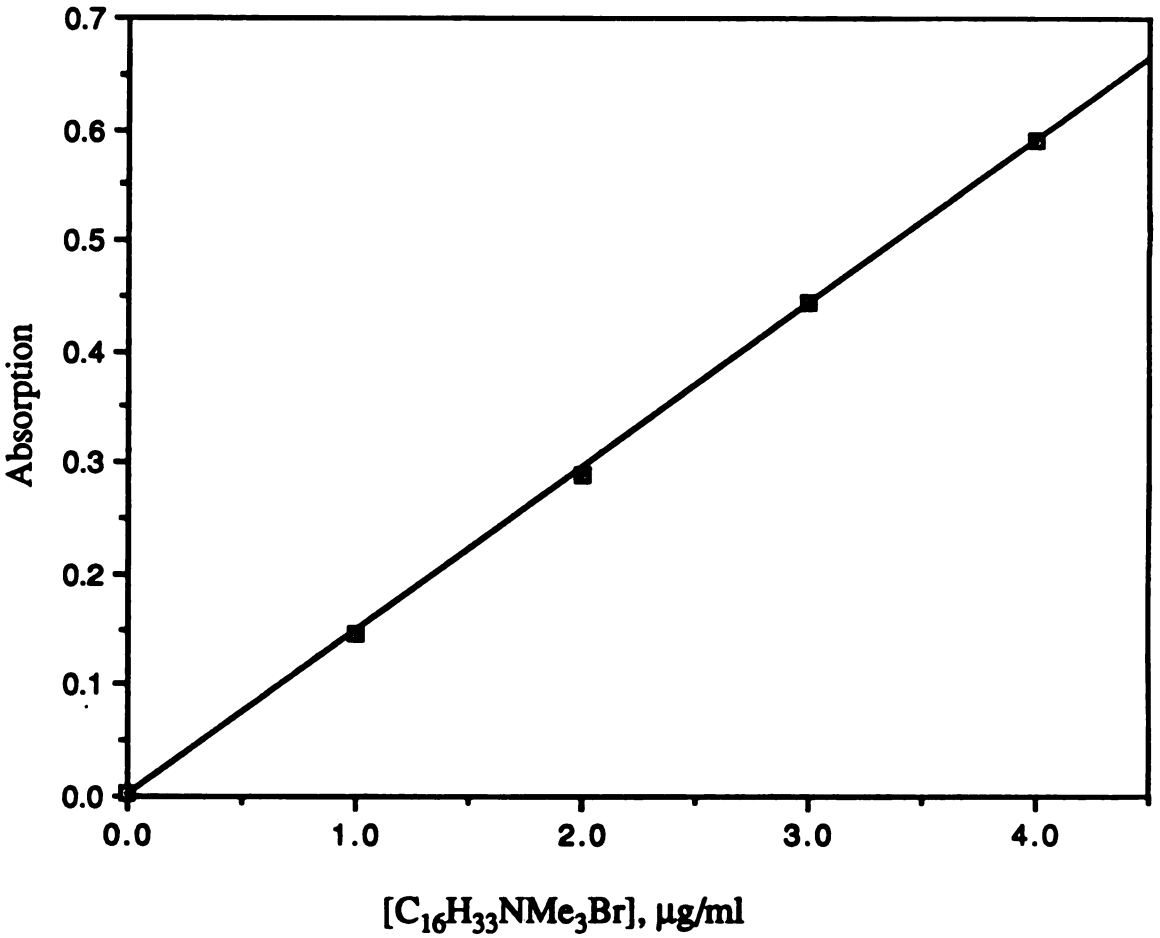
2. Recyclabilities of Organoclays for Chlorination

Aliquots of 4 mL 2.5N NaCl aqueous solution and 4 mL of a toluene solution containing 2 mmole of pentyl bromide and an internal standard of 0.15 g decane were added to 0.100 g of the organoclay catalyst. The mixture was stirred at 90°C for 8 hours. The conversion was determined from the change in the integral GLC intensity for pentyl bromide and the internal standard. The catalyst was filtered and washed with 10 mL fresh water and ethanol. The same catalytic reaction was repeated using the recycled catalyst.

3 Surfactant Desorption of Organoclays

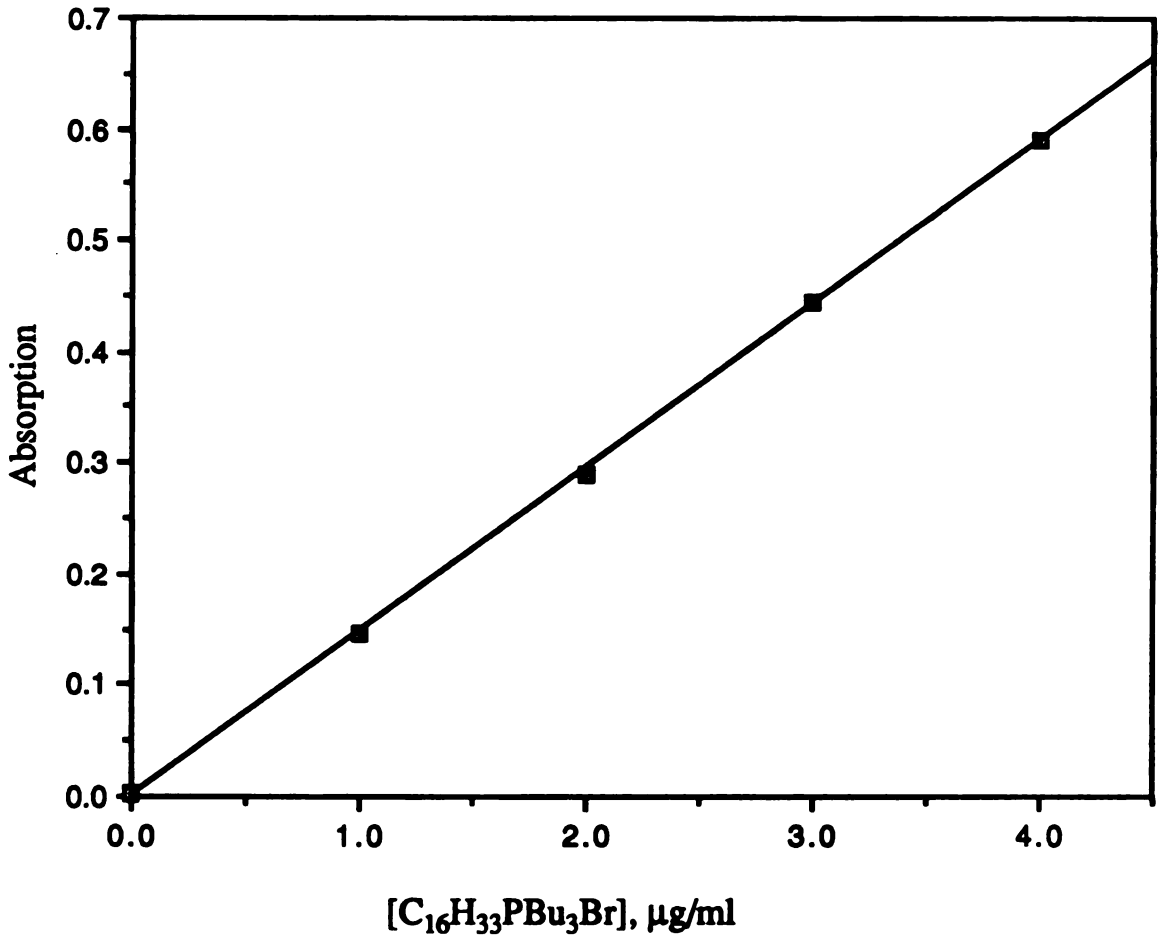
The desorption of surfactants from clay hosts was determined by measuring the concentration of cationic surfactants in bulk liquid phase after ion-exchange reactions. The desorbed cationic surfactant concentration in liquid solution was determined by the method developed by Wang and Langley[98]. Mixtures containing 0.03g organoclay, 4 mL aqueous solution with desired electrolyte concentrations and 4 mL of organic solvents were stirred at 90°C or room temperature for the desired time. After the ion-exchange reactions were finished, 1 mL of both organic and aqueous solutions were transfered to a 50 mL buffer solution containing citric acid and 1.0 mg methyl orange. If the desorption of onium ion was very high, the quantity of methyl orange was doubled or increased further to ensure an excess of indictor. The aqueous solutions were extracted using 25 mL of chloroform. Standard curves of UV-Vis absorptions in chloroform solution with a 10 mm length cell against known surfactant concentrations (Figures 14 and 15) were determined. The absorption for the surfactant-dye ion pairs in chloroform were measured at 418 nm. If absorbancies were over the limit of the

Figure 14 Dependence of the UV-Vis absorption of $C_{16}H_{33}NMe_3Br^+$-methyl orange chloroform solution at 418 nm on concentration of $C_{16}H_{33}NMe_3Br$ aqueous solution.



Various concentrations of $C_{16}H_{33}NMe_3Br$ in aqueous solution were added to excess amount of methyl orange. The ion pairs of the cationic surfactant and anionic dye were extracted into 25 mL of chloroform. The absorptions of the chloroform solutions in a 10 mm length cell were determined bya UV-Visible spectrophotometer at the wavelength 418 nm.

Figure 15 Dependence of the UV-Vis absorption of $C_{16}H_{33}PBu_3Br^+$-methyl orange chloroform solution at 418 nm on concentration of $C_{16}H_{33}PBu_3Br$ aqueous solution.



Various concentrations of $C_{16}H_{33}PBu_3Br$ in aqueous solution were added to excess amount of methyl orange. The ion pairs of the cationic surfactant and anionic dye were extracted into 25 mL of chloroform. The absorptions of the chloroform solutions in a 10 mm length cell were determined by a UV-Visible spectrophotometer at the wavelength 418 nm.

instrumental measurement, the solution was diluted by adding more chloroform until the absorption was within the standard curve. According to Beer's Law, the concentration of the surfactant-dye adducts were proportional to absorption. Thus, desorption of surfactants from clay hosts to liquid phases were derived by measuring the UV-Vis absorption and finding the relative surfactant concentration from the standard curve.

4. Effect of Co-surfactant on Phase Transfer Catalysis Reactions.

To a Corning culture tube was added 2 mmole potassium cyanide in 3 mL of water, 0.100g of clay supported catalyst (equivalent to 0.060 mmole of onium salt), and then 1.511 g (20 mmole) of pentyl bromide and the desired amount of co-surfactants in 6 mL of toluene. Subsequently 0.100 g of decane, the internal standard, was added to the mixture, the tube sealed and vigorously stirred at 90° for 4 hours. The conversions of pentyl bromide were determined from the GLC integrated intensity of pentyl cyanide relative to the decane integral intensity. A standard GLC curve for the integration ratio of pentyl cyanide to decane is determined (Figure 13) to quantify the amount of pentyl cyanide in the reaction mixtures.

5. Conversion of n-Bromoalkan-1-ol to n-Cyanoalkan-1-ol by Using Phase Transfer Catalysts

To a Corning culture tube containing 0.100 g of the organoclay catalyst (equivalent to 0.06 mmole of $C_{16}H_{33}NMe_3Br$) was added on aqueous solution containing 10 mmole potassium cyanide in 3 mL of water, and then 2 mmole of n-bromoalkan-1-ol in 6 mL of toluene. After the internal standard, decane, was added to the mixture, the tube was sealed and stirred vigorously at 90°C in an oil bath for 4 hours. The

conversion of n-bromoalkan-1-ol was determined from the integrated intensities of n-bromoalkan-1-ol to decane peaks by GLC.

6. Conversion of n-Bromoalkane to n-Cyanoalkane Using Phase Transfer Catalysts

To a Corning culture tube was added an aliquot solution containing 10 mmole potassium cyanide in 3 mL of water, 0.100 g of the organoclay catalyst (equivalent to 0.06 mmole of $C_{16}H_{33}NMe_3Br$) and 2 mmole of n-bromoalkane in 6 mL of toluene. After 0.15 g of decane, the internal standard, was added to the mixture, the tube was sealed and stirred vigorously at 90°C in an oil bath for 4 hours. The conversion of n-bromoalkan-1-ol was determined from the ratio change of the integrated intensities of n-bromoalkan-1-ol to decane peaks by GLC analysis.

7. Recyclability of Crown Ether Clays for Cyanation

A toluene solution containing 2 mmole of benzyl bromide and 0.15 g of decane as the internal standard was added to 0.100 g of the crown ether clay and 5 mmole of potassium cyanide in 1 mL of water. THis mixture was placed in a Corning tube which was then sealed and stirred at 90°C in an oil bath for 12 hours. After the catalytic reaction was stopped, the conversion was determined by GLC. The solid material was filtered and washed using 10 mL of ethanol. The same catalytic reaction was repeated by using the recycled material.

E. Application of Organoclay Triphase Catalysis to Organic Synthesis

1. Synthesis of Symmetrical Formaldehyde Acetals (Equation 10-12)

Mixtures of 10 mL methylene chloride solution containing 10 mmole of the desired alcohol, 10 g of dibromomethane and 10 mL of 50% NaOH aqueous solution were added to 0.2 g of the desired organoclay catalyst. The mixtures were refluxed with stirring at 90°C for 12 hours. After reaction, the liquid phases were easily filtered. The organic layer was dried over $MgSO_4$ and the organic residue was obtained by evaporating the volatile organic solvent under reduced pressure. The structure and the yield of the product were determined by ^1H NMR spectra.

2. Synthesis of Alkyl Bromide by Dehydration of Alkyl Alcohol in Strongly Acidic Conditions (Equation 13)

To a Corning tube was added a mixture of 2.5 mmole of octanol, 0.1 g of decane, 1 mL 47% HBr and 0.1 g of organoclay. The mixture was stirred at 90°C in an oil bath for 11 hours. The yield was determined by GLC.

For the reaction with diluted reactants, 1 mL of water and 1 mL of toluene were added to the mixture indicated above. This reaction was also carried out at 90°C in an oil bath for 11 hours.

3. Dehydrohalogenation of 2-Bromoethylbenzene (Equation 14)

A mixture of benzene containing 0.2 g of decane as the internal standard, 4 mmole of 2-bromoethylbenzene, 2 mL 50% NaOH aqueous, and 0.1 g organoclay were introduced to a Corning tube which was sealed and heated at an elevated temperature. Yields were determined by GLC.

4. Oxidation of trans-Stilbene (Equation 15)

A mixture of 3 mmole of trans-stilbene in 10 mL benzene, 6 mmole of $KMnO_4$ in 6 mL water and 0.200g organoclay catalyst, were refluxed with stirring at the room temperature for 8 hours. After filtering the reaction mixture, the acidic product in the organic layer was extraction with 20% NaOH aqueous solution. The aqueous layer was combined with the alkaline washing solution. The basic aqueous solution was acidified by hydrochloric acid, followed by extracted with 40 mL of methylene chloride. The pure benzoic acid was obtained by evaporating the organic solvent under reduced pressure and the yields were determined by weighing the product.

5. Synthesis of 2,4-Dinitrophenyl Ether (Equation 16)

In a round bottomed flask a mixture of 5 mmole of 1-chloro-2,4-dinitrobenzene and 6 mmole of phenol in 8 mL of benzene, 4 mL 1.5 N NaOH aqueous solution and 0.100 g of the organoclay catalyst were stirred at room temperature for 6 hours. After the organic layer was washed with deionized water, the product residue was obtained by evaporating the organic solvent under reduced presure. The purity of the organic residue was determined by ^1H NMR spectra

F. Physical Measurements

1. Infrared Spectroscopy

Infrared spectra were recorded using an IBM Single Beam FT IR44 model spectrophotometer. Liquid spectra were obtained by using 0.1 mm NaCl cells and solid spectra were recorded by mixing the samples with KBr and pressing them into disks.

2. Gas Liquid Chromatography

All product mixtures together with solvent and internal standard were analyzed by gas liquid chromatography either on a model 5880 Hewlett-Packard instrument filled with a flame ionization detector and a 25 m x 0.25 mm cross-linked dimethylsilicone capillary column or on a model 5890 Hewlett-Packard chromatograph with a flame ionization detector and a capillary 60 m x 0.25 mm column. Products were identified by comparison of GLC retention times with those of authentic samples. The percentage yield of products was determined by integration of the absorption peaks of the starting reagents and the internal standard.

3. NMR Spectroscopy

Proton and carbon-13 nuclear magnetic resonance spectra were recorded on a Bruker WM-250 or Gemini-300 MHz spectrometer. Chemical shifts were usually measured relative to tetramethylsilane as internal standard and reported in units of ppm.

4. X-Ray Diffraction

X-ray d_{001} basal spacing were determined for oriented film samples with either a Philips X-ray or a Rigaku X-ray diffractometer using Cu-Ka radiation with wavelength equals to 1.5405 Å. The film specimens were prepared by allowing an aqueous suspension of the samples to evaporate on a microscope glass and monitoring the diffraction over a 2-theta range from 1^{o} to 40^{o}. Peak positions in the angle 2 theta were converted to d-spacing with a standard chart.

5. UV-Vis spectroscopy

UV-Vis spectra were recorded by a 9430 UV-Visible IBM Spectrophotometer. Sample concentrations were determined by absorption measurements. Sample and reference solutions were contained in 10 mm quartz cells.

6. BET Surface Area Measurement

The BET surface area were recorded by a QUANTASORB Jr. Sorption Analyzer. The specific surface area of the samples was determined by measuring sorption of nitrogen on the sample at liquid nitrogen temperature.

CHAPTER III

RESULTS AND DISCUSSION

A. The Preparation and Structures of Clay Derivatives

1. The Preparation of Organoclays

The reaction of sodium smectite in liquid suspension with stoichiometric amounts of onium salts dissolved in water, ethanol or acetone results in products in which the sodium ion is displaced by onium cations. A series of organoclays shown in Table 1 were prepared using this method. The first letter designates the clay source or type, e.g. "A" is Arizona montmorillonite and "F" represents the clay host, fluorohectorite. The number designates the onium ion in the clay interlayer and the reaction solvents are represented by the last two letters. For example, "AA" of A26AA means that the organoclay is synthesized in aqueous solution. Likewise, H24AB is synthesized in ethanol and H24AC is generated in acetone, and the number "26" designates the onium ion, $C_{16}H_{33}PBu_3^+$.

Table 1 Surfactant-intercalated clay catalyst.

Catalyst	Clay	CEC (Meq/100g)	Solvent	Surfactant	d001 (Å)	Interlayer Distance(Å)	L (Å)
L24AA	Laponite	55	Water	$C_{16}H_{33}N(CH_3)_3^+$	14.5	4.9	44
H24AA	Hectorite	73	Water	$C_{16}H_{33}N(CH_3)_3^+$	17.8	8.2	62
H24AB	Hectorite	73	Ethanol	$C_{16}H_{33}N(CH_3)_3^+$	17.8	8.2	47
H24AC	Hectorite	73	Acetone	$C_{16}H_{33}N(CH_3)_3^+$	14.0	4.4	66
W24AA	W-Mont.*	75	Water	$C_{16}H_{33}N(CH_3)_3^+$	18.3	8.1	137
A24AA	A-Mont.*	118	Water	$C_{16}H_{33}N(CH_3)_3^+$	21.8	12.2	61
F24AA	F-hectorite	140	Water	$C_{16}H_{33}N(CH_3)_3^+$	27.2	17.6	237
R24AA	Rectorite	60	Water	$C_{16}H_{33}N(CH_3)_3^+$	31.0	12.0	187

Continued

Table 1 (Continued)

Catalyst	Clay	CEC (Meq/100g)	Solvent	Surfactant (Å)	d001 (Å)	Interlayer Distance (Å)	L (Å)
L26AA	Laponite	55	Water	$C_{16}H_{33}PBu_3^+$	16.0	6.4	52
H26AA	Hectorite	73	Water	$C_{16}H_{33}PBu_3^+$	19.6	10.0	52
W26AA	W-Mont.*	75	Water	$C_{16}H_{33}PBu_3^+$	19.5	9.9	104
A26AA	A-Mont.*	118	Water	$C_{16}H_{33}PBu_3^+$	27.6	18.0	85
F26AA	F-hectorite	140	Water	$C_{16}H_{33}PBu_3^+$	28.0	19.4	229
R26AA	Rectorite	60	Water	$C_{16}H_{33}PBu_3^+$	32.7	13.7	232
L30AA	Laponite	55	Water	$(C_{12}H_{25})_2N(CH_3)_3^+$	17.7	8.1	45
H30AA	Hectorite	73	Water	$(C_{12}H_{25})_2N(CH_3)_3^+$	20.1	10.5	65
W30AA	W-Mont.*	75	Water	$(C_{12}H_{25})_2N(CH_3)_3^+$	20.1	10.5	113
A30AA	A-Mont.*	119	Water	$(C_{12}H_{25})_2N(CH_3)_3^+$	30.2	20.6	90
F30AA	F-hectorite	140	Water	$(C_{12}H_{25})_2N(CH_3)_3^+$	30.2	20.6	234
H18AA	Hectorite	73	Water	$(C_4H_9)_4N^+$	14.5	5.0	52
F18AA	F-hectorite	140	Water	$(C_4H_9)_4N^+$	14.5	5.0	94

* W-mont. is Wyoming montmorillonite and A-mont. is Arizona montmorillonite.

If the reaction condition involved water or ethanol as solvent, displacement of the sodium cation by onium cations was strongly favored. Nearly complete cation exchange was achieved by using stoichiometric amounts of reagents. However, the ion exchange reaction could not be completed in acetone because of the low acetone dielectric constant which limits swelling of the silicate layer. The organoclay (H24AC) is not completely ion-exchanged, so its d-spacing of 14.0Å is smaller than those of products H24AA and H24AB with values of 17.8Å.

2. The Structure of Organoclays.

The X-ray d-spacings of organoclays depend on the smectite clay layer charge densities and on the structure of the surfactant onium ions. Figure 16 lists the representative XRD patterns of organoclays: (a). L24AA; (b) H24AA; (c) W24AA; (d) A24AA; (e) F24AA. High d-spacing organoclays are formed for smectites with high layer charge densities. For example, the d-spacing of $C_{16}H_{33}NMe_3^+$laponite (L24AA) with the CEC of 55meq/100g is 14.5Å, but the d-spacing of $C_{16}H_{33}NMe_3^+$F-hectorite (F24AA) with the CEC 140meq/100g is 27.2Å. The BET-Surface areas are dramatically reduced when sodium is replaced by surfactants in the interlayer due to the absence of space accessible for nitrogen adsorption in the interlayers (Table 2). The surfactant hydrocarbons are packed in the clay gallery and more of the cationic surfactants are loaded in higher layer charge density clays to balance the negative charge of the silicate layers.

Table 2 The BET surface area of sodium clays and organoclays in which the surfactant, [$C_{16}H_{33}NMe_3^+$], is intercalated in the clay interlayers.

Clay Host	BET Specific Area (m^2/g)	
	Sodium Clay	$C_{16}H_{33}NMe_3^+$ clay
Laponite	413	160
Hectorite	108	10.1
Arizona Montmorillonite	104	4.2
F-hectorite	4.2	3.5

Figure 16 The X-Ray diffraction pattern of various organoclays.
(a) L24AA; (b) H24AA; (c) W24AA; (d) A24AA; (e) F24AA.

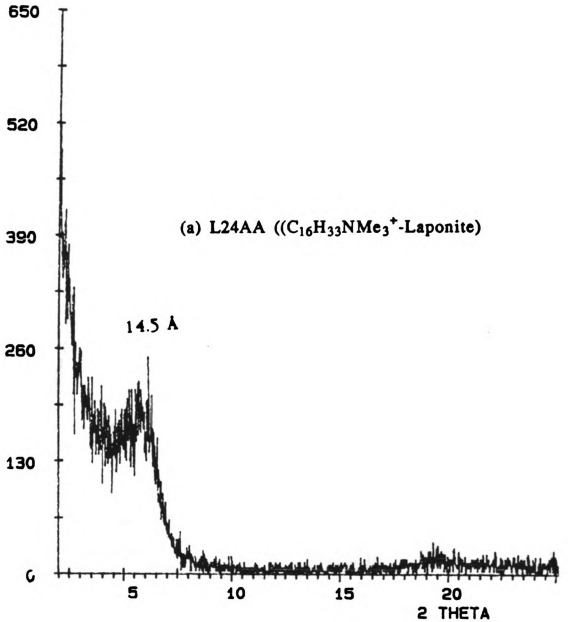


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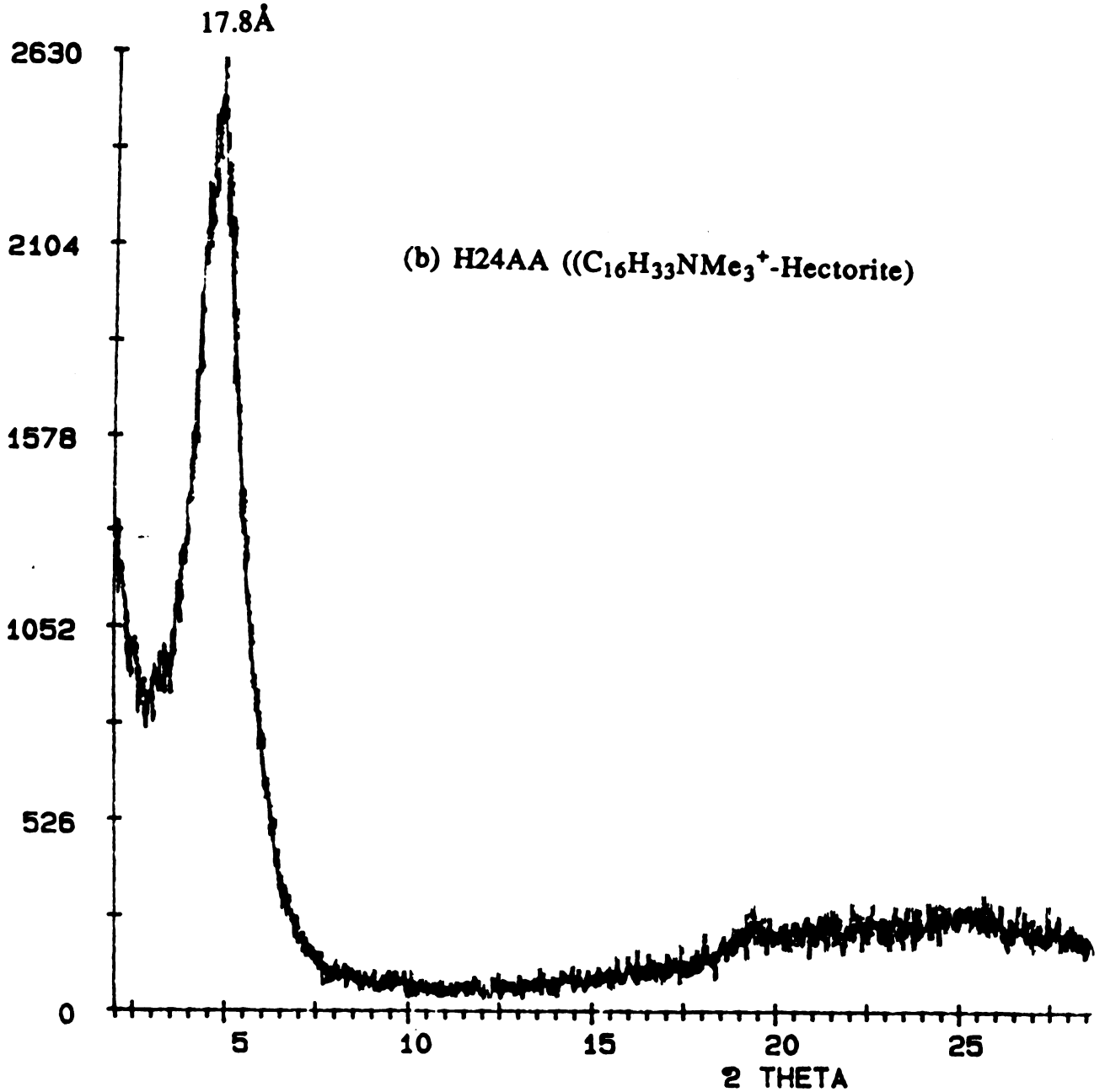
Figure 16 (continued)



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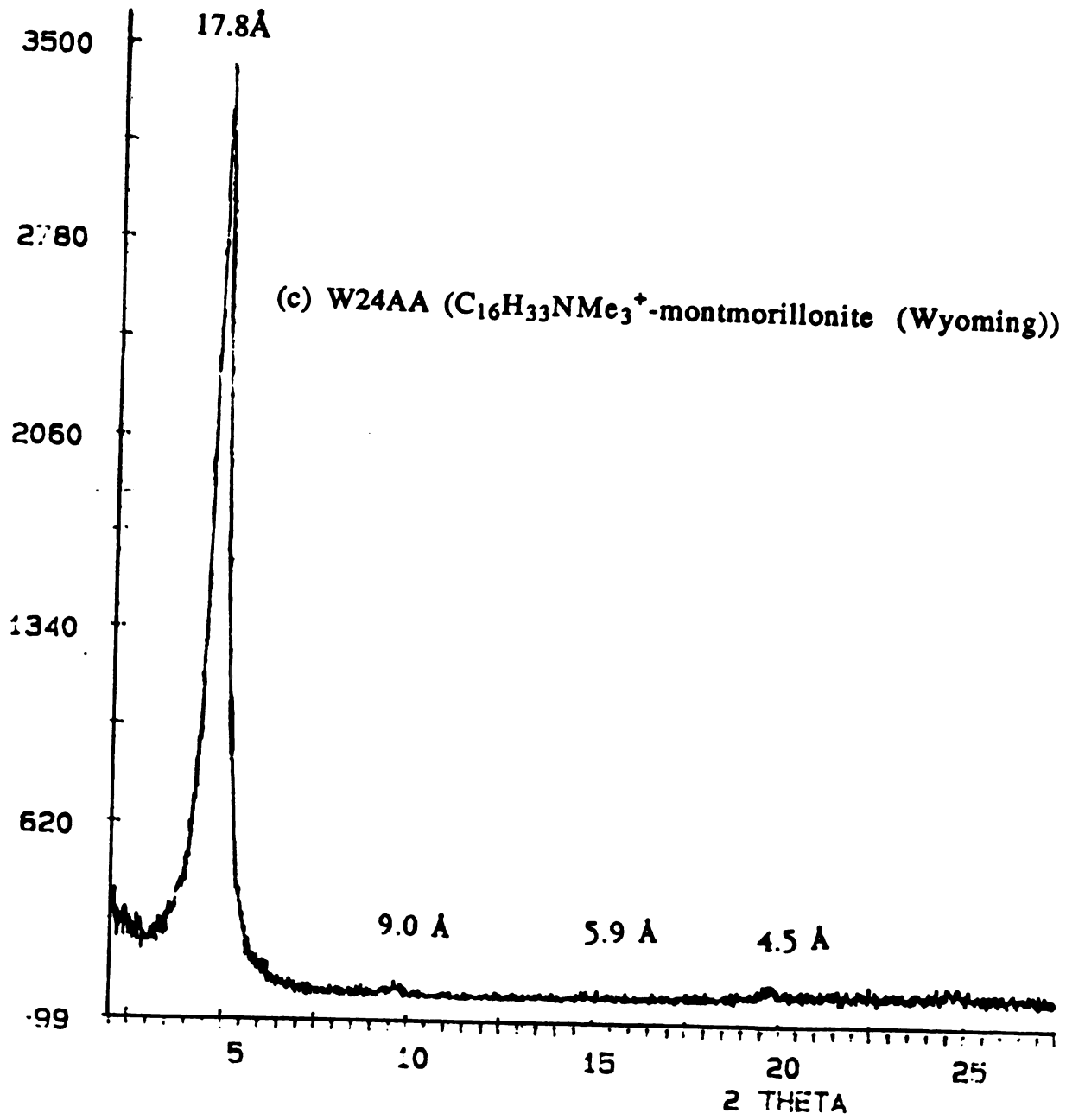

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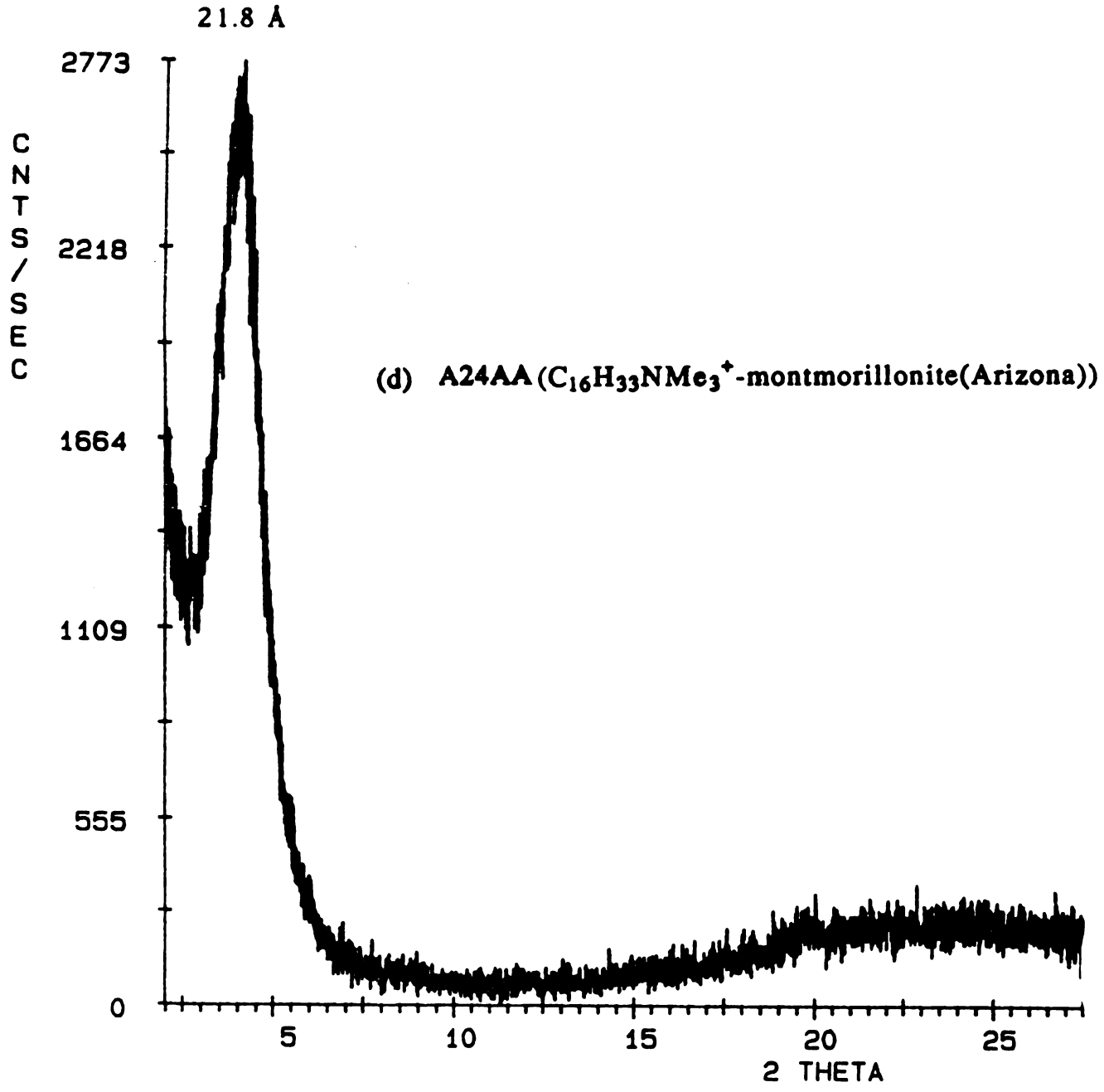

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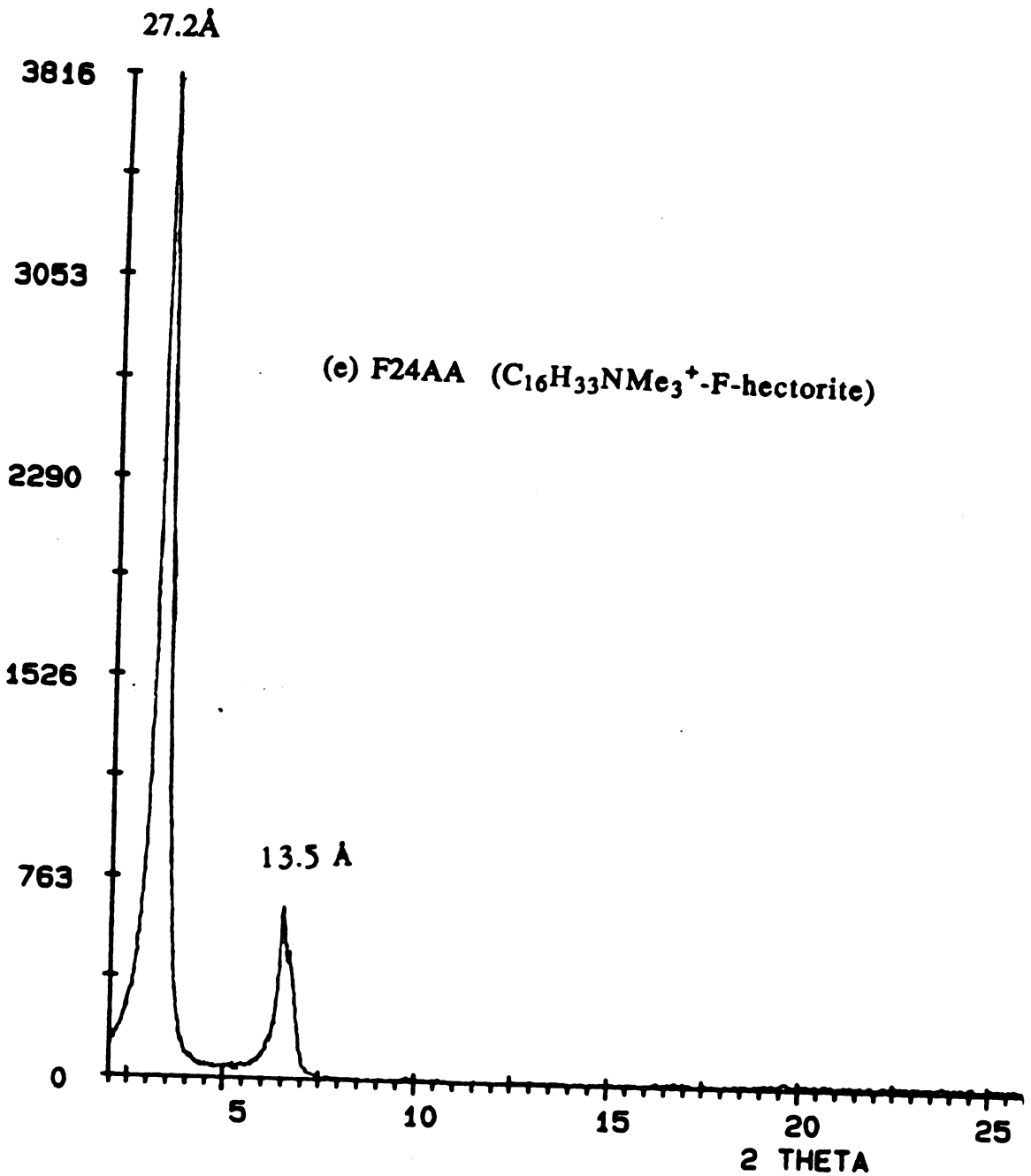

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The synthetic F-hectorite derivatives show better C-axis stacking order than the analogous natural smectite and synthetic laponite derivatives. Laponite derivatives show the poorest crystal size as determined by XRD (Figure 16a). The first order reflection of L24AA is much broader than the those of the other organoclays (Figure 16). From Equation 7, the scattering domain L can be calculated[1]:

$$L = \lambda K/\beta\cos\theta \qquad (7)$$

L is the mean of crystallite dimension in Å along a line normal to the reflection plane, λ is the wavelength of X-ray, K is a constant near unity and β is the width of a reflection at half-height expressed in radians. Values of L are listed in Table 2. Crystallinity is dependent on the particle size of the silicate layers. The surfactant in the clay interlayers can not alter the crystallinity due to the constant particle size of silicate layers. Large particle smectite clays afford small hydrophilic edge surface area and this edge surface area can not be coated by cationic surfactants. Therefore, small particle size smectite clays such as laponite are difficult to convert to an amphiphilic material by intercalation of cationic surfactants.

The orientations of linear cationic surfactants in the interlayer of clays with various layer charge densities have been studied by Lagaly and Weiss[71,72]. Laponite intercalated by surfactants with only one long chain alkyl group (L24AA and L26AA) orient in the gallery with a monolayer arrangement parallel to the surface of the silicate layer (Figure 7a) The external surface of the clay particle should be half-covered by surfactants. The surfactant orientation on the layered silicate surface is significant because it can influence the hydrophobicity of the material. For hectorite and Wyoming montmorillonite

derivatives, (H24AA, H26AA W24AA and W26AA), two surfactant hydrocarbon chains lie parallel to the silicate surfaces of the clay interlayers adopting a lateral bilayer structure (Figure 7b). The external silicate layer of these materials are covered with a monolayer of surfactant so that the surface wettability is totally changed. As the clay layer charge densities increase, pseudo-trimolecular and paraffin-like surfactant structures are obtained. Arizona montmorillonite and rectorite derivatives containing C_{16} chains (A24AA, A26AA, R24AA and R26AA) are suggested to adopt pseudo trimolecular structures (Figure 7c), and the surfactants in organo-F-hectorite (F24AA and F26AA) interlayers are oriented as in paraffin-like structures (Figure 7d). However, the orientation of the surfactants might differ from the above structures if the surfactants contain two long hydrocarbon chains. For instance, the organo laponite (L30AA) with didodecyldimethyl ammonium in the interlayer, the surfactant exhibits a bilayer structure rather than a monolayer structure (Figure 7e). Likewise, a lipid-like surfactant orientation is found in the gallery of F-hectorite (F30AA) and a paraffin-like structure most likely forms on its external surface (Figure. 7f).

3. The Preparation and Structure of Crown Ether Clay Complexes

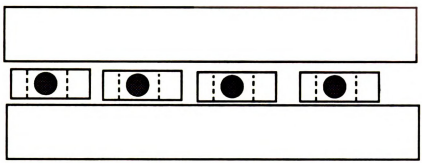
Two crown ethers, 18-crown-6 and dicyclohexano-18crown-6, have been employed as pillars in hectorite and Arizona montmorillonite. The complexes were synthesized by mixing the sodium clay and two times the CEC of crown ether in methanol suspension. The d-spacing are dependent on the smectite clay layer charge density and the structure

Table 3 The d-spacings of crown ether-clay complexes derived from X-Ray diffraction measurement

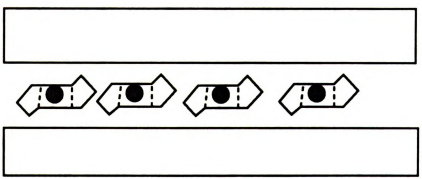
Clay-Crown	Clay Host	Crown Ether	d-spacing
18C6Hect	Na-Hectorite	18-Crown-6	15.6Å
18C6Mont	Na-Mont. (Arizona)	18-Crown-6	17.4Å
Hex18C6Hect	Na-Hectorite	Dicyclohexano18-Crown-6	17.8Å
Hex18C6Mont	Na-Mont. (Arizona)	Dicyclohexano18-Crown-6	19.0Å

Figure 17 The orientations of crown ethers in hectorite and Arizona montmorillonite interlayers. These figures are adapted from E. Ruiz-Hitzky and H. Casal, NATO ASI Series: Chemical Reaction in Organic and Inorganic Constrained Systems, 213 (1986)

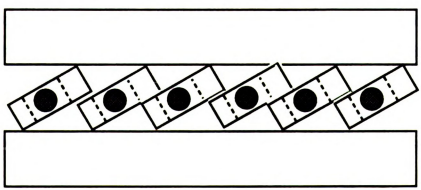
(a) 18-Crown-6 Hectorite



(b) Cyclohexa18-Crown-6 Hectorite and 18-Crown-6 Montmorillonite (Arizona)



(c) Cyclohexa18-Crown-6 Montmorillonite (Arizona)



of the crown ether (Table 3). The orientations of crown ethers in complex clay interlayers have been investigated by Ruiz-Hitzky and Casal[82]. The clay supported crown ether complex, sodium 18C6Hect, has an interlayer distance (gallery height) of close to 4.5 Å, which corresponds to the thickness of the crown ether assuming a planar arrangement of ligand parallel to the silicate surface (Figure 17a). In sodium exchange forms of Hex18C6Hect and 18C6Mont, with d-spacings of 15.6Å and 17.4Å, respectively, a distortion of the crown ethers occurs in order to fill the space of the clay gallery (Figure 17b). The crown ether, dicyclohexano-18-crown-6, in Arizona montmorillonite exhibits a gallery height of 19.0Å. The complex probably adopts a tilted orientation to fit the interlayer distance (17c).

B. The Catalytic Properties of Organoclays

1. Wettabitity and Catalytic Capacities of Organoclays

The cyanation of pentyl bromide (Equation 1) is employed as the probe reaction in which the

$$C_5H_{11}Br + CN^- \text{--------}> C_5H_{11}CN + Br^- \qquad (1)$$

nucleophile, CN^-, was held in ten fold equivalent excess over the organic substrate, $C_5H_{11}Br$, so that the observed rate constant (k_{obs}) could be measured and calculated by Equation 5.

$$-d[C_5H_{11}Br]/dt = k_{obs}[C_5H_{11}Br] \qquad (5)$$

Organo clays that facilitate formation of water and organic emulsions were usually good phase transfer catalysts due to the efficient mixing of the two immiscible liquid phases.

The organo laponites (L24AA and L26AA) containing $C_{16}H_{33}NMe_3^+$ and $C_{16}H_{33}PBu_3^+$, respectively, always show poor

Table 4 The catalytic activities[a] and the colloidal properties of the organoclays and the onium salts as phase transfer catalysts.

Catalyst	Wetting of the clay under reaction conditions	$10^5 x k_{obs}$, sec^{-1}
L24AA	water	0.31
H24AA	emulsion	2.93
H24AB	emulsion	3.07
H24AC	water	0.25
W24AA	emulsion	3.64
A24AA	emulsion	4.07
F24AA	emulsion	4.09
R24AA	Paste in toluene	1.40
L26AA	water	1.10
H26AA	emulsion	12.9
W26AA	emulsion	27.2
A26AA	ion desorption	54.6
F26AA	ion desorption	56.5
R26AA	Paste in toluene	8.20

Continued

Table 4 (Continued)

Catalyst	Wetting of the clay under reaction conditions	$10^5 x k_{obs}$, sec^{-1}
L30AA	partial emulsion	1.96
H30AA	emulsion	2.92
W30AA	emulsion	4.45
A30AA	emulsion	8.39
H18AA	water	2.01
$C_{16}H_{33}NMe_3Br$[b]	emulsion	2.43
$C_{16}H_{33}PBu_3Br$[b]	toluene	62.2
NMe_4Br[b]	toluene	15.6

a. Reaction and wetting conditions: 2.0 mmole pentyl bromide in 6 mL toluene; 20.0 mmole potassium cyanide in 3 mL water; 0.100g organoclay; 90°C.

b Biphase catalyst: The amount of $C_{16}H_{33}NMe_3Br$, $C_{16}H_{33}PBu_3Br$ and NMe_4Br are 0.60, 0.55 and 0.61 mmole respectively.

catalytic activities with k_{obs}' of 0.31 $x10^{-5}$ and $1.10x10^{-5}$ sec^{-1}, respectively, in triphase catalysis (Table 4), owing to inability to form the emulsion. The hydrophobicity of the material can not be effectively enhanced because of the large edge surface area versus the lamellar surface area of the clay. In Table 2, laponite derivatives are seen to exhibit larger surface areas than the other organoclays, resulting from the small particle size of the lamella laponite particles. The surface area receives significant contribution from the particle edge, which can not be covered by the alkyl chains of the surfactants. The incomplete coverage of the basal laponite surface by surfactant (Figure 7a) also results in poor amphiphilic properties. When the interlayer surfactant in hexadecyltrimethyl laponite was replaced by didodecyldimethyl ammonium(L30AA), k_{obs} increased from $0.31x10^{-5}$ to $1.96x10^{-5}$ sec^{-1}, but the improvement was not satisfactory. For the lattice onium ions, the surfactant chains adopt a lateral bilayer structure in the clay interlayer and a monolayer structure on the external clay surface (Figure 7e), so that the external surface is totally covered by surfactant alkyl chains.

As the clay layer charge density increases and the surface area of the organo clay decreases, the triphase catalytic activity of an organoclay increases (Table 4). Hectorite derivatives, H24AA and H26AA, with k_{obs} values of $2.93x10^{-5}$ and $12.9x10^{-5}$ sec^{-1} respectively, facilitate the catalytic reactions more readily than laponite derivatives, L24AA and L26AA, with k_{obs} values of $0.31x10^{-5}$ and $1.10x10^{-5}$ sec^{-1} respectively. For H24AA in which hexadecyltrimethyl ammonium is in the interlayer cation the triphase catalysis rate constant ($2.93x10^{-5}sec^{-1}$) for cyanation is slightly larger than that k_{obs} for the micellar biphase

catalysis when using the same equivalent surfactant, hexadecyltrimethyl ammonium bromide with k_{obs} of 2.43×10^{-5} sec^{-1}. The organo hectorite H26AA with hexadecyltributyl phosphonium as the interlayer onium ion (k_{obs} = 12.9×10^{-5} sec^{-1}) does not perform any better as a triphase catalyst than the corresponding biphase catalyst (k_{obs} = 62.3×10^{-5} sec^{-1}). However, the recyclability and the greater convenience of workup after catalytic reaction more than compensates for the disadvantage of a lower reaction rate. The hectorite derivative with tetrabutyl ammonium in the interlayer (H18AA) is not a good triphase catalyst (k_{obs} = 2.01×10^{-5} sec^{-1}) owing to the instability of this clay to a toluene/water emulsion although tetrabutyl ammonium bromide is a powerful biphase catalyst (k_{obs} = $1.56 \times 10^{-4} sec^{-1}$). This lack of amphiphilic character results from the short alkyl chain in the onium ion and the incomplete coverage of the external hectorite basal surface leading to poor enhancement on the material hydrophobicity. Therefore, the contact area of the two immiscible liquids partitioned by H18AA is much smaller than the emulsion stabilized by the high d-spacing organo hectorite, H24AA and H26AA.

The solvent used for intercalation of the cationic surfactant into the hectorite interlayers also plays an important role in determining the extent of onium ion exchange and, hence, the colloidal and catalytic properties for the organo hectorite. Water and ethanol have high dielectric constants and produce good swellability for the clay silicate layers. This facilitates the interlayer exchange of the metal cations by the cationic surfactants. The d-spacings of organo hectorites, H24AA and H24AB, prepared in water and ethanol, respectively, exhibit no difference in d-spacing (17.8Å) (Table 1). Also, the catalytic capacities

for the two materials are comparable. However, the $C_{16}H_{33}NMe_3^+$ surfactant can not be completely ion-exchanged into the hectorite interlayer using acetone (14.0Å) as the solvent for the intercalation reaction and the d-spacing for the material synthesized in acetone is lower than that of H24AA and H24AB. Therefore, the catalytic capacity of H24AC with k_{obs} $0.25x10^{-5}$ sec^{-1} is very poor. The silicate layer does not swell very well in low dielectric organic solvents.

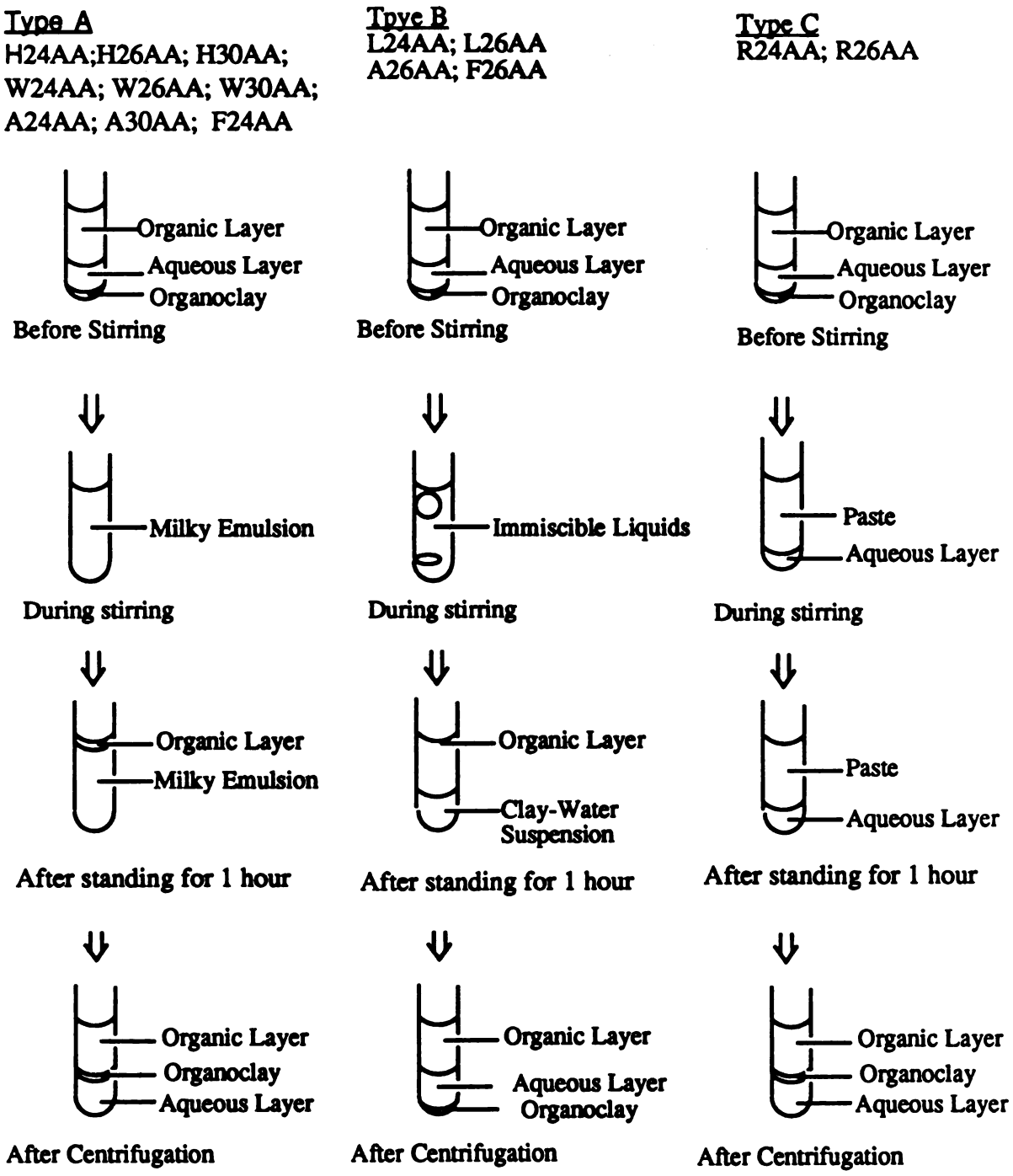
The triphase catalytic reactivities of the organo montmorillonites and F-hectorite, A24AA and F24AA interlayered by hexadecyltrimethyl ammonium are also high (k_{obs} = $4.07x10^{-5}$ and $5.65x10^{-5}$ sec^{-1} respectively). These clays have high layer charge densities. However, F26AA and A26AA do not stabilize emulsion formation even though they show unusually high k_{obs} values. In this case, however, the surfactant is desorbed from the clay hosts. In fact, the observed reaction occurs by biphase catalysis. That is, A26AA and F26AA catalysis occurs by the desorbed and soluble surfactant instead of by solid organoclays.

Although rectorite derivatives, R24AA and R26AA, are also amphiphilic materials, they only form a paste-like gel with the water phase of the triphase catalyst system instead of forming a milk-like emulsion. A paste-like gel retards dynamical stirring during reaction. Thus the catalytic activities for the two rectorite derivatives with k_{obs} $1.40x10^{-5}$ (R24AA) and $8.20x10^{-5}$ sec^{-1} (R26AA) respectively, are not as good as those of the other high layer charge density layered silicate derivatives. The thickness of the rectorite layer (19.0Å) is twice that of smectite layer (9.6Å) because rectorite layer stacking consists of a mica and an expandable smectite sheet[3]. Rectorite particles with a thickness

double that of the corresponding smectite particle may have a lower suspension extent in liquid solution than the smectite particle. Therefore, the rectorite particle aggregated and a paste formed.

The colloidal properties of organoclays for triphase catalysis reactions as listed in Table 1 can be classified into three categories, as shown in Figure 18. The first class of organoclays, designated Type A clays, is amphiphilic and stabilizes emulsions of 3 mL 2.5 N NaCl aqueous and 6 mL toluene solutions (Figure 18a). The density of unsolvated organoclays should be greater than the density of water and toluene. However, when toluene is adsorbed by the amphiphilic organoclay, the density of the organoclays become intermediate between the density of water and toluene. After the amphiphilic clay/water/toluene mixtures are centrifuged, the solid organoclays are located between the aqueous and organic phases (Figure 18a). The second type of the organoclays, designated by Type B in Figure 18b, does not support emulsions of aqueous and organic solutions. Organo F-hectorite undergoes surfactant desorption and organo laponites become suspended in the water liquid phase. Toluene is not adsorbed on the hydrophilic organo laponite or ion exchanged sodium F-hectorite formed by the surfactant desorption. Upon centrifugation, the Type B clay materials collect at the bottom of the two liquid phases shown in Figure 18b. Type C organoclay is unique in rectorite derivatives. A paste is formed in the organic phase which retards dynamic stirring (Figure 18c). Since Type C materials also absorb toluene, these organoclays will be located at the boundary of the aqueous and organic solutions after the mixtures of organo rectorite, toluene and aqueous phases are centrifuged.

Figure 18 Classification of the colloidal behavior of 0.100 g of organoclay in liquid mixtures containing 3 mL of 6.25M potassium cyanide aqueous solution, 6 mL of toluene and 2 mmole of pentylbromide.



2. Dependence of Catalytic Reactivity on the Bulk Reactant Concentration of Liquid Phases

Under triphase reaction condition, the nucleophile and organic substrate are segregated into separate phases. Thus, one or both of the reactants must be adsorbed on the organoclay to interact with each other either at the solid liquid interface or within the solid phase. As described in the Introductory Chapter three different triphase process are possible and are characterized by the three following equations.

$$\text{Rate} = k[\text{organo clay}\cdot RX][CN^-]_{(aq)} \quad (2),$$

$$\text{Rate} = k[\text{organo clay}\cdot CN^-][RX]_{(org)}, \text{ or} \quad (3)$$

$$\text{Rate} = k[\text{organoclay}\cdot CN^- RX] \quad (4)$$

Equation 2 describes the catalytic reaction occurring at the clay-aqueous interface. If the equation holds for the pseudo first order condition, i.e., $[CN^-] >> [RX]$, a pseudo first order rate constant, is designated k_{obs}, is equal to $k[CN^-]$. The observed constant, k_{obs}, was calculated from Equation 5 in which the [RX] value was traced by GLC at different reaction time during the triphase reaction.

$$d[RX]/dt = k_{obs}[RX] \quad (5)$$

then, $\ln[RX]/[RX]_o = -k_{obs}t$

Figure 19a is an example of determining the $-k_{obs}$ value by finding the slope of $\ln[RX]/[RX]_o$ against the reaction time, t. The observed rate constant, k_{obs}, is proportional to the bulk cyanide concentration if the triphase reaction occurs at catalyst aqueous interface.

For this assumption, four aliquots of cyanide solution with 5, 10, 15 and 20 mmole in 3 mL aqueous solution versus 2 mmole of pentyl bromide in 6 mL of toluene were prepared. According to Lin's investigation[95], k_{obs} is linear to [CN^-] (Figure 20a), indicating that equation 2 is an appropriate description of the reaction rate under pseudo first order rate condition and the catalytic reaction are suggested to occur at the catalyst-aqueous boundary. For polymer supported phase transfer catalysts, the catalytic reactivity is insensitive to the bulk concentration of cyanide[43]. Organoclay triphase catalysis reactions are carried out in different reaction environment from the polymer supported triphase catalysis.

If the condition for organoclay phase transfer catalysis are first order in electrophile (Equation 5) by varying pentyl bromide from 5 to 20 mmole in 6 mL organic phase which keeping cyanide constant at 2 mmole in 3 milliliter of aqueous solution, the k_{obs}' was not linear with the concentration of [RX] (Figure 20b). This pesudo orer rate constant, k'_{obs}, is derived from Equation 6.

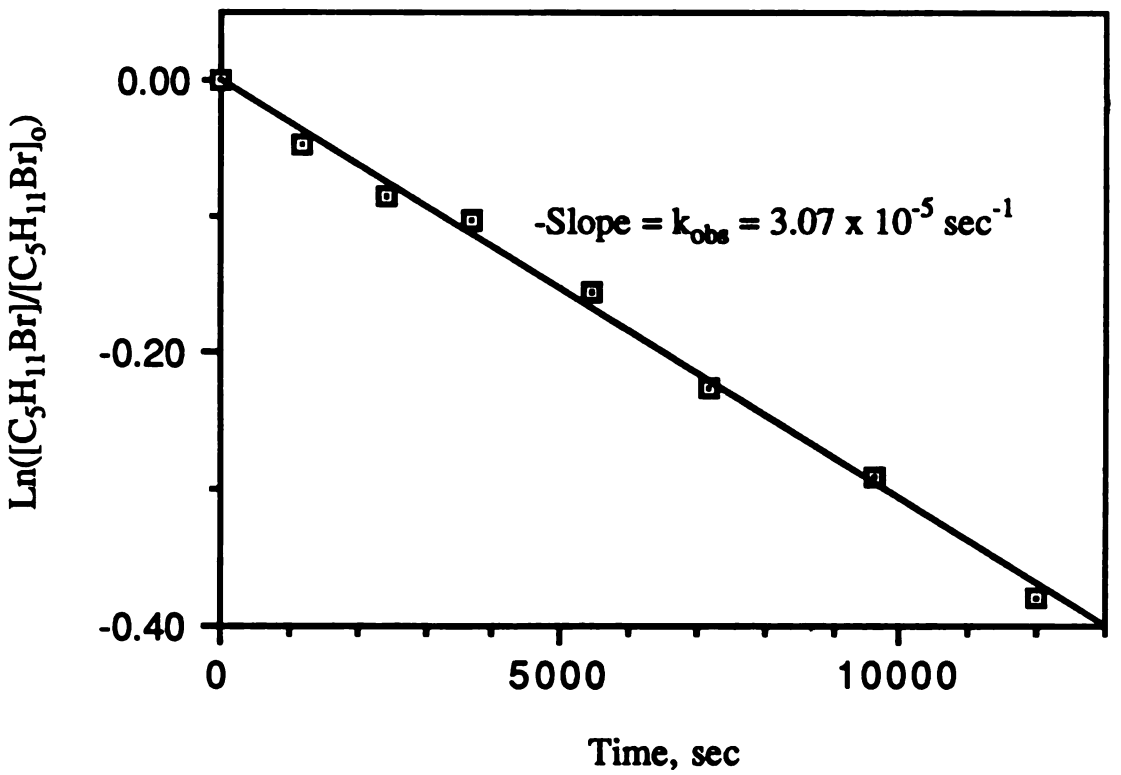
$$d[CN^-]/dt = k_{obs}'[CN^-] \qquad (6)$$

Then, $Ln([CN^-]/[CN^-]_o) = k_{obs}'t$

or, $Ln((2-[C_5H_{11}CN])/2) = k_{obs}'t$

where the [$C_5H_{11}CN$] designates the miniequivalent of $C_5H_{11}CN$.

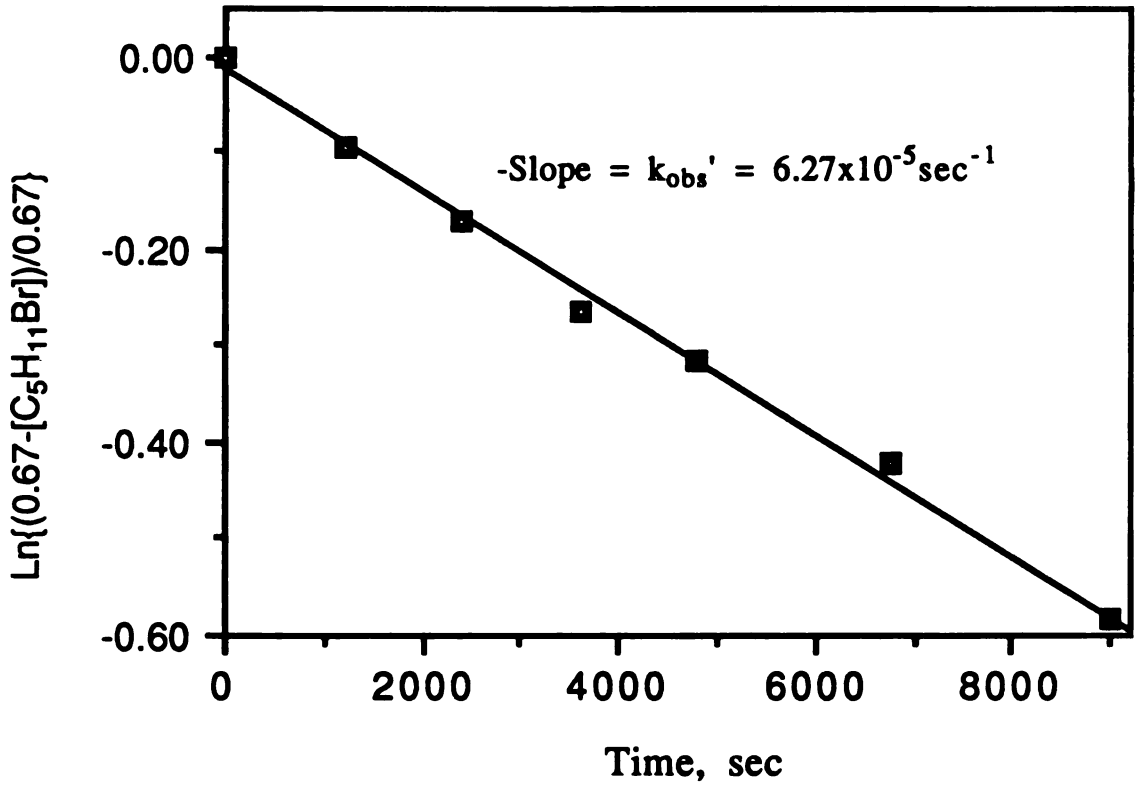
Figure 19 (a) Determination of a k_{obs} from the slope of a plot of $[C_5H_{11}Br]/[C_5H_{11}Br]_o$ versus reaction time in the presence of 0.100 g $C_{16}H_{33}NMe_3$hectorite.



The initial concentration of CN^- was 20 mmole in 3 mL aqueous solution and $[C_5H_{11}Br]$ was 2 mmole in 6 mL toluene solution. The equivalent of the CN^- was ten times that of $C_5H_{11}Br$, that was recognized that the nucleophile, CN^-, was far more than electroophile, $C_5H_{11}Br$. Thus, the observed rate constant was first order in $[C_5H_{11}Br]$ and the kinetic equation was represented by $d[C_5H_{11}Br]/dt = -k_{obs}[C_5H_{11}Br]$. Therefore,$k_{obs}$ could be derived from $\ln([C_5H_{11}Br]/[C_5H_{11}Br]_o) = -k_{obs}t$.

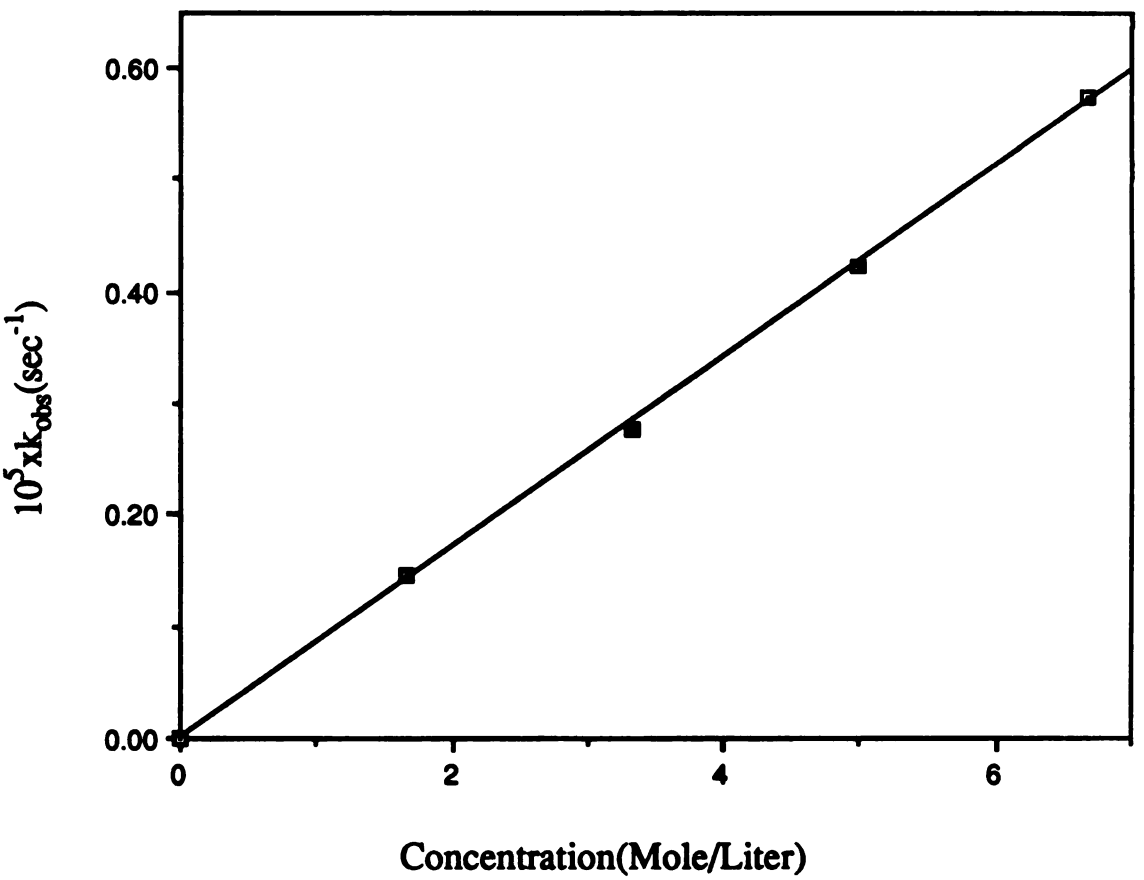
Figure 19 (Continued)

(b) Determination of a k_{obs}' from the slope of a plot of $[CN^-]/[CN]_0$ against reaction time in the presence of 0.100g $C_{16}H_{33}PBu_3$hectorite (H26AA) .



The initial concentration of CN^- was 2 mmole in 3 mL aqueous solution and $[C_5H_{11}Br]$ was 10 mmole in 6 mL toluene solution. The equivalent of the $C_5H_{11}Br$ was five times that of CN^-. Thus, the reaction was first order in the concentration of the nucleophile $[CN^-]$ and the kinetic equation was represented by $d[CN^-]/dt = k_{obs}'t$. Then the observed rate constant (k_{obs}') could be derived from $\ln([CN^-]/ [CN^-]_o) = -k_{obs}'t$. The depletion of CN^- was equal to the production of $C_5H_{11}CN$, which could be analyzed by GLC. The equivalent of CN^- was equal to (2 - $C_5H_{11}CN$).

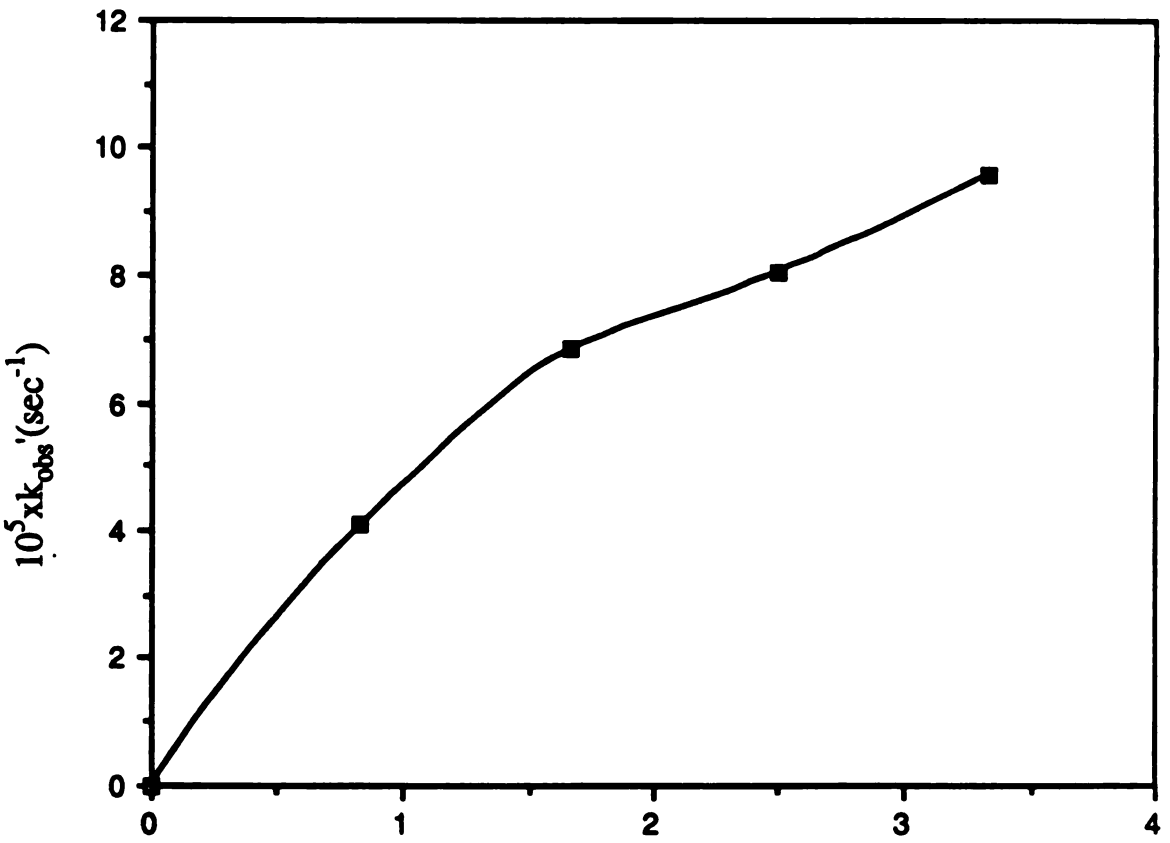
Figure 20 (a) Dependence of the observed rate constant (k_{obs}) on nucleophile concentration for the cyanation reaction (Equation 1) at 90°C in the presence of 0.100 g $C_{16}H_{33}PBu_3$hectorite (H26AA) as the triphase catalyst.



The pseudo order rate constant k_{obs} was determined under conditions when the reactant is first order in electrophile; i.e., the nucleophile concentraction was much larger than the organic electrophile concentration, which was kept at 0.33M in toluene.

Figure 20 (continued)

(b)Dependence of the observed rate constant (k_{obs}') on the organic electrophile concentration for the reaction at 90°C in the presence of 0.100 g $C_{16}H_{33}PBu_3$hectorite as the triphase catalyst.



The pseudo first order rate constant k_{obs}' was determined under conditions when the reaction is first order in nucleophile. That is, the electrophile concentration was far larger than the nucleophile concentration, which was kept at only 0.67 M in aqueous solution.

Figure 19b is an example of determining k_{obs}' from the slope of a plot of ln((0.67-[$C_5H_{11}CN$])/0.67) against reaction time, t. This result demonstrates that the mechanism represented by Equation 2 does not hold. This behavior is explained by a model in which the organic electrophile is initially adsorbed on the boundary of the clay and the organic solution and then the clay is transferred to the aqueous phase to react with the nucleophile in the aqueous solution. The catalytic reaction rate depends on the nucleophile bulk concentration and the surface concentration of the organic electrophile on the organoclay (Equation 2). The surface concentration of adsorbed pentyl bromide on the clay may be increased by increasing the bulk electrophile concentration, but the adsorption relation is not linear. Consequently, the k_{obs}' curve in Figure 19b is not a straight line.

3. Dependence of Organoclay Catalytic Reactivity on the Polarity of the Organic Solvent

The solvent polarity dependence of organoclay triphase catalysis can also afford information on the catalytic reaction mechanism. Lin has investigated the influence of polarity on the cyanation reaction by using $C_{16}H_{33}PBu_3^+$hectorite as the catalyst[95]. Organic solvents of lower polarity result in higher catalytic reactivity for the organoclay triphase catalysis. In contrast, Montanari, et al.[61,62] using polystyrene-supported phosphonium bromide as a triphase catalyst, found that higher polarity organic solvents led to higher iodination reaction rates. The organo hectorite, H26AA, when used for iodination (Equation 7), exhibits a reactivity dependence on the solvent polarity which is opposite that derived for polymer supported catalysts. The data in Table 5 indicate that with H26AA as the triphase catalyst solvents of low

polarity produce high reactivity for the iodination of pentyl bromide. If the onium ion is supported in

$$C_5H_{11}Br + I^- \text{-----> } C_5H_{11}I + Br^- \qquad (7)$$

inorganic matrices such as SiO_2 or Al_2O_3, the reactivity of cyanation increases with decreasing polarity of the organic solvents[47,49]. The dependence of solvent polarity on the inorganic based triphase catalysts parallels that of organoclays. Because of the good swellability of the polymer-based catalysts in polar organic solvents, anionic nucleophiles are carried more easily to the ionic center of the polymer. Consequently, nucleophilic substitution reactions proceed easily in the polar organic medium. While organoclays swellability increases with organic solvent polarities, catalytic reactivity under the triphase catalysis does not improve. This is because the reaction site for an organoclay triphase catalysis is not located in the organic medium. Organoclays as catalysts for nucleophilic substitution reactions require pre-adsorption of the organic electrophiles on the organoclay surfaces. Highly polar organic solvents exhibit strong affinity for organic reactants. Also, adsorption of organic electrophiles on the organoclay is retarded by competitive adsorption of the polar organic solvent. Thus, the surface concentration of organic reactants will be lowered by increasing the polarity of the organic solvent and the catalytic reactivity of organo clays for triphase catalysis will decrease.

Table 5 Solvent effect on k_{obs} for the iodonation reaction of pentyl bromide (Equation 8) under condition with pseudo first order in nucleophile

Catalyst	Solvent	$10^4 k_{obs}$, sec^{-1}
H26AA	o-Dichlorobenzene	0.81
H26AA	Toluene	1.29
H26AA	Decane	3.42

Reaction condition: 8 mmole of potassium iodide; 2 mmole of pentyl bromide; 0.15 g decane as internal standard; 3 ml water and 6 mL organic solvent; 0.100g of H26AA; 90°C

4. Dependence of O/C Alkylation on Biphase and Triphase Catalysts

There are two possible products for the alkylation of naphthoxide by benzyl bromide[65,68] as shown in Figure 7. In protic solvents such as water, trifluoroacetic acid, methanol or ethanol, the C-alkylation product is predominant. C-alkylation is favored in protic solvents because the enolate of the C-alkylation precursor has an carbonyl group as shown in Figure 7 which can be stabilized by hydrogen bonding between the solvent and the intermediate anionic complex, whereas the negative charge is not favored to locate on the low electroaffinitive carbon. On the other hand, the O-alkylation product is favored in aprotic solvents, such as toluene, benzene, DMF, DMSO and dichloromethane. The enolate resonance structure of the O-alkylation precursor is energetically stable because the negative charge is located on the high electroaffinitive oxygen. Since the aprotic solvent can not form a hydrogen bond with the hydroxy group of the potential intermediate, the intermediate favors the energetically stable form which will result in the O-alkylation product. The ratio of the two alkylation products in a triphase catalysis system can provide information about the location of the reaction.

As shown in Table 6, the major products for the alkylation of naphthoxide by benzyl bromide with organo hectorites (H26AA and H24AA) as catalysts are C-alkylated derivatives. This suggests that the catalytic reaction occurs in the aqueous environment. In contrast to organoclays, nucleophilic substitution reactions for polymer supported

Table 6 The product ratios of the O/C alkylation reaction[a] of sodium naphthoxide with benzyl bromide when organoclays and onium salts were used as the phase transfer catalysts

Catalyst	Solvent	% of O-alkylation[b]	% of C-alkylation[b]	k_{obs} for depletion of benzyl bromide[c]
H26AA	benzene	17.8	82.2	
$C_{16}H_{33}PBu_3Br$	benzene	42.9	57.1	
H26AA	CH_2Cl_2	48.9	51.1	
$C_{16}H_{33}PBu_3Br$	CH_2Cl_2	83.7	17.3	
$C_{16}H_{33}NMe_3Br$	benzene	59.7	40.3	$5.79 \times 10^{-5} sec^{-1}$
H24AA	benzene	20.7	79.3	$1.89 \times 10^{-5} sec^{-1}$
$C_{16}H_{33}NMe_3Br$	CH_2Cl_2	71.8	28.2	$8.88 \times 10^{-5} sec^{-1}$
H24AA	CH_2Cl_2	22.4	77.6	$1.57 \times 10^{-5} sec^{-1}$

a. Reaction conditions: 2 mmole of benzyl bromide in 5 ml organic solution; 3 mmole of sodium naphthoxide in 5 ml of water; 0.24 mmole of catalyst; 25°C, 4 hour reaction time.
b. The O/C alkylation ratios were determined by ^1H NMR.
c. The depletion k_{obs} constants of benzyl bromide were determined by monitoring the integration ratios of benzyl bromide and the internal standard (decane) by GLC.

catalysts proceed in organic instead of aqueous medium[61,63,64]. For alkylations with $C_{16}H_{33}NMe_3Br$ and $C_{16}H_{33}PBu_3Br$ as the biphase catalysts, O-alkylation process dominates the reactions (Table 6), since the biphase catalyst carries the nucleophile from the aqueous phase to the organic phase where the nucleophilic substitution reaction occurs. The O-alkylation percentage of the biphase catalysis is sensitive to organic solvent polarity. The ion pair of the O-alkylation intermediate and onium ion in polar organic solvents such as methylene chloride shows greater solubility than in less polar solvents such as benzene. The results is a higher O-alkylation percentage in methylene chloride (72%) than in benzene (60%) when $C_{16}H_{33}NMe_3Br$ is the biphase catalyst. However, for organo clay triphase catalysis, the O/C alkylation ratios are not significantly influenced by the polarity of organic solvent as determined by $C_{16}H_{33}NMe_3^+$hectorite (H24AA) as triphase catalyst. The O-alkylation percentages using H24AA as catalyst are 21% and 22% in benzene and methylene, respectively. For $C_{16}H_{33}PBu_3^+$hectorite (H26AA) as the triphase catalyst, the O-alkylation yield is high when reacted in methylene chloride (49%) but low when in benzene (18%).

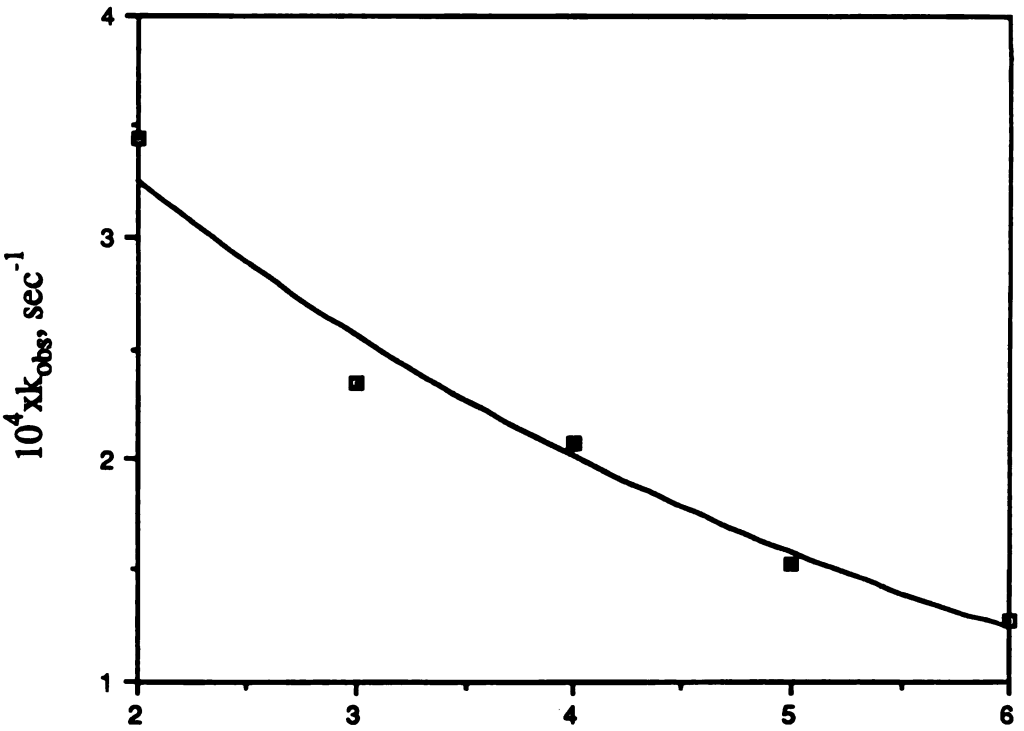
Organoclays afford predominate by C-alkylation. This result is very unusual. Organoclays provide a unique selectivity for reaction products which can only be rationalized if the reaction occurs at the clay-aqueous interface.

5. The Dependence of Organoclay Catalytic Reactivity on the Volume of the two Liquid Phases

A stirred mixture of the organoclay, aqueous and organic solutions forms a water in oil emulsion. Organo hectorite is homogeneously distributed in the emulsion and the water droplets are incorporated into the organic phase. When the volume of water is more than needed for an emulsion, a clear aqueous phase appears in the triphase system. A typical emulsion of 6 mL of organic liquid, 3 mL aqueous solution and 0.1g organo hectorite formed by stirring is milky white in appearance and no excess organic phase or aqueous phase is evidenced. A small excess organic liquid segregates from the emulsion when the mixture is allowed to remain for more than five minutes. As the volume of aqueous phase is increased higher than 3 mL and the volume of organic solution phase is decreased lower than 6 mL, a clear aqueous solution phase can be observed during stirring. The excess aqueous solution can not be incorporated into the emulsion of supported organo hectorite in the organic phase.

Since the triphase system is a water-in-oil emulsion, a part of the aqueous phase does not participate the emulsion system. The activity of an organoclay triphase catalysis is only influenced by the volume of organic solution and not affected by the volume of aqueous solution (Figure 21). The catalytic activity decreases when the volume of the organic phase is increased while the concentration of reactants, as the total volume of aqueous and organic solution and the amount of organoclay catalyst, H26AA were kept constant (Figure 21a). Based on the same amount of organoclay catalyst, increasing the volume of the

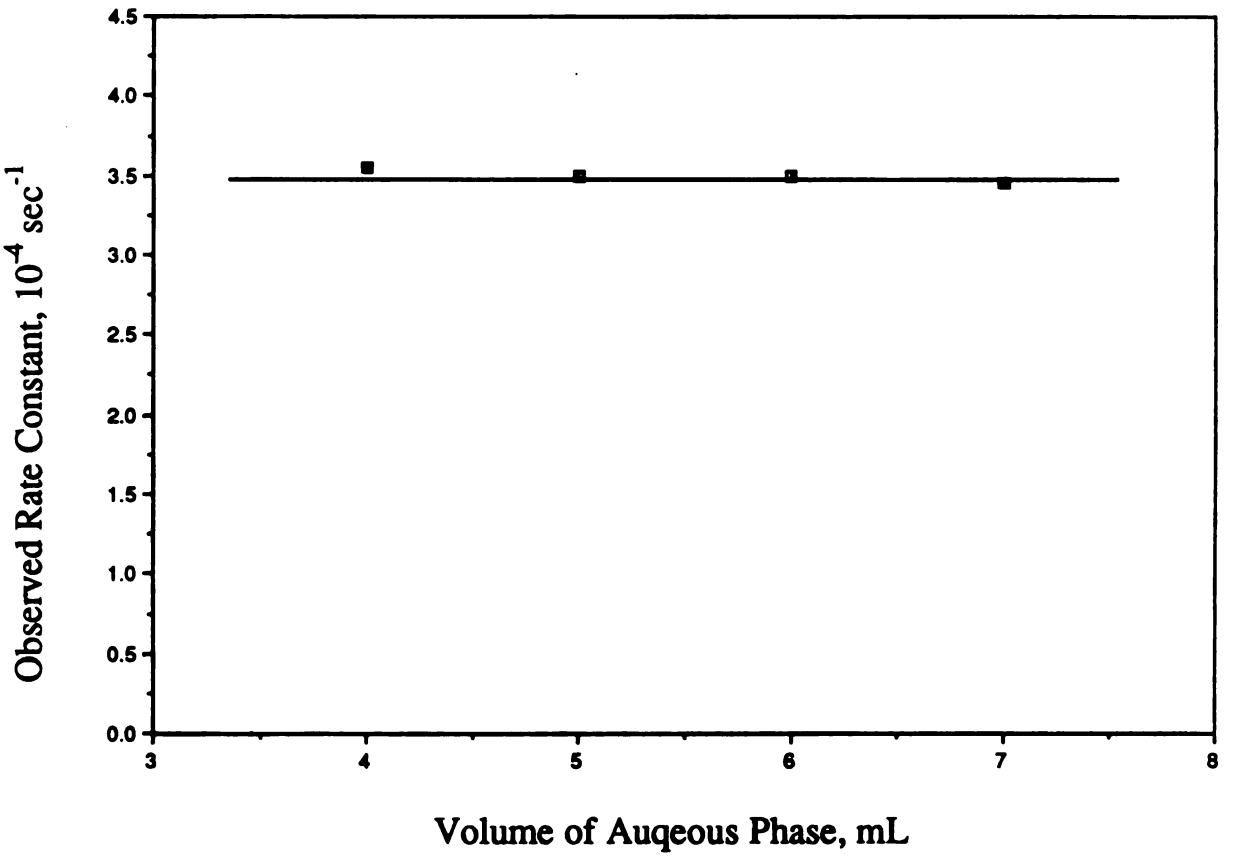
Figure 21 (a) The dependence of k_{obs} on the volume of toluene for the reaction of pentylbromide with KCN.



Reaction was carried out under a condition that was pseudo first order in electrophile. The total volume of organic and aqueous phase was 9 mL. The concentration of cyanide in aqueous solution was 6.25 M and the pentyl bromide concentration was 0.33 M in toluene.

Figure 21 (Continued)

(b) The observed rate plotted against the volume of aqueous solution while the volume of toluene solution was kept constant at 2 mL.



Reaction was carried out under a condition that was pseudo first order in electrophile. The concentration of cyanide in aqueous solution was 6.25 M and the pentyl bromide concentration was 0.33 M in toluene.

organic phase will decrease the suspended catalyst concentration in the organic solution. Thus, a low efficiency of adsorbing organic reactants on organoclay results in low catalytic reactivity when the volume of the organic phase is increased. However, when the volume of organic phase is kept constant, the catalytic reactivity is not apparently changed by changing the volume of aqueous solution (Figure 21b). Since only a certain amount of aqueous solution can be incorporated into the emulsion, the excess aqueous phase which can not be incorporated into the emulsion does not participate in the organoclay triphase catalysis. Therefore, the reactivity is not influenced by the volume of aqueous solution if the concentration of the nucleophile, CN^-, is kept constant.

6. Organoclay Catalytic Reaction in the Absence of Water.

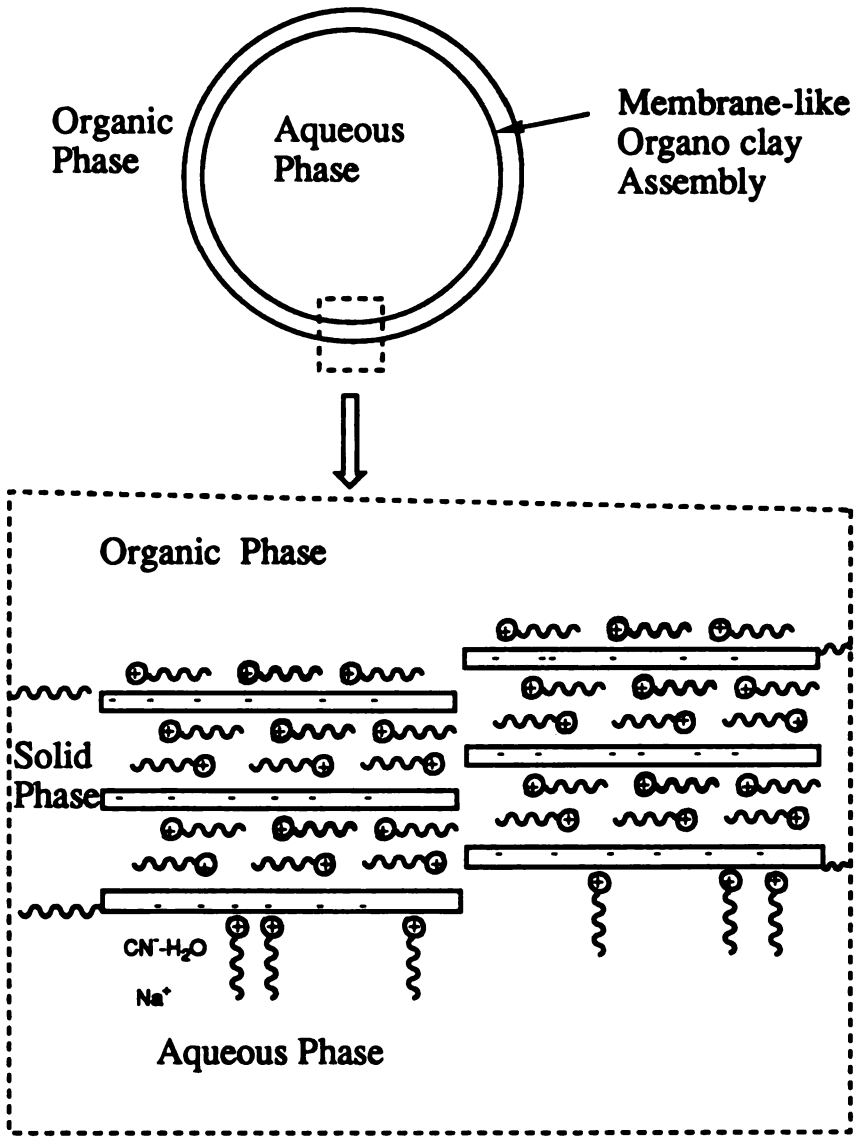
Nucleophilic substitution reactions are not catalyzed by the organoclay H26AA in the absence of water. For the cyanation of pentyl bromide, potassium cyanide can not be transferred by the organoclay from the solid phase into the toluene solution to react with the organic reactant. Potassium cyanide is hydrophilic, but it can be suspended in the organic solution. However, a phase transfer catalysis reaction is known to occur in the absence of water when a polymer supported catalyst or an onium salt is employed as the phase transfer catalyst[62,99]. A polymer supported catalyst can transfer the nucleophile by ion-exchanging the anion on the polymer-attached onium group. This onium-nucleophile ionic pair is accessible to the electrophile in organic solution for nucleophilic substitution reaction. An organoclay does not have an ionic center for ion-exchange reaction with a nucleophile. Instead, the organoclay facilitates the nucleophilic substitution by forming an emulsion mixture of aqueous and organic solution. The

nucleophile can not be transferred from the solid state into the organoclay. Therefore, if the nucleophile can not be dissolved in the liquid solution of the phase transfer catalysis reaction, catalytic reaction can not proceed. Consequently, water is required for catalytic nucleophilic substitution reactions in the presence of organoclay.

7. Mechanism of the Organoclay Triphase Catalysis

The assembly of an organoclay emulsion is the decisive factor for the efficient triphase catalysis. Levine and Spence and co-workers[100,101] have investigated emulsions of organic and aqueous solution stabilized by fine clay particles containing adsorbed surfactant. In our organoclay triphase catalysis reaction system, the organoclays act as an emulsifier to minimize the particle size of the dispersion droplet (Figure 22). At the aqueous interface, the onium surfactant orient vertically on the surface to explore the hydrophilic silicate surface and increase hydrophilic interaction[102]. At the organic liquid catalyst boundary, the surfactant may orient horizontally on the silicate surface to shield the polar clay surface and maintain the hydrophobicity of the material surface. For the purpose of forming an emulsion, the organo clay should have a high layer charge density and be interlayered by an onium ion with at least one long alkyl chain. Therefore, the inherent hydrophilic layered silicate will be modified to an amphiphilic material. Hectorite derivatives (H24AA and H26AA) with long chain alkyl ammonium can form emulsions and are good triphase catalysts.

Figure 22 The emulsion of aqueous and organic solutions stabilized by an amphiphilic organo hectorite.

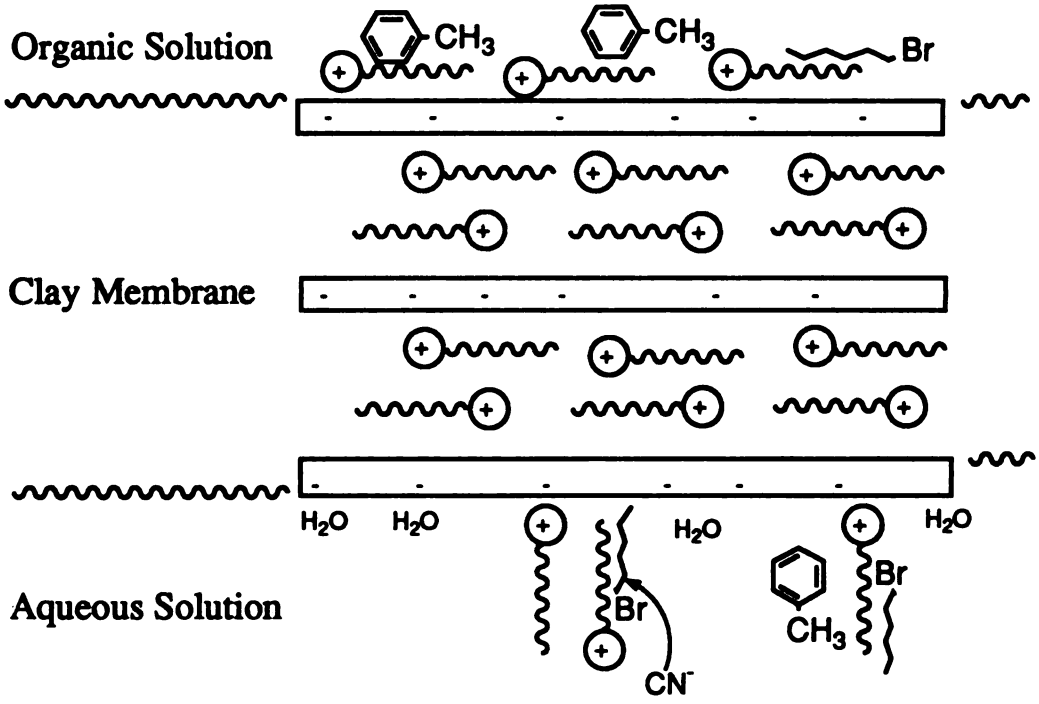


However, not all organoclays are efficient triphase catalysts. Hectorite derivative, H18AA, with tetrabutyl ammonium in the interlayer, fails to form an emulsion and is a poor triphase catalyst. The onium ion in this case fails to shield the clay surface for wetting by the organic phase. Laponite derivatives do not form emulsions due to the low layer charge density of the layer silicate, which limits adsorption of onium ion on the silicate surface and the degree of hydrophobicity. Also, the inherently small particle size of laponite affords a large edge surface area which can not be covered by the hydrophobic surfactant tail, and this also contributes to the hydrophilicity of the surface.

The mechanism of efficient triphase catalysis by organo hectorites (H24AA and H26AA) as triphase catalysts is elucidated by the solvent effect and the dependence on reactant concentrations. Also, the experiment on O/C alkylation and the study of the volume ratio of the two liquid phases provides mechanistic information for the organoclay triphase catalysis reaction. All these results suggest that the reaction occurs at the clay-aqueous liquid boundary. Figure 23 shows the proposed mechanism for nucleophilic substitution reaction by organo hectorites as triphase catalysts. An organo hectorite particle which stabilizes the organic-aqueous emulsion is a part of the assembled organo clays. They behave as emulsifiers, or better, as membranes between the aqueous and organic phases. The catalyst swellability in organic solvents is not a significant factor for catalytic reactivity.

Figure 23 The mechanism of the triphase catalysis reaction with organo hectorites as the catalysts.

Binding of RX occurs at the clay-organic interface.



Nucleophilic attack occurs at the clay-aqueous interface.

However, the adsorption of organic electrophile on the organo clay surfaces and the concentration of anionic nucleophile in aqueous solution are the two most important factors for the catalytic reactivity of nucleophilic substitution reaction.

Asorption of the organic molecule is occurring at the organic-aqueous interface. Solvents of low polarity produce high adsorption of the organic electrophile. Thus, the surface concentration of organic reactant is high and the catalytic reaction is more efficient when non-polar organic solvents are used in the triphase catalysis system. The nucleophilic substitution reaction occurs at the boundary of the catalyst and the aqueous solution. The nucleophile in the aqueous solution is directly reacting with the organic electrophile which has been adsorbed on the organoclay surface, since the reaction rate is proportional to the bulk concentration of the nucleophile in the aqueous solution.

C. The Longevity of Organoclays for Triphase Catalysis

1. Recyclability of Organoclays as Triphase Catalysts

The structural stability and catalytic recyclability of organoclays for TPC are dependent on the layer charge densities of the silicate layer hosts, and on the solubilities of the ion-pair formed between nucleophile anions and surfactant cations in the organic solvents. In order to study stability and catalytic recyclability, organoclays containing either $C_{16}H_{33}NMe_3^+$ or $C_{16}H_{33}PBu_3^+$ as the intercalated cations were employed as the catalysts.

The hectorite derivative, H26AA, containing the interlayer $C_{16}H_{33}PBu_3^+$ cation shows excellent recyclability for triphase catalysis (Figure 24). Another hectorite derivative, H24AA, with $C_{16}H_{33}NMe_3^+$ gallery cation shows fair catalytic recyclability (Figure 25) for the probe cyanation reaction (Equation 1). After 10 cycles of cyanation reaction, in which the total reaction time was 30 hours and the reaction temperature 90°C, both of the hectorite derivatives retained their d-spacings, as judged by the XRD. The loss of catalytic activity after use for vigorous cyanation reaction was approximately 10% and 55% for H26AA and H24AA respectively. The catalysts were recycled by simple filtration and resuspension in fresh reaction mixture. This recycle procedure could result in incomplete recovery of the solid catalyst and an apparent loss of reactivity. The loss of the catalytic reactivity of H26AA is most likely due to incomplete catalyst recovery by the filtration procedure. However, the 55% loss in activity for H24AA

Figure 24 The recyclability of $C_{16}H_{33}PBu_3^+$hectorite (H26AA) over 10 reaction cycles for the cyanation of pentyl bromide at 90°C.
Reaction conditions for each cycle were the same as those described in Figure 19a.

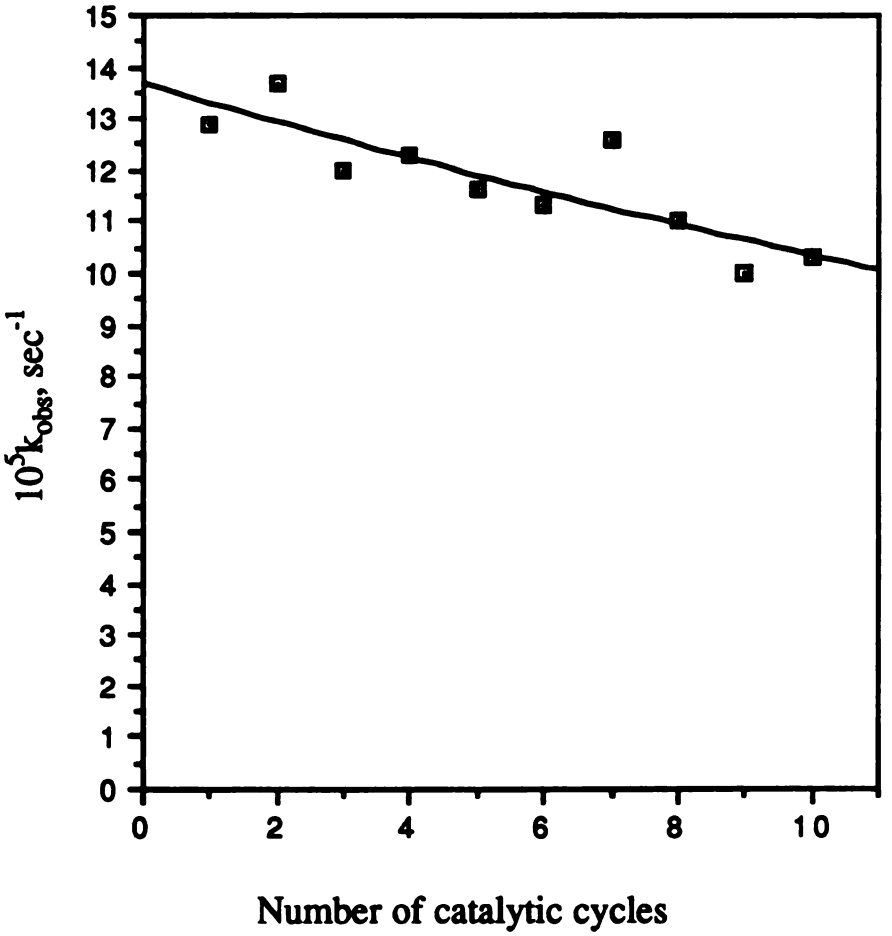
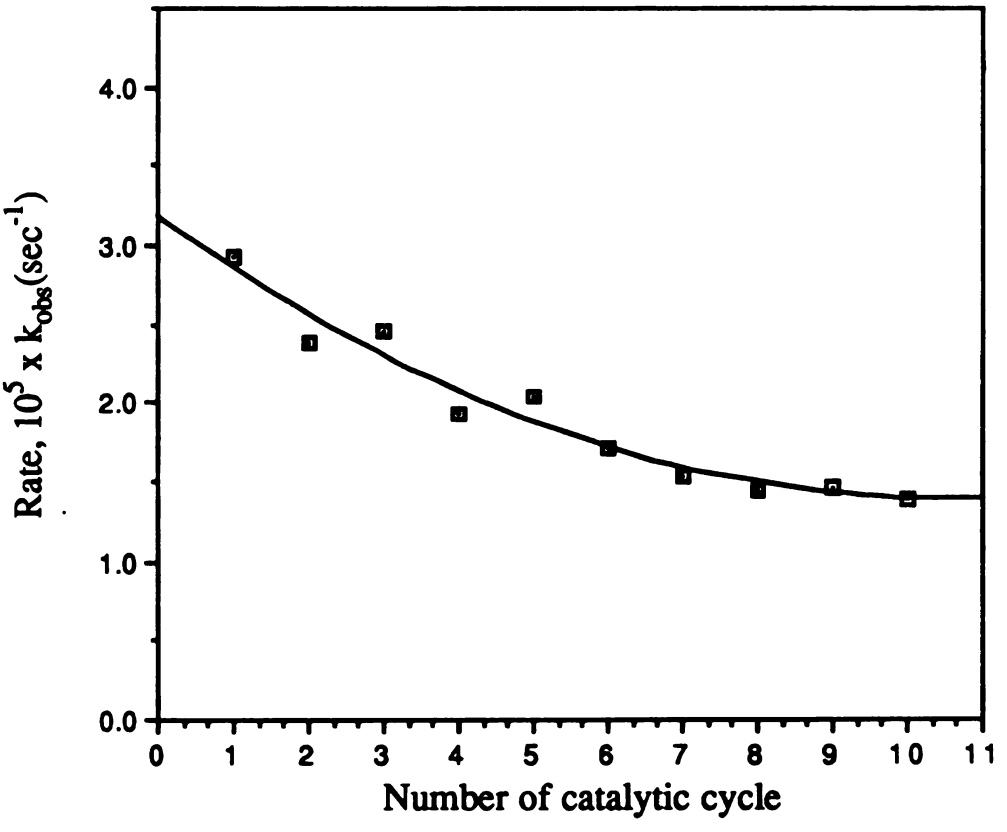


Figure 25 The recyclability of $C_{16}H_{33}NMe_3^+$hectorite (H24AA) over 10 reaction cycles for the cyanation of pentyl bromide at 90°C.
Reaction conditions for each cycle were the same as those described in Figure 19a.



after 10 reaction cycles can not be due to loss of catalyst by the filtration.

Quaternary ammonium ions may undergo Hoffmann elimination, the result of which is production of trialkyl amines and alkenes in strongly alkaline solution[42]. For example, the interlayer surfactant, $C_{16}H_{33}NMe_3^+$, which contains b-hydrogens may decompose into an amine and alkene in the basic solution at elevated temperature[85-87].

The structural stability of the extremely high layer charge density onium ion F-hectorite derivative F26AA, in which the surfactant adopts a paraffin-like structure, is almost negligible. More than 98% of the catalytic capacity is lost after one reaction cycle (Table 7). The X-ray pattern shows the catalyst is transformed to the potassium form of F-hectorite, an indication that the surfactant does not remain bound to the clay host. For $C_{16}H_{33}NMe_3^+$-F-hectorite F24AA which adopts a paraffin-like structure in the interlayer, the catalytic recyclability is satisfactory (Figure 26) but the solid catalyst is converted to a mixture of potassium F-hectorite and an interstratified form of F-hectorite in which the gallery are alternately occupied by potassium and surfactant cations. This regularly interstratified form of F-hectorite will be discussed in the later section. The difference in recyclability between F26AA and F24AA is due to the nature of the surfactants themselves. The carbon-rich surfactant, $C_{16}H_{33}PBu_3^+$ dissolves into the liquid phase but the other surfactant, $C_{16}H_{33}NMe_3^+$ remains intercalated in the silicate host. This desorption mechanism will be discussed in more detail in the section D.3.

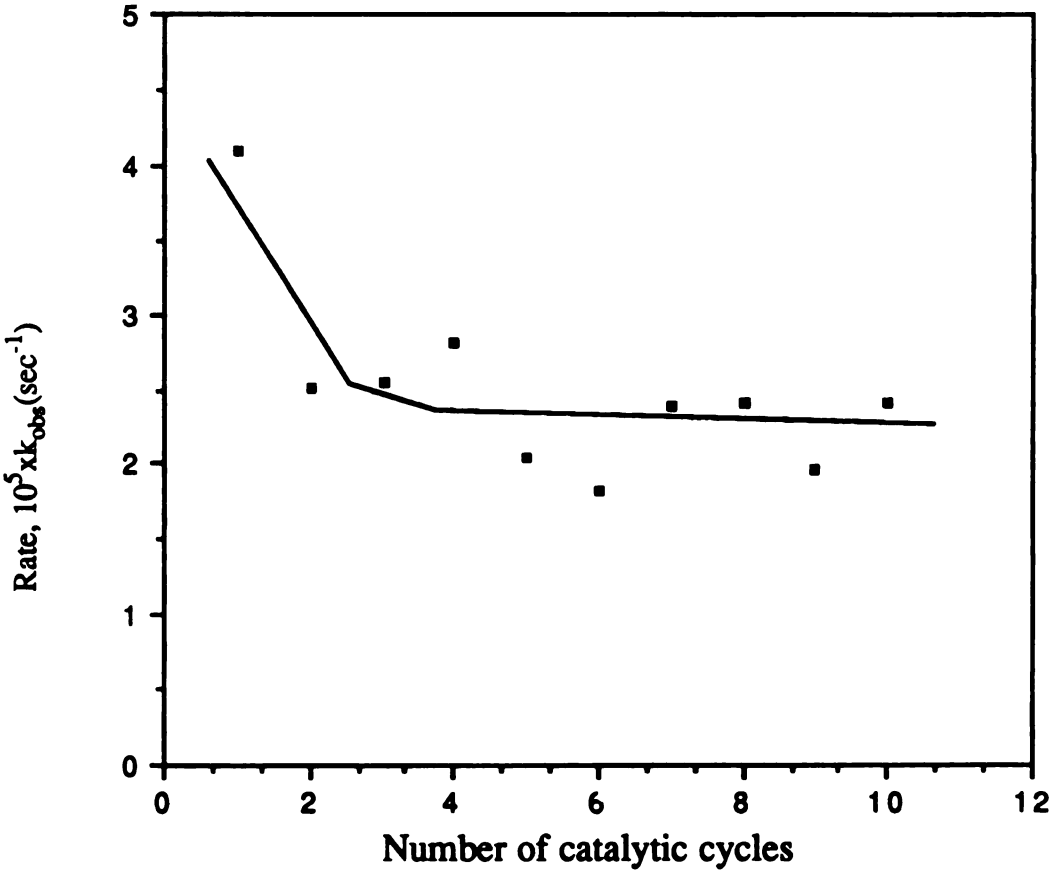
Table 7 The catalytic activity of the high layer charge density $C_{16}H_{33}PBu_3^+$-Clay after multiple reaction cycle for cyanation and chlorination of pentyl bromide[a].

Organoclay	Organic Solvent	Nucleophile	Pseudo First Order Rate Constant (10^5 x k_{obs}, Sec^{-1})		
			Reaction Run		
			1	2	3
W26AA	Toluene	CN^-	27.2	10.7	4.33
A26AA	Toluene	CN^-	54.6	9.44	2.11
F26AA	Toluene	CN^-	56.5	1.91	0.98
A26AA	Decane	CN^-	71.8	49.6	
F26AA	Decane	CN^-	46.9	4.96	
A26AA	Toluene	Cl^-	24.3%[b]	22.7%[b]	

a. Reaction Conditions: 2 mmole pentyl bromide; 20 mmole potassium cyanide or 7.5 mmole sodium chloride; 3 mL aqueous solution; 6 mL organic solution; reaction temperature 90°C.

b The reactivity is determined by the chemical yield of the chlorination product after 8 hour reaction.

Figure 26 The recyclability of $C_{16}H_{33}NMe_3^+$-F-hectorite (F24AA) over 10 reaction cycles for the cyanation of pentyl bromide at 90°C.
Reaction conditions for each cycle were the same as those described in Figure 19a.



The two montmorillonite derivatives, W26AA and A26AA, which contain $C_{16}H_{33}NMe_3^+$ and $C_{16}H_{33}PBu_3^+$ onium ions respectively, are between F-hectorite and hectorite supported catalysts in structural stability and catalytic recyclability (Table 7). Although the Wyoming montmorillonite derivative, W26AA, shows the same lateral bilayer surfactant structure as the hectorite derivative, H26AA, W26AA does not exhibit catalytic recyclability as good as that of H26AA. For the Arizona montmorillonite derivative (A26AA) which adopts a pseudo trimolecular structure, the catalytic recyclability for pentyl bromide cyanation is also poor (Table 7). The surfactant ($C_{16}H_{33}PBu^+$) appears to desorb from the montmorillonite host after the phase transfer catalysis reaction. The extent of desorption of $C_{16}H_{33}PBu_3^+$ from the clay hosts is correlated with the clay layer charge density.

When the reaction conditions are changed, the recyclability properties of organoclays for PTC are also changed. The recycled $C_{16}H_{33}PBu_3^+$-Montmorillonite(Arizona) (A26AA) after pentyl bromide cyanation is a poor catalyst for the next cycle of the same reaction if toluene is employed as the organic solvent. However, if a non-polar solvent such as decane is used on a reaction solvent, the catalytic stability for cyanation can be greatly improved. The poor solubility of the surfactant-cyanide ion pair in the non-polar organic solvent undoubtedly contributes to the stability of the intercalate. This low solubility of the ion pair in the non-polar organic solvent can limit the desorption of the surfactant from the clay hosts. Also, the recyclability

of A26AA for catalytic chlorination is much better than for the cyanation reaction with the same solvent. The surfactant-chloride ion pair is not as soluble as surfactant-cyanide pair in the toluene solution. Therefore, the instability of the organoclay structure and the loss of catalytic recyclability is due to the desorption of the surfactants by ion pairing with the nucleophiles in the organic solvent.

2. Surfactant Desorption

The desorption of onium ion surfactants from clay interlayers is the main cause of the loss of catalytic capacity for organoclay catalysts. This desorption process has been investigated by treating the organoclays under various condition and analyzing the concentration of the desorbed surfactants dissolved in liquid solution.

(a) Influence of aqueous electrolyte solution on surfactant desorption of organoclays.

Onium ion surfactants are expected to remain adsorbed on the clay hosts in the presence of concentrated electrolyte aqueous solution without an organic solvent. The affinity between the surfactant-anion pair and water is less than the electrostatic force between the surfactant and silicate layer. The results of the surfactant desorption for different organoclays in 2.5 N sodium chloride solution is shown in Table 8. The amount of surfactant desorption was determined by spectrometric analysis of the surfactant in liquid solution[98]. The cationic surfactants in the aqueous phase were extracted into the chloroform layer in the

Table 8. The desorption of onium ion from the organoclays in the presence of 2.5N NaCl aqueous solution[a].

Organoclay	onium ion Desorption	Temp. °C	Original d-Spacing	d-Spacing after treatment with 2.5N NaCl	Change of Surfactant Orientation after treatment with NaCl
$C_{16}H_{33}NMe_3^+$Laponite (L24AA)	< 0.5%	25°	14.5Å	14.5Å	None
L24AA	< 0.5%	90°	14.5Å	14.5Å	None
$C_{16}H_{33}NMe_3^+$Hect. (H24AA)	< 0.5%	25°	17.8Å	17.8Å	None
H24AA	< 0.5%	90°	17.8Å	17.8Å	None
$C_{16}H_{33}NMe_3^+$Mont(W) (W24AA)	< 0.5%	25°	18.3Å	18.3Å	None
W24AA	< 0.5%	90°	18.3Å	18.3Å	None
$C_{16}H_{33}NMe_3^+$Mont(A) (A24AA)	< 0.5%	25°	21.8Å	39.4Å	Interstratified
A24AA	< 0.5%	90°	21.8Å	39.4Å	Interstratified
$C_{16}H_{33}NMe_3^+$F-Hect. (F24AA)	< 0.5%	25°	27.2Å	52.6Å	Interstratified
F24AA	0.54%	90°	27.2Å	52.6Å	Interstratified
$C_{16}H_{33}PBu_3^+$Laponite (L26AA)	< 0.5%	25°	16.0Å	17.2Å	None
L26AA	< 0.5%	90°	16.0Å	17.3Å	None
$C_{16}H_{33}PBu_3^+$Hect. (H26AA)	< 0.5%	25°	19.6Å	19.5Å	None
H26AA	< 0.5%	90°	19.6Å	19.5Å	None
$C_{16}H_{33}PBu_3^+$Mont(W) (W26AA)	< 0.5%	25°	19.5Å	19.5Å	None
W26AA	< 0.5%	90°	19.5Å	19.5Å	None
$C_{16}H_{33}PBu_3^+$Mont(A) (A26AA)	<0.5%	25°	27.6Å	28.1Å	None
A26AA	<0.5%	90°	27.6Å	28.1Å	None
$C_{16}H_{33}PBu_3^+$F-Hect. (F26AA)	0.66%	25°	28.0Å	40.0Å	Interstratified
F26AA	0.71%	90°	28.0Å	40.0Å	Interstratified

(Continued)

Table 8 (Continued)

Organoclay	onium ion Desorption	Temp. °C	Original d-Spacing	d-Spacing after treatment with 2.5N NaCl	Change of Surfactant Orientation after treatment with NaCl
$(C_{12}H_{25})_2NMe_2^+$Lapon L30AA	< 0.5%	25°	17.7Å	17.3Å	None
$(C_{12}H_{25})_2NMe_2^+$Hect. (H30AA)	< 0.5%	25°	20.1Å	18.8Å	None
$(C_{12}H_{25})_2NMe_2^+$Mont(W) W30AA	< 0.5%	25°	20.1Å	19.9Å	None
$(C_{12}H_{25})_2NMe_2^+$Mont(A) A30AA	<0.5%	25°	30.2Å	30.5Å	None
$(C_{12}H_{25})_2NMe_2^+$F-Hect. F30AA	<0.5%	25°	30.2Å	43.3Å	Interstratified
NBu_4^+Hect. (H18AA)	< 0.5%	25°	14.5Å	14.5Å	None
NBu_4^+F-Hect. (F18AA)	< 0.5%	25°	14.5Å	14.5Å	Onium ion was removed from gallery

a. Aliquot of 4 ml 2.5N NaCl aqueous solution and 0.030 g organoclay were stirred in 90°C for 3 hours or at room temperature for 15 hours. The onium ion desorption was determined by analyzing the onium ion concentration in the liquid phase.

b. The interlayer onium ion was ion-exchanged by sodium ion but no onium ion was found in liquid solution.

presence of anionic methyl orange as an indicator. The UV-Visible absorption of the organic cation-organic anion pairs is shifted to 418 nm in chloroform solution[103,104]. According to Beer's Law, the maximum absorption at 418 nm is proportional to the concentration of the cationic surfactant-dye pairs in the chloroform solution. As shown in Table 8, the onium ion surfactants do not desorb from clay hosts in the absence of water.

(b)Dependence of the surfactant desorption on the surfactant structure in the presence of the sodium chloride aqueous solution and toluene

The onium ion surfactants do not desorb from clay host in the absence of organic solutions but they may desorb when both an aqueous electrolyte and a polar organic solvent are present. The solubilities of the surfactant-anion pairs in the organic liquid phase and the clay layer charge density are important factors in determining surfactant desorption from the clay hosts as expressed as the following overall reaction.

$$\overline{S^+} + NaCl_{(aq)} \longrightarrow \overline{Na^+} + S^+Cl^-_{(Org)} \qquad (9)$$

where the horizontal bars represent the intercalated species and S^+ is the onium ion surfactant.

The desorption of low lipophilic surfactants containing one long and three short alkyl chain, such as $C_{16}H_{33}NMe_3^+$, is always negligible (Table 9), regardless of the clay layer charge density. Although the

Table 9 Desorption of surfactant from organoclays in the presence of NaCl aqueous solution and toluene[a].

Organoclay	onium ion Desorption	Temp. °C	Original d-Spacing	d-Spacing after being treated with 2.5N NaCl and toluene	Change of Surfactant Orientation after being treated with NaCl and Toluene
$C_{16}H_{33}NMe_3^+$Laponite (L24AA)	< 0.5%	25°	14.5Å	14.4Å	None
L24AA	< 0.5%	90°	14.5Å	14.4Å	None
$C_{16}H_{33}NMe_3^+$Hect. (H24AA)	< 0.5%	25°	17.8Å	18.1Å	None
H24AA	< 0.5%	90°	17.8Å	18.0Å	None
$C_{16}H_{33}NMe_3^+$Mont(W) (W24AA)	< 0.5%	25°	18.3Å	18.0Å	None
W24AA	< 0.5%	90°	18.3Å	18.4Å	None
$C_{16}H_{33}NMe_3^+$Mont(A) (A24AA)	< 0.5%	25°	21.8Å	37.4Å	Interstratified
A24AA	< 0.5%	90°	21.8Å	38.0Å	Interstratified
$C_{16}H_{33}NMe_3^+$F-Hect. (F24AA)	< 0.5%	25°	27.2Å	42.6Å	Interstratified
F24AA	0.54%	90°	27.2Å	53.5Å	Interstratified
$C_{16}H_{33}NMe_3^+$Rectorite (R24AA)	<0.5%	25°	31.0Å	48.5Å	Interstratified
R24AA	<0.5%	90°	31.0Å	48.5Å	Interstratified
$C_{16}H_{33}PBu_3^+$Laponite (L26AA)	< 0.5%	25°	16.0Å	17.1Å	None
L26AA	< 0.5%	90°	16.0Å	17.0Å	None
$C_{16}H_{33}PBu_3^+$Hect. (H26AA)	< 0.5%	25°	19.6Å	20.5Å	None
H26AA	< 0.5%	90°	19.6Å	20.2Å	None

(Continued)

Table 9 (Continued)

Organoclay	onium ion Desorption	Temp. °C	Original d-Spacing	d-Spacing after being treated with 2.5N NaCl and Toluene	Change of Surfactant Orientation after being treated with 2.5 NaCl and Toluene
$C_{16}H_{33}PBu_3^+$Mont(W) (W26AA)	< 0.5%	25°	19.5Å	18.8Å	None
W26AA	< 0.5%	90°	19.5Å	18.2Å	None
W26AA	< 0.5%	90°	19.5Å	18.2Å	None
$C_{16}H_{33}PBu_3^+$Mont(A) (A26AA)	3.8%	25°	27.6Å	34.6Å	Interstratified
A26AA	12.2%	90°	27.6Å	26.0Å	Interstratified
$C_{16}H_{33}PBu_3^+$F-Hect. (F26AA)	88.2%	25°	28.0Å	12.5Å	Na^+Exchange
F26AA	83.2%	90°	28.0Å	12.5Å	Na^+Exchange
$C_{16}H_{33}PBu_3^+$Rectorite (R26AA)	2.8%	25°	32.7Å	37.0Å	Interstratified
R26AA	8.6%	90°	32.7Å	35.3	Interstratified
$(C_{12}H_{25})_2NMe_2^+$Lapon L30AA	< 0.5%	25°	17.7Å	16.7Å	None
$(C_{12}H_{25})_2NMe_2^+$Hect. (H30AA)	< 0.5%	25°	20.1Å	19.6Å	None
$(C_{12}H_{25})_2NMe_2^+$Mont (Wyoming) W30AA	< 0.5%	25°	20.1Å	20.7Å	None
$(C_{12}H_{25})_2NMe_2^+$Mont. (Arizona) A30AA	<0.5%	25°	30.2Å	30.57	None
$(C_{12}H_{25})_2NMe_2^+$F-Hect. F30AA	<0.5%	25°	30.2Å	37.5Å	Interstratified
NBu_4^+Hect. (H18AA)	< 0.5%	25°	14.5Å	14.5Å	None
NBu_4^+F-Hect. (F18AA)	< 0.5%	25°	14.5Å	12.6Å	Onium ion was removed from gallery[b]

a. Aliquot of 4 mL 2.5N NaCl aqueous solution, 4 mL toluene and 0.030 g organoclay were stirred in 90°C for 3 hours or at room temperature for 15 hours.

b. Only the diffraction peak of Na F-hectorite was found in XRD pattern but no onium ion could be observed in liquid solutions.

surfactant re-orients in the F-hectorite and Arizona montmorillonite to form a regular ordered mixed ion species, surfactant desorption does not occur. However, highly lipophilic surfactants, such as $C_{16}H_{33}PBu_3^+$, in the interlayers of F-hectorite, will almost totally desorb by Na^+ exchange and dissolve into the toluene phase by ion pair formation. For laponite, hectorite and Wyoming montmorillonite derivatives (L26AA, H26AA and W26AA, respectively) in which the surfactants adopt monolayer or bilayer structures, desorption of all surfactants is negligible (Table 9) even in the presence of toluene and aqueous sodium chloride solution. Moreover, low layer charge density organoclay structures are not altered by the electrolyte and organic solvent treatment.

For the Arizona montmorillonite and rectorite derivatives (A26AA and R26AA) in which the surfactants adopt pseudo trimolecular structures in the clay interlayers, the surfactants partially desorb from the clay hosts (Table 9). There are 2.8% and 3.8% of $C_{16}H_{33}PBu_3^+$ desorbed from Arizona montmorillonite and rectorite, respectively, at room temperature. The desorption increases to 12.3% and 8.6% for A26AA and R26AA respectively as the temperature is elevated to 90°C (Table 9). The reaction products in each of these systems are the mixture of Na^+-exchange and interstratified forms of the clays.

(c)Desorption of surfactant from clay hosts in the presence of aqueous sodium bromide solution and toluene

The anion in the electrolyte solution can also influence surfactant desorption from the organoclay in a water-organic liquid emulsion. As the hard and hydrophilic chloride ion is substituted by the softer and more lipophilic bromide anion, more of [$C_{16}H_{33}PBu_3^+$] desorbs from

the organoclays with pseudo-trimolecular structures due to the improved solubilities of the surfactant-anion pairs in the organic solution. Comparing the two surfactant-ion pairs, [$C_{16}H_{33}PBu_3^+Br^-$] and [$C_{16}H_{33}PBu_3^+Cl^-$], we expect the former ion to have a higher solubility in toluene. Consequently, the desorption of the surfactants from both A26AA and R26AA increases when sodium bromide is substituted for sodium chloride (Table 9 and 10). However, when the sodium chloride was substituted by by sodium bromide in the aqueous solution does not increase the desorption of hexadecyltributyl phosphonium from the F-hectorite derivative (F26AA), but it even dramatically reduces the desorption percentage.

(d)The dependence of surfactant desorption on electrolyte concentration.

The desorption of hexadecyltributyl phosphonium ($C_{16}H_{33}PBu_3^+$) from F-hectorite increases with increasing electrolyte concentration. Figure 29 shows a plot of surfactant desorption versus the concentration of aqueous solution in the presence toluene and F26AA at room temperature.

The XRD patterns also show the changes that occur in the 001 reflection peaks upon increasing the sodium chloride concentration (Figure 28). While the concentration is increased, the 28Å and 14Å reflections, which are the 001 and 002 reflections of F26AA, become weaker and a new peak at 12.5Å is present due to formation of sodium F-hectorite. As the sodium chloride concentration is decreased below 0.5N, peaks in the range from 42Å to 49Å are observed; these are due to the interstratified F-hectorite derivatives with the ordered stacking of

Table 10 Desorption of surfactant from the organoclay in the presence of aqueous 2.5N NaBr and toluene solutions[a].

Organoclay	Onium Ion Desorption	Temp °C	Original d-Spacing	d-Spacing after being treated with NaBr and Toluene	Change of Onium ion Orientation
$C_{16}H_{33}NMe_3^+$Lapon. (L24AA)	< 0.5%	25	14.5Å	14.7Å	None
$C_{16}H_{33}NMe_3^+$Hect. (H24AA)	< 0.5%	25	17.8Å	17.7Å	None
$C_{16}H_{33}NMe_3^+$Mont. (Wyoming) (W24AA)	< 0.5%	25	18.3Å	16.3Å	None
$C_{16}H_{33}NMe_3^+$Mont. (Arizona) (A24AA)	< 0.5%	25	21.5Å	38.4Å	None
$C_{16}H_{33}NMe_3^+$F-Hect. (F24AA)	< 0.5%	25	27.2Å	47.5Å	Interstratified
$C_{16}H_{33}NMe_3^+$Rect. (R24AA)	< 0.5%	25	31.0Å	39.4Å	Interstratified
$C_{16}H_{33}PBu_3^+$Lapon. (L26AA)	< 0.5%	25	16.0Å	17.1Å	None
$C_{16}H_{33}PBu_3^+$Hect. (H26AA)	< 0.5%	25	19.6Å	18.8Å	None
$C_{16}H_{33}PBu_3^+$Mont. (Wyoming) (W26AA)	< 0.5%	25	19.5Å	19.3Å	None
$C_{16}H_{33}PBu_3^+$Mont. (Arizona) (A26AA)	42.6%	25	27.6Å	37.9Å	Interstratified
$C_{16}H_{33}PBu_3^+$F-Hect. (F26AA)	48.7%	25	28.0Å	34.7Å(w) 12.5Å(s)[b]	Na-Exchange (Not Complete)
$C_{16}H_{33}PBu_3^+$Rect. (R26AA)	44.4%	25	32.7Å	26.6Å	Interstratified

a The experimental conditions were the same as described in Table 9, except the nucleophile was changed to bromide.

b. The weak diffraction peak at 34.7Å results from organo F-hectorite and that at 12.5Å results Na-F-hectorite.

Figure 27 Dependence of [$C_{16}H_{33}PBu_3^+$] desorption from organo F-hectorite (F26AA) on the concentration of sodium chloride in an aqueous-toluene emulsion.

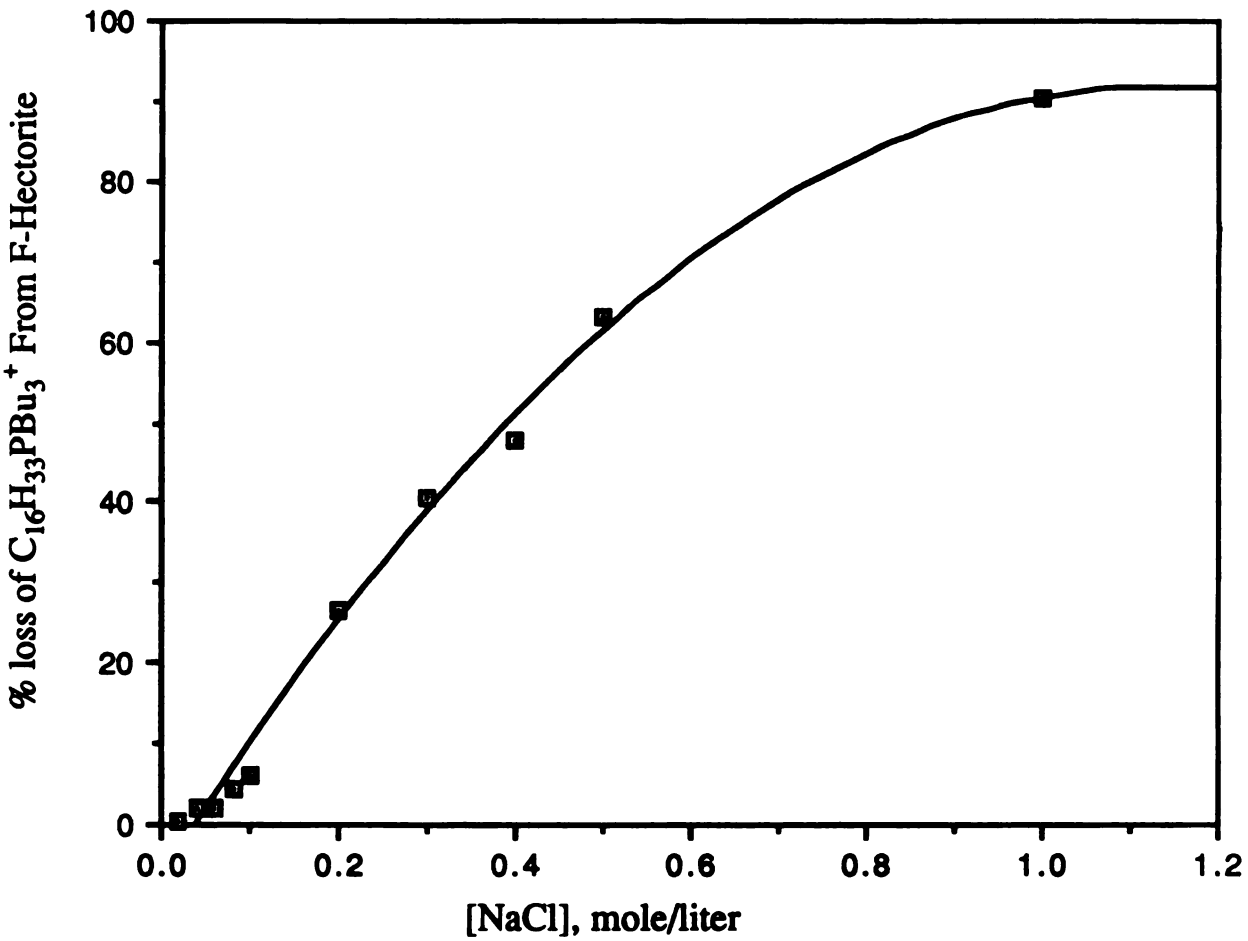
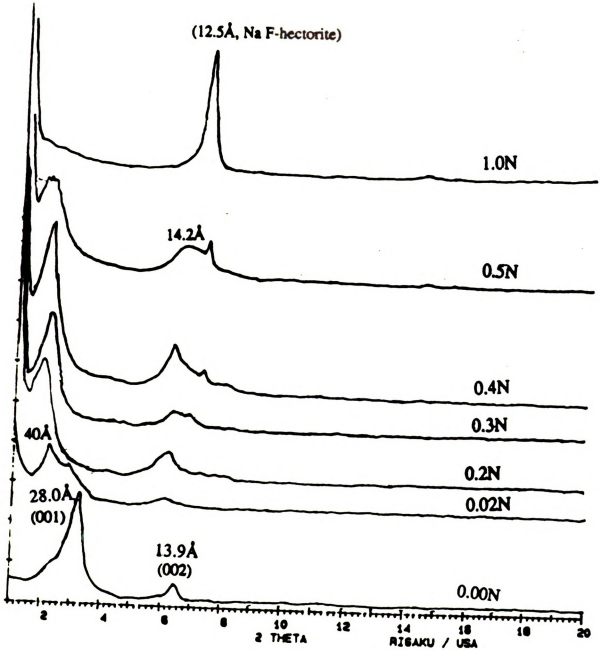


Figure 28 The X-ray diffraction patterns of $C_{16}H_{33}PBu_3^+$-F-Hectorite (F26AA) reaction products formed by reaction of aqueous solution-toluene emulsions at various NaCl concentration.



the Na-F-hectorite and [$C_{16}H_{33}PBu_3^+Br^-$]-F-hectorite layers. When the concentration reaches 1.0N, all of the interlayer surfactant is dissolved into the toluene phase and the only diffraction peak is that at 12.5Å which results from Na^+-F-hectorite formed after the ion-exchange reaction. If the desorption is due to the one-by-one ion exchange of surfactant to sodium ion, all the surfactants would be substituted at the concentration of 0.02N. However, less than 1% of the surfactant is exchanged (Figure 27) by the sodium cation at the sodium chloride concentration at which the sodium molarity equals that of the interlayer surfactant. Therefore, the desorption of the onium ion surfactant, $C_{16}H_{33}PBu_3^+$ is related to the electrolyte concentration instead of the total amount of metal cation.

(e) Dependence of the surfactant desorption on organic solvent polarity.

The desorption of surfactants from organoclays under TPC reaction conditions can be prevented by using a non-polar organic solvent to form the emulsion. If the organic solvent is decane instead of toluene, desorption of hexadecyltributyl phosphonium form A26AA drops from 12.3% to less than 0.5% at 90°C. Also, the desorption of the same surfactant from the F-hectorite derivative (F26AA) decreases from 83% in toluene to 8.78% in decane at 90°C (Table 11). Non-polar decane not only exhibits good catalytic reactivity, but also promotes catalyst longevity by inhibiting ion exchange of the organoclay structure.

Table 11. The desorption of the surfactant under the triphase condition with other organic solvents[a].

organoclay	Surfactant Desorption	Temp. °C	Organic solvent
$C_{16}H_{33}PBu_3^+$F-Hect. (F26AA)	1.2%	25°	Decane
F26AA	8.8%	90°	Decane
$C_{16}H_{33}PBu_3^+$Mont. (Arizona) (F26AA)	<0.5%	25°	Decane
A26AA	<0.5%	90°	Decane
$C_{16}H_{33}NMe_3^+$F-Hect. (F24AA)	<0.5%	25°	o-Dichlorobenzene
F24AA	<0.5%	90°	o-Dichlorobenzene
$C_{16}H_{33}NMe_3^+$Mont. (Arizona) (A24AA)	<0.5%	25°	o-Dichlorobenzene
A24AA	<0.5%	90°	o-Dichlorobenzene

a. A 4 mL of aliquot of 2.5N NaCl aqueous solution, 4 mL organic solvent and 0.030 g organoclay were stirred at 90°C for 3 hours or at room temperature for 15 hours.

A surfactant of low lipophilic character such as hexadecyltrimethyl ammonium, does not desorb from the clay host even in the presence of a highly polar organic solvents such as o-dichlorobenzene (Table 11). The attractive force between a clay layer and [$C_{16}H_{33}NMe_3^+$] is still stronger than the affinity between the [$C_{16}H_{33}NMe_3^+Br^-$] ion pair and o-dichlorobenzene.

3. Co-Surfactant Effects on Phase Transfer Catalysis

(a)Influence of co-surfactant on [$C_{16}H_{33}NMe_3^+$] desorption

For smectite clay derivatives intercalated by hexadecyltrimethyl ammonium ion $C_{16}H_{33}NMe_3^+$, the surfactant always remains bound to the clay hosts instead of being desorbed into the liquid solution. The cationic surfactant is almost insoluble in toluene, but can be dissolved in aqueous solution in the form of a micelle if the surfactant concentration is larger than the critical micelle concentration (CMC). Dobias[88] found that the adsorption of hexadecyl pyridinium chloride on natural minerals such as quartz decreases tremendously when the surfactant concentration was higher than the CMC. It was suggested that the surfactant is more stable as a three-dimensional emulsion mixture than on a two-dimension quartz surface. However, a similar surfactant, hexadecyltrimethyl ammonium, in the smectite clays does not desorb when the surfactant concentration is more than the CMC owing to the strong electrostatic affinity between the clay and the surfactant. However, when an alcohol co-surfactant with more than 5 carbon atoms is introduced into this system, the surfactant may dissociate to form a more thermodynamically stable microemulsion which is composed of the surfactant, co-surfactant, water and the organic phase (Figure 12). This co-surfactant effect on the surfactant desorption is especially

significant for clays with high layer charge density. Table 12 lists for [$C_{16}H_{33}NMe_3^+$] the desorption from clays of various layer charge density that results by adding different concentrations of the co-surfactant, octanol. The desorption of [$C_{16}H_{33}NMe_3^+$] increases with increasing co-surfactant concentration in the microemulsion system.

The difference between "macroemulsion" and "microemulsion" is that the later includes a co-surfactant. The function of the co-surfactants is to separate the positive charge on the polar portion of cationic surfactants[28,91](Figure 12). Therefore, the electric double layer charge density on the interface of the surfactant and aqueous phase is lowered, leading to reduction of the interfacial tension of the water and oil phase[25,27,28,29,30,89,90,91,105]. Generally, the microemulsion droplet sizes are 10 to 100 fold smaller than those of the emulsion[27,28]. In addition, unlike an emulsion which is only kinetically stable, a microemulsion is not only kinetically stable, but also thermodynamically stable[27,29].

(b) Influence of co-surfactants on biphase and triphase catalysis.

Nucleophilic substitution reactions which use the cationic surfactant, $C_{16}H_{33}NMe_3Br$, as a biphase catalyst are strongly influenced by the addition of co-surfactant. Brown and Fendler et al[18,20,22,23,24,106] have utilized cationic surfactants that form micellar aggregates to catalyze nucleophilic substitution reactions. When a co-surfactant is added to a reaction mixture containing a cationic surfactant, toluene and an aqueous solution, a small droplet-size microemulsion is formed. Nucleophilic substitutions proceed more readily in the microemulsion mixture. However, the co-surfactant,

Table 12. Desorption of $[C_{16}H_{33}NMe_3]^+$ from organoclays in the presence of octanol as co-surfactant[a].

	Percentage Desorption of Surfactant from Organoclay						
mmole of Octanol	1 mmole	2 mmole	3 mmole	4 mmole	5 mmole	7 mmole	19 mmole
Organo clay[b]							
L24AA	0.4%	0.4%	0.7%	0.7%	1.1%	2.5%	12.8%
H24AA	0.5%	0.4%	0.4%	0.9%	1.1%	2.2%	8.2%
W24AA	0.2%	0.3%	0.4%	0.9%	1.7%	2.5%	15.0%
A24AA	0.2%	0.2%	0.9%	2.0%	3.3%	5.4%	44.2%
F24AA	0.4%	1.6%	5.3%	6.6%	9.1%	17.3%	57.2%

a. A 4 mL aliquot 2.5N NaCl aqueous solution and 4 mL toluene solution with the indicated amount of octanol was stirred at room temperature for 18 hours.

b. L24AA: $C_{16}H_{33}NMe_3^+$Laponite;
H24AA: $C_{16}H_{33}NMe_3^+$Hectorite
W24AA: $C_{16}H_{33}NMe_3^+$Montmorillonite (Wyoming);
A24AA: $C_{16}H_{33}NMe_3^+$Montmorillonite (Arizona);
F24AA: $C_{16}H_{33}NMe_3^+$F-Hectorite.

octanol, does not alter the colloidal properties of the emulsion formed by organoclay aggregates.

For biphase catalysis reactions which use cationic surfactants as catalysts, the reaction site is assumed to be near the Gouy layer of the micelle. Upon addition of co-surfactants, a smaller micelle droplet of microemulsion is formed, leading to greater efficiency for the catalytic reaction, since the concentration between the two immiscible liquid phases is increased. Table 13 shows the cyanation reactivity for various concentrations of octanol as the co-surfactant when $C_{16}H_{33}NMe_3Br$ or an organoclay are the phase transfer catalysts. These results indicate cyanation reactivity increases with increasing co-surfactant concentration for the biphase $C_{16}H_{33}NMe_3Br$ catalyst. For cyanation of pentylbromide catalyzed by an organoclay, the effect of co-surfactant on reactivity is dependent on the layer charge density of the organoclay.

For organoclay triphase catalysis, the co-surfactant does not change the structure of the organoclay assemblies under triphase conditions. The co-surfactants can merely be adsorbed on the catalyst surface, just as other organic materials are. Consequently, the co-surfactant has little or no influence on the catalytic reaction rate under triphase conditions (Table 13). However, if the onium ion desorbs from the clay, then biphase catalysis reactions will occur and the co-surfactant will increase the catalytic reactivity. Onium ion desorption is especially significant for those organoclays with high layer charge densities, such a F-hectorite and Arizona montmorillonite. From the data in Tables 12 and 13, the increase in the catalytic reactivity caused by adding the co-surfactants is correlated with the desorption of the surfactant from the

Table 13 Influence of octanol and tetradecanol co-surfactants on the cyanation of pentylbromide by biphase catalysts and triphase catalysts[a].

	Chemical conversion of pentyl bromide to pentyl cyanide[a]					
Mmole of Co-Surfactant	0	1	2	3	5	7
Catalyst[c]/ Co-Surfactant						
$C_{16}H_{33}NMe_3^+Br^-$[b] /Tetradecanol	23.3%	27.7%	30.8%	33.7%	46.5%	55.9%
L24AA /Tetradecanol	11.0%	12.8%	13.1%	11.6%	12.1%	11.7%
H24AA /Tetradecanol	22.4%	18.5%	18.2%	19.7%	19.6%	18.9%
A24AA /Tetradecanol	27.7%	30.5%	31.7%	33.0%	33.9%	34.8%
F24AA /Tetradecanol	43.0%	42.5%	43.5%	46.2%	54.7%	

(Continued)

Table 13 (Continued)

	Chemical conversion of pentyl bromide to pentyl cyanide[a]					
Mmole of Co-Surfactant	0	1	2	3	5	7
Catalyst[c]/ Co-Surfactant						
$C_{16}H_{33}NMe_3^+Br^-$[b] /Octanol	23.3%	28.4%	30.4%	36.7%	46.1%	52.1%
L24AA /Octanol	11.0%	10.4%	9.5%	8.9%	9.1%	10.5%
H24AA /Octanol	22.4%	19.7%	18.8%	22.6%	20.3%	20.8%
A24AA /Octanol	27.7%	28.2%	27.0%	35.3%	34.9%	37.0%
F24AA /Octanol	43.0%	41.5%	43.4%	42.9%	49.3%	56.9%

a. Reaction conditions: 3 mL aqueous solutions containing 2 mmole potassium cyanide, 6 mL toluene solution containing 10 mmole of pentylbromide and indicated amounts of co-surfactants; 0.100 g organoclays were stirred in 90°C oil bath for 4 hours .

b. The surfactant, $C_{16}H_{33}NMe_3Br$.was used as a micellar biphase catalyst. The amount of surfactant used in this experiment was equal to the amount of interlayer surfactant contained in 0.100 g H24AA.

c. L24AA: $C_{16}H_{33}NMe_3^+$Laponite; H24AA:$C_{16}H_{33}NMe_3^+$Hectorite
A24AA: $C_{16}H_{33}NMe_3^+$Montmorillonite (Arizona);
F24AA: $C_{16}H_{33}NMe_3^+$F-Hectorite

clay. The organo laponite (L24AA), organo hectorite (H24AA) and organo Wyoming montmorillonite (W24AA) with lower layer charge densities are not influenced by less than 7 mmole of co-surfactant. The organo F-hectorite, F24AA, behaves almost the same as a biphase catalyst, and the Arizona montmorillonite derivative, A24AA, is moderately influenced by the co-surfactants. The high layer charge density organoclays result in surfactant desorption when the co-surfactant is added and the desorbed cationic surfactants undergo biphase catalysis reaction.

(c) Catalytic properties of organoclays and surfactants for the cyanation of alkyl bromide and bromoalkyl alcohol.

Organic reactants that have co-surfactant character such as 8-bromooctan-1-ol are much more reactive for cyanation under biphase reaction conditions than the analogous n-bromoalkanes. Under triphase catalysis reaction conditions with organo hectorites as the catalysts, the cyanation rates for bromoalkanols and bromoalkanes are comparable (Table 14).

The activation energy for cyanation of a bromoalkanol and bromoalkane are similar, provided the reaction conditions are not different. The relative reaction rates for the two organic electrophiles are determined from the concentrations of the organic electrophile on the clay surface (Figure 23). For organo hectorite triphase catalysis reaction, reaction occurs at the catalyst-aqueous interface and the concentration discrepancy between bromoalkanol and bromoalkane on the clay surface is very small. Consequently, the cyanation rates for these two reactants are comparable.

Under the biphase catalysis reaction conditions with $C_{16}H_{33}NMe_3Br$ as the catalyst, the co-surfactant reactants can form a microemulsion with the cationic surfactant, and the aqueous and organic solution. The co-surfactants are positioned at the reactive site, which is at the interface of the surfactant in the aqueous phase (Figure 12). Moreover, the reactive site for biphase micellar catalysis is also at the micelle and liquid interface[18,19,107,108]. Consequently, the co-surfactant reactants, bromoalkanol's, have higher surface concentration in the region where reaction occurs. Since bromoalkane does not have a hydroxyl group, the organic molecules are mainly located in the toluene phase, which is not close to the liquid and micelle interface, causing this reactant to have a low concentration in the region where reaction occurs. Therefore, the cyanation reactivity of a bromoalkane is much lower than the reactivity of a bromoalkyl alcohol under biphase micellar catalysis reaction conditions with $C_{16}H_{33}NMe_3Br$ as the catalyst.

The results in Table 14 also provide information about some clay derivatives in which the surfactants desorb during the phase transfer catalysis reaction. The F-hectorite derivative, F24AA, exhibits behavior similar to that of biphase catalysts, due to the similar discrepancy in catalytic reactivity between bromoalkane and bromoalkanol. The surfactant in the organo F-hectorite, F24AA, can potentially desorb from the silicate layer to carry out the reaction under biphase catalysis condition. Organo clays with low charge densities do not have the problem of surfactant desorption, so the reactivities between bromoalkane and bromoalkyl alcohol are comparable.

Table 14. The cyanation of bromoalkanes and bromoalkanols under biphase and triphase catalysis conditions[a].

Catalysts	Conversion (%)	
	$C_8H_{17}Br$[b]	$BrC_8H_{16}OH$[b]
None	0	4
$C_{16}H_{33}NMe_3Br$	17	50
H24AA	21	27
A24AA	27	49
F24AA	23%	63
	$C_{10}H_{21}Br$	$BrC_{10}H_{20}OH$
None	0	0
$C_{16}H_{33}NMe_3Br$	14	65
H24AA	21	27
A24AA	25	26
F24AA	21	62

a. Reaction condition: 3 mL aqueous solution containing 10 mmole potassium cyanide; 6 mL of toluene solution containing 3 mmole of bromo compound; 0.100g organoclays or 0.060 mmole of $C_{16}H_{33}NMe_3Br$ were stirred in 90°C oil bath for 4 hours.

4. The Catalytic Properties of Crown Ether Clay Complexes

Crown ethers are well known biphase catalysts,[15,16,32109,110]. These molecules can be pillared into the clay interlayer[82] and this pillar clay can also facilitate the phase transfer catalysis reaction. However, crown ethers supported in smectite clay interlayers desorb from the clay host during the phase transfer catalysis reactions. Chemical yields for benzyl bromide cyanation with clay crown ether complexes are shown in Table 15. The chemical yields for cyanation with the clay crown ether complexes are about twice those obtained in the absence of catalyst under the same conditions. The crown ethers in the clay interlayer are replaced by metal cations after the catalytic reactions, but the crown ethers are not completely dissolved in the liquid solutions. The recovered solid catalysts after one cycle do not have the same diffraction pattern as the original clay crown ether complexes (Table 15), but they exhibit the IR absorption of the crown ether vibration (Figure 29c). Figure 29a and 29b are the IR spectra of sodium hectorite and 18C6Hect respectively. The IR absorptions at 1355, 1470 and 2900cm^{-1} are due to the crown ether vibration. Both the recycled and original catalysts exhibit these absorptions.

The recovered solid catalyst still possesses good catalytic capacity for cyanation (Table 15), although the structure of the clay crown ether complex is changed after the catalytic reaction. While the catalytic reactions employ the same amount of crown ether for phase transfer catalysis, no insoluble crown ether can be isolated from liquid solutions. The crown ethers are believed to adsorb onto the clay matrices after the

Table 15 Chemical yields for the cyanation of benzylbromide to benzyl cyanide[a].

Catalyst	d_{001}-Spacing (Å)		Chemical Yield[b] (%)	
	Fresh Catalyst	Recycled Catalyst	1st Cycle	2nd Cycle
18-crown-6	___	____	71[c]	___
18C6Hect	15.6	13.2	58	53
18C6Mont	17.4	13.1	69	68
Dicyclohexo 18-Crown-6	____	____	76[c]	___
Hex18C6Hect	17.8	13.5	56	55
Hex18C6Mont	19.0	14.1	74	52
None	____	____	45	___

a. Reaction condition: 2 mmole of benzyl bromide in 6 mL of toluene; 2.5 mmole of potassium cyanide in 1 mL of water; 0.100 g clay supported catalyst or 0.060 mmole crown ether; Reaction temperature 90°C; Reaction time 12 hours

b. The yields were determined by GLC.

c. No catalyst can be recovered after the catalysis reaction.

catalytic reaction. The smectite clays does not change the crown ether biphase catalysis mechanism, but the clay do act as an adsorbent for the expensive crown ether after the nucleophilic substitution reaction.

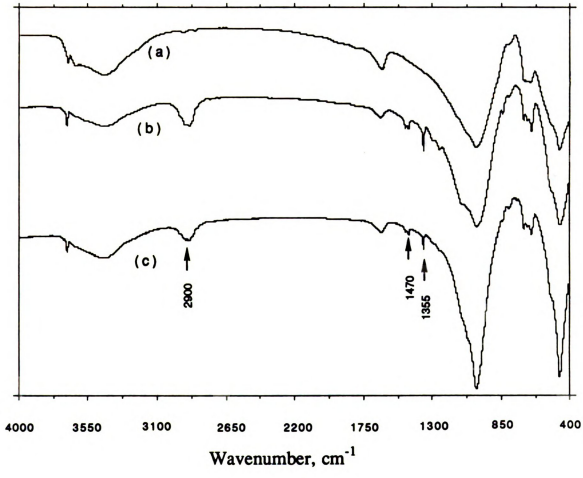
D. The Applications of Organoclays in Other Triphase Catalysis Reactions

1. The Synthesis of Symmetrical Formaldehyde Acetals

Many formaldehyde acetals can be synthesized by using organoclays as triphase catalysts (Equation 10, 11 and 12). The hectorite supported catalysts, H24AA, H26AA and the Arizona montmorillonite supported catalysts, A24AA and A26AA, are employed as catalysts for nucleophilic substitution reactions. Corneleis et al.[54,111,112] have used Tixogel VP, a montmorillonite organic derivative, as the phase transfer catalyst to synthesize formaldehyde acetal derivatives.

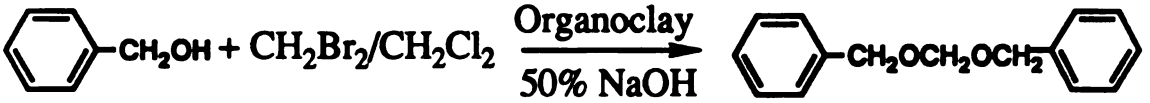
The catalytic reactions proceeded by refluxing the mixture of the alcohol, dihalomethane and 50% sodium hydroxide aqueous solution at 90°C in an oil bath for 12 hours. The chemical structures and yields were obtained by ^{1}H and ^{13}C NMR. The chemical yields of all the formaldehyde acetals are shown in Table 16 and the NMR spectra data for the acetal products are listed in Table 17. The yields of formaldehyde benzyl acetal are almost 100% by using all the indicated catalysts. The yield of the blank reaction is only 12% at the same condition but in the absence of the triphase catalysts. The chemical yields for the synthesis of formaldehyde n-butyl acetal and formaldehyde iso-pentyl acetal (Equation 11 and 12) are low,

Figure 29 The IR spectra of (a) sodium hectorite, d_{001}=12.1Å (b) 18C6Hect, d_{001}=15.6Å and (c) recycled 18C6Hect after one cycle of reaction, d_{001}=13.2Å. The absorptions at 1355,1470 and 2900 cm^{-1} are due to a crown ether vibration.



apparently due to the low acidity of the aliphatic alcohols. Reactions represented by Equation 11 and 12 can not proceed without a phase transfer catalyst.

All of these catalytic reactions employed a 50% alkaline solution, which is highly destructive toward the layer silicates. Corneleis et al.[54,111,112] did not investigate the thermal stability of the organoclay, Tixogel VP, after vigorous catalytic reactions. In fact, the montmorillonite equivalent of Tixogel VP, in which the onium ion is a dialkyldimethylammonium, undergoes surfactant desorption under reaction conditions. Thus much of the reaction observed by Corneleis et al. was due to biphase reaction. However we found that the hectorite derivatives, H24AA and H26AA, can be recovered by filtration and recycled many times for the same catalytic reactions (Table 16). The XRD pattern (Figure 30) of the recycled H24AA shows that the organoclay structure is unchanged after catalytic reactions. Surprisingly, sodium hectorite is destroyed after treatment with 50% sodium hydroxide solution even at room temperature, because the original d_{001} reflection peak of Na-hectorite disappears (Figure 31). Therefore, the surfactants in organo hectorite not only increase the hydrophobicity of the material but also protect the silicate layer from attack by the alkaline solution. The Arizona montmorillonite derivatives, A24AA and A26AA, do not have the advantage of resisting the alkaline solution. Trace amount of solid material could be recovered by centrifuging the catalytic reaction mixture after the catalytic reactions. The catalysts, A24AA or A26AA, are decomposed

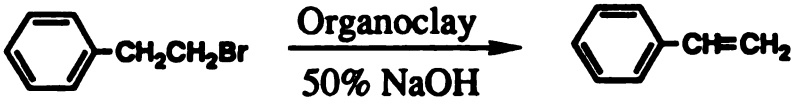


(10)

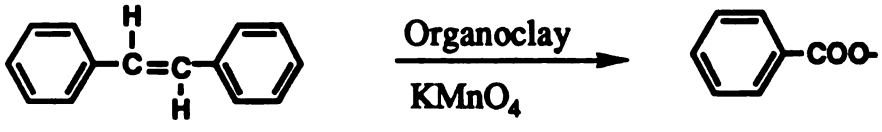
$$C_4H_9OH + CH_2Br_2/CH_2Cl_2 \xrightarrow[50\%\ NaOH]{Organoclay} C_4H_9OCH_2OC_4H_9 \qquad (11)$$

$$(CH_3)_2CH(CH_2)_2OH + CH_2Br_2/CH_2Cl_2 \xrightarrow[50\%\ NaOH]{Organoclay} CH_2[O(CH_2)_2CH(CH_3)_2]_2 \qquad (12)$$

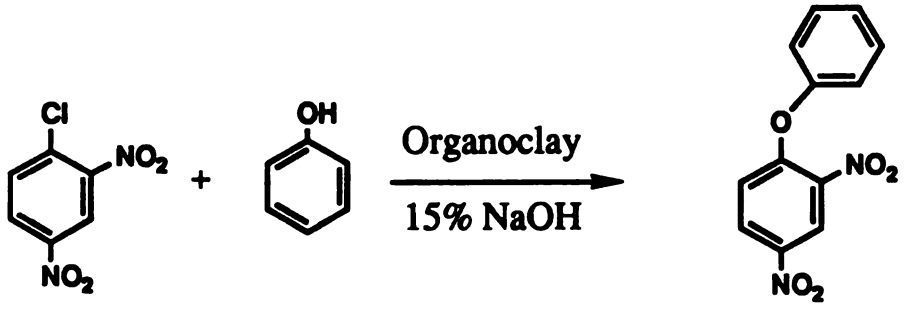
$$C_8H_{17}OH + HBr(47\%) \xrightarrow{Organoclay} C_8H_{17}Br \qquad (13)$$



(14)



(15)



(16)

Table 16. The chemical yields of the acetal synthesis (Equation 10-12)[a].

Entry	R Group	Catalyst	Chemical Yield (%)
1	Benzyl	H24AA	>95
2	Benzyl	H26AA	>95
3	Benzyl	A24AA	>95
4	Benzyl	A26AA	>95
5	Benzyl	$C_{16}H_{33}NMe_3Br$	>95
6	Benzyl	$C_{16}H_{33}PBu_3Br$	>95
7	Benzyl	No	18
8	Benzyl	Recycled H24AA	>95
9	Benzyl	Recycled H24AA	>95
10	Butyl	H24AA	37
11	Butyl	H26AA	50
12	Butyl	A24AA	63
13	Butyl	A26AA	58
14	Butyl	$C_{16}H_{33}NMe_3Br$	55
15	Butyl	$C_{16}H_{33}PBu_3Br$	56
16	Butyl	No	0
17	Butyl	Recycled H24AA	35
18	Butyl	recycled H26AA	49
19	iso-Pentyl	H24AA	32
20	iso-Pentyl	H26AA	28
21	iso-Pentyl	A24AA	58
22	iso-Pentyl	A26AA	38
23	iso-Pentyl	$C_{16}H_{33}NMe_3Br$	36
24	iso-Pentyl	$C_{16}H_{33}PBu_3Br$	33
25	iso-Pentyl	No	0
26	iso-Pentyl	Recycled H24AA	30
27	Iso-Pentyl	recycled H26AA	24

a. Reaction condition: 10 mmole of alcohol; 10g CH_2Br_2; 10g CH_2Cl_2; 10 mL 50% NaOH aqueous solution; reaction temperature, 90°C; reaction time 12 hours.

Table 17 The chemical shifts in the ^1H NMR of the starting materials and the reaction products of the acetal synthesis reaction (Equation 10-12).

Chemical	Chemical shift (ppm)
$C_6H_5CH_2OCH_2OCH_2C_6H_5$	4.68 ppm (s, 4H)[a] 4.87 ppm (s, 2H) 7.3-7.4 ppm (m, 10H)
$C_4H_9OCH_2OC_4H_9$	0.86-0.94 ppm (t, 6H) 1.3-1.4 ppm (m, 4H) 1.45-1.55 ppm (m, 4H) 3.45-3.55 ppm (t, 4H)[a] 4.62 ppm (s, 2H)
$[(CH_3)_2CH(CH_2)_2O]_2CH_2$	0.90-0.92 ppm (d, 12H) 1.40-1.51 ppm (q, 4H) 1.60-1.80ppm (m, 4H) 3.45-3.55 ppm (t, 4H)[a] 4.62 ppm (s, 2H)
$C_6H_5CH_2OH$	4.70 ppm (s, 2H)[a] 7.3-7.4 ppm (m, 5H)
C_4H_9OH	0.86-0.94 ppm (t, 3H) 1.3-1.4 ppm (m, 2H) 1.45-1.55 ppm (m, 2H) 3.55-3.65 ppm (t, 2H)[a]
$(CH_3)_2CH(CH_2)_2OH$	0.90-0.92 ppm (d, 6) 1.40-1.51 ppm (q, 2H) 1.60-1.80ppm (m, 2H) 3.65-3.71 ppm (t, 2H)[a]

a. The underline marks are the absorption peaks used for measuring the integration ratio of starting materials and reaction products.

and converted to smaller particles suspended in the aqueous phase. The trace amounts of recycled Arizona montmorillonite derivatives, A24AA and A26AA, do not retain their original structure following reaction, as evidenced by X-Ray diffraction.

As is mentioned in this chapter, the surfactants in the high layer charge density smectite clay group, such as Arizona montmorillonite, will dissociate from the interlayer if the clay derivatives are suspended in electrolyte solutions. Since the surfactants do not coat the surface of the silicate layer, hydroxide ion can destroy the unprotected surface and decompoe the mineral. The surfactant in a relatively low layer charge density hectorite will not dissociate so the silicate layer surface is always protected by the surfactant.

2. Synthesis of Alkyl Bromide

The long chain alkyl bromide can be synthesized by refluxing a mixture of alkyl alcohol in concentrated hydrobromic acid. Montanari et al.[113] have utilized hexadecyltributyl phosphonium bromide as a phase transfer catalyst to facilitate this reaction. The organo clay (H26AA) is employed as the phase transfer catalyst for the alkyl bromide synthesis (Equation 13). The catalytic reaction conversions are better than the conversion for the blank reaction (Table 18). However, the organo clay is totally decomposed by the strong acid and the recycled solid material does not show any catalytic activity. The XRD pattern of the recycled material is amorphous, with the original d001 absorption peak of H26AA absent. The hectorite supported catalysts can tolerate alkaline solution but are destroyed by strongly acidic solution. Fortunately, most phase transfer catalysis reactions are carried out under neutral or basic condition.

Figure 30 The X-ray diffraction pattern of $C_{16}H_{33}NMe_3^+$hectorite (H24AA) after the catalysis reaction in which the reaction mixture contains 50% NaOH aqueous solution and 10 mL of methylene chloride solution.
The peaks at 19Å arises from H24AA. The 10Å, 4.7Å and 2.4Å peaks belong to the reactants.

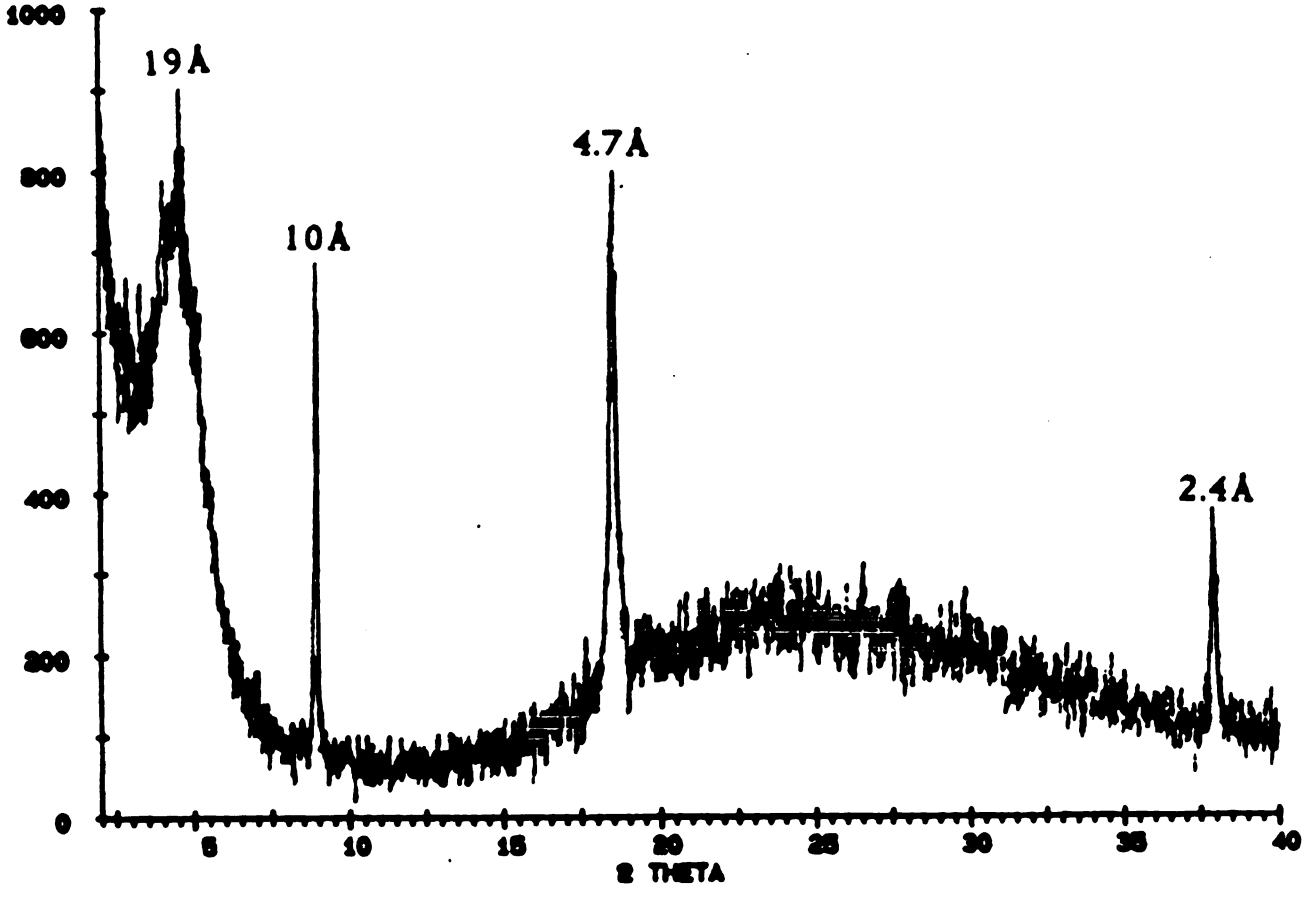
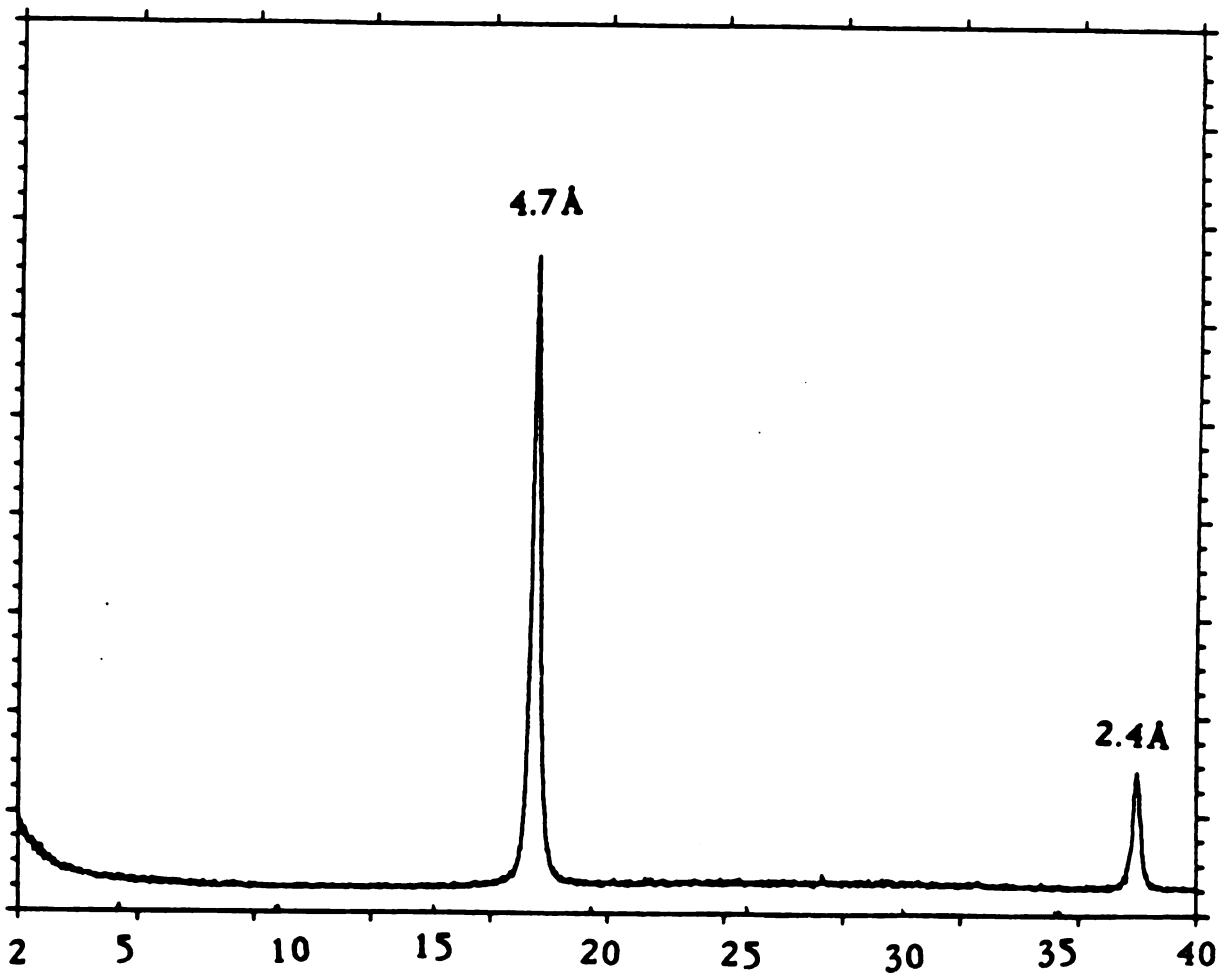


Figure 31 The X-ray diffraction pattern of sodium hectorite treated with 50% NaOH aqueous solution. No reflection peak at 12.5Å ccould be found. The reflection peaks at 4.7Å and 2.4Å are due sodium hydroxide.



3. Dehydrohalogenation of 2-Bromoethylbenzene

Styrene, which is a very important industrial chemical for polymerization, can be generated by treating 2-bromoethylbenzene in strong alkaline aqueous solution using triphase catalysts such as polyethylene glycol or organoclay (Equation 14). The chemical yields of the reaction are determined by the GLC. Commercial styrene from Aldrich Chemical Company shows the same retention time in the GLC as the product obtained in the catalytic reaction. The chemical yield of the styrene in the reaction catalyzed by H26AA and H24AA are shown in Table 19. No styrene is formed in the absence of organo clay as triphase catalyst. The organo hectorite preserves its original layer structure after this catalytic reaction.

4. Oxidation of trans-Stilbene

Organo clays can facilitate the oxidation of trans-stilbene under the triphase catalysis condition (Equation 15). The product, benzoic acid, is identified by its melting point and NMR spectrum. Table 20 shows that the chemical yields of the oxidation using organoclays as catalysts are much better than the blank reaction without a phase transfer catalyst. However, the organo clay catalysts are difficult to recycle due to the large amount of manganese dioxide precipitate mixed-in with the catalyst.

Table 18 The synthesis of octyl bromide from octanol by hydrobromic acid dehydration[a] (Equation 13).

Catalyst	Concentration of HBr (%)	Reaction Time	Chemical yield[b]
$C_{16}H_{33}PBu_3^+$ Hectorite (H24AA)	47%	11 Hours	79%
None	47%	11 Hours	37%
$C_{16}H_{33}PBu_3^+$ Hectorite (H24AA)	23%	11 Hours	0%
None	23%	11 Hours	0%

a. Reaction Condition: 1 mL of 47% HBr or 2 mL or 23% of HBr; 2.5 mmole octanol; 0.060 mmole catalyst; Reaction temperature 90°C.

b. The chemical yields were determined by GLC.

5. Synthesis of 2,4-Dinitrophenyl Ether

Organo clay triphase catalyst can also be employed for the synthesis of 2,4-dinitrophenyl ether by treating 1-chloro-2,4-dinitrobenzene and phenol in 1.5N NaOH solution (Equation 16). The chemical yield of the nucleophilic substitution reaction is almost 100% (Table 21). The reaction product and chemical yield were determined by ^{1}H NMR and ^{13}C NMR (Figure 32). Tundo and Venturello[47] have used silica gel supported onium ions as the triphase catalysts to synthesize 2,4-dinitrophenyl ether. However, the reaction occurs in strongly basic solution. Since organo hectorite is stable in alkaline solution, this hectorite derivative is a more suitable triphase catalyst for this synthesis reaction.

Table 19 Synthesis of styrene from 2-bromoethylbenzene under alkaline solution[a] (Equation 14).

Catalyst	Reaction Time	temperature	Yield[b]	d001(Å)[c]
$C_{16}H_{33}PBu_3^+$ -Hectorite (H26AA)	13 hours	65°C	73%	21
$C_{16}H_{33}PBu_3^+$ -Hectorite (H24AA)	13 hours	65°C	70%	18
$C_{16}H_{33}PBu_3^+$ -Hectorite (H26AA)	10 hours	75°C	76%	21
$C_{16}H_{33}PBu_3^+$ -Hectorite (H26AA)	14 hours	75°C	83%	21
None	13 hours	65°C	9%	___

a. Reaction Condition: 4 mmole 2-bromoethylbenzene; 0.300g Decane (Internal Standard); 4 mL Benzene; 0.100g Organoclay; 3 mL 50% NaOH aqueous solution.
b. The chemical yields were determined by GLC.
c. The d-spacing of the recovered catalyst.

Table 20 The formation of benzoic acid by the oxidation of trans-stilbene[a] (Equation 15).

Catalyst	Reaction Time	Yield (%)[b]
$C_{16}H_{33}PBu_3^+$Hectorite (H26AA)	10 Hours	78
None	10 Hours	63
$C_{16}H_{33}PBu_3^+$Hectorite (H26AA)	18 Hours	94
None	18 Hours	81

a. Reaction Condition: 0.200 g H26AA; 3 mmole trans-Stilbene; 6 mmole $KMnO_4$; 10 mL Benzene; 6 mL Water.

b. The yields were obtained by weighing the isolated benzoic acid after the reactions.

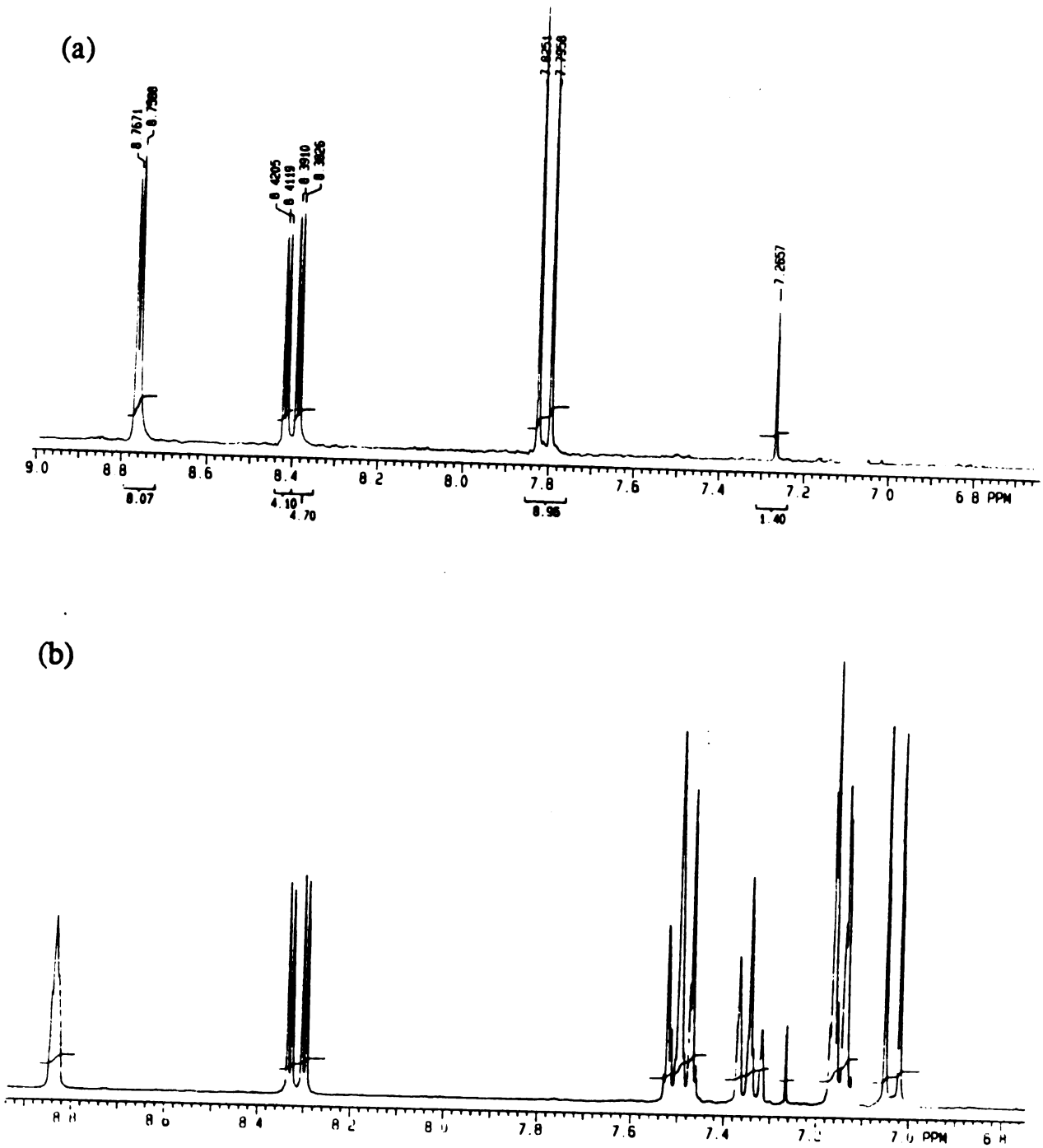
Table 21 The synthesis of 2,4-dinitrophenyl ether from 1-chloro-2,4-dinitrobenzene and phenolate[a] (Equation 16).

Catalyst	Reaction Time	Chemical Yield[b] (%)
$C_{16}H_{33}PBu_3^+$ Hectorite (H26AA)	4 Hours	>95
$C_{16}H_{33}PBu_3^+Br$	4 Hours	>95
None	4 Hours	0

a. Reaction Condition: 6 mmole phenol and 1-chloro-2,4-dinitrobenzene in 5 mL benzene; 6 mmole sodium hydroxide in 5 mL of aqueous solution; 0.060 mmole catalyst; reaction temperature 25°C.

b Yields were determined by the ^1H NMR integration area of starting material and reaction product (Figure 34).
The chemical product, 2,4-dinitrophenyl ether, was also characterized by its melting point (68-71°C).

Figure 32 The ^{1}H NMR spectra of (a) 1-chloro-2,4-dinitrobenzene and (b) 2,4-dinitrophenyl ether.



CHAPTER IV

CONCLUSIONS

Organoclays provide different properties in triphase catalysis from those of typical polymer supported triphase catalysts. The mechanistic property of the clays in which the onium salts are immobilized on polystyrene is similar to that of onium ion biphase catalysis. In this mechanism[13,14,16,17,61,62,114] the anionic nucleophile is paired with an onium cation in the aqueous phase followed by extraction into the organic phase to undergo the nucleophilic substitution reaction. With the polymer supported catalyst the reactant must undergo mass transfer to the catalyst surface, diffuse to the active site which is close to the region of the onium ion, proceed with chemical reaction, and the reaction product must leave the site. Any or all of these fundamental steps may limit the catalytic reactivity.

Organo hectorite does not remove the nucleophile from the aqueous phase to the organic phase. The clay organic derivative provides an amphiphilic property which can stabilize a water in oil emulsion. Because the nucleophilic substitution reaction can only occur at the liquid-liquid interface in the absence of a phase transfer catalyst, formation of an

emulsion can dramatically increase the interfacial area of the oil and water phase resulting in a higher probability for chemical reaction. In organo hectorite triphase catalysis, only the organic reactant must undergo the process of mass transfer and diffuse to the active site on the catalyst surface. The nucleophile can freely transfer to the active site without the two limiting steps. This is evidenced by the linear relationship between the reaction rates and nucleophile concentration in bulk aqueous phase (Figure 19a). However, the stronger solvation of the nucleophile in aqueous solution results in a low nucleophilic ability for the anion. The activation energy of reactions catalyzed by organo hectorites is theoretically equal to that of the reaction proceeding in aqueous solution.

The function of the organo hectorite is to increase reactant concentration in the active site. The nucleophilic substitution reaction catalyzed by polymer supported catalyst is carried out in the organic phase[61,63,64,115]. The function of the polystyrene supported catalyst is (a) to lower the activation energy of the reaction pathway and (b) to provide a phase with a high effective concentration of the potential reactant[116,117]. The first function, which can be achieved by changing the chemical reaction environment from the aqueous to the organic phase, results in enhanced nucleophilic ability of the anionic nucleophile. The second can be fulfilled by increasing the lipophilic property of the polymer supported catalyst. The catalytic ability of polystyrene supported and free onium salts sometimes depend on the extraction coefficient of the nucleophile between the aqueous phase and the organic phase[15,17]. Hydrophobic anions such as SCN^- and I^- have high extraction coefficients. However, high hydrophilic nucleophiles such as hydroxide or chloride which have low extraction coefficients in these two liquid

solutions mediated by phase transfer catalysts, lead to a low effective concentration of the nucleophile at the reaction site.

The typical phase transfer catalysts used for reactions that employ the hydroxide ion as the nucleophile are expensive crown ether, cryptates or derivatives of poly(ethylene glycol)[31,42,55,57,118]. These analogues can hydrogen bond with the hydroxide, and then be extracted into the organic phase. Organo hectorite is also a good triphase catalyst for reactions in this strongly basic system. The hydrophilic anion does not have to be transferred from the aqueous to the organic phase so the reaction is not limited by the extraction coefficient. The organic solvents in triphase catalysis systems also influence catalytic reactivity. In a triphase catalysis reaction with a polystyrene supported catalyst, use of non-polar organic solvents results in low catalytic reactivity[46,61]. The extraction coefficients of anionic nucleophiles are low in non-polar organic solvents. In addition, the low swellability of the ion pair, onium cation and anionic nucleophile, in the non-polar organic solvent leads to difficulty with mass transfer and diffusion of reactants to the active site. Use of inexpensive and non-toxic non-polar organic solvents such as decane in organoclay triphase catalysis reactions can improve the chemical reactivity relative to that of more expensive polar organic solvents, such as toluene and o-dichlorobenzene. The low affinity of the non-polar organic solvent and the organic reactant results in ease of mass transfer of the organic electrophile from the bulk organic phase to the organoclay surface. Then the catalytic reactivity is high because of the high concentration of the organic reactant on the organoclay surface. Although an organoclay triphase catalyst does not significantly reduce the activation energy of the chemical reaction, the independence of the extraction coefficient of the

anionic nucleophile provides the advantage that a larger variety of nucleophiles and non-polar organic solvents can be appropriately used in the triphase catalysis system. Another kind of triphase catalyst is that in which the onium ions are supported in inorganic matrices such as silica gel or alumina[47,48]. Chemical reactions using these inorganic-based materials as triphase catalysts are believed to occur at the liquid-catalyst interface[49,50]. The catalytic reactivity of the inorganic-based material also increases with decreasing the polarity of organic solvent[47,49,69]. The advantage of these materials are their physical strength and the lack of swelling[119]. Smectite clays also have strong rigidity[120]. Organoclays swell in organic solvents. A high polar organic solvent, such as o-dichlorobenzene, dramatically swells organo hectorite. However, a high polar organic solvent strongly solvates the organic electrophile and limits mass transfer of the organic molecule with the result of poor catalytic activity.

The swellability of polystyrene supported onium salts in organic solvents plays an important role in the catalytic reactivity of the triphase catalysis reaction. All other factors being equal, reaction rates decrease with increased cross-linking whenever rate is limited by intraparticle diffusion [58,59,64,67,119]. The more highly cross-linked the catalyst, the lower is the diffusion of reactants to the active sites. However, the most common 1% and 2% cross-linked resin in solvent-swollen form is too gelatinous to be recovered by filtration[119]. Although catalytic activity is most studied in phase transfer catalysis, recyclability is an aspect in triphase catalysis that is sometimes the most important. Good polymer supported catalysts with great swellability in organic solvent may be difficult to recycle. High cross-linked polystyrene supported catalysts

more easily recovered but are lower in catalytic activity than those of low cross-linked polymers. Organoclay is easily recovered by filtration or centrifugation after the chemical reaction. The main disadvantage of organoclay for recycling is that some of the onium ions in the clay interlayer may desorb from clay hosts with high layer charge densities. Because the bond between the clay layer and the onium ion guests is electrostatic, metal cations from the aqueous phase may substitute for the onium ions. However, hectorite as the host overcomes the problem of onium ion desorption. The interlayer onium ions in this medium layer charge density clay host are not ion-exchanged by metal cations from the aqueous solution. This makes the hectorite derivative a good triphase catalyst in terms of longevity.

The chemical instability of the triphase catalyst under reaction conditions also results in poor recyclability. Ammonium and phosphonium salts may be destroyed during the reaction. This is especially true for quaternary ammonium salts, which undergo Hoffmann elimination in strongly alkaline solution and produce trialkylamine and alkene products[15]. Most triphase catalysts have encountered this problem[80,121] and so does organoclay. The catalytic activity of hexadecyltrimethyl ammonium hectorite gradually decays in each cyanation reaction. Before 50% of the catalytic activity of the organo hectorite is lost, more than 100 turnovers of the chemical reaction have been achieved. This organo hectorite is still valuable in this triphase catalysis cyanation reaction. Quaternary phosphonium is generally more stable than quaternary ammonium under reaction conditions[15]. Thus hexadecyltributyl phosphonium hectorite can preserve its catalytic capacity better than the quaternary ammonium hectorite. More than 300

turnovers of the reaction have been achieved while the hectorite supported phosphonium still maintains 85 % of the catalytic activity. The 15 % loss of reactivity is believed to caused by loss of the solid catalyst during reaction work-up. The hectorite matrix can sometimes reduce the chemical decomposition of the interlayer guests. For example, triphenylbenzyl phosphonium and benzaldehyde in hydroxide solution will undergo the Witting reaction to form trans-stilbene[122]. When the triphenylbenzyl phosphonium ion was intercalated into the hectorite interlayer, the reaction could not be observed under the same reaction conditions. Therefore, hectorite can more or less prevent the interlayer guest from participating in the chemical reaction. Silica gel and alumina are unstable in hydroxide solution and this may limit the use of the inorganic-based catalysts for some chemical reaction. Silica gel is even unstable in cyanide solution[119]. Sodium smectite clays including hectorite are also unstable in strongly basic solutions. However, as the interlayer sodium cations of hectorite are ion-exchanged by cationic surfactants, the material is durable in this vigorous reaction environment. This organo hectorite can be recovered after use in a triphase catalysis reaction with hydroxide as a reagent and the recycled catalyst is still active.

Generally, the reactivity of triphase catalysis is less than that of biphase catalysis or homogeneous reaction with different polar aprotic compounds as solvents. The catalytic functional groups anchored on the macromolecule supports can not move as freely as the analog dissolved in liquid solution. Hexadecyltributyl phosphonium ion performs catalytic activity five times more than that of the similar phosphonium group supported on polystyrene[61]. This phosphonium ion also shows four times

more catalytic activity than the organo hectorite which contains the same equivalent of phosphonium in the hectorite interlayer. An exceptional situation is that in which the hexadecyltrimethyl ammonium hectorite is more catalytically active than the free surfactant. This surfactant proceeds by micellar catalysis[18,24,123,124] which is slower than the typical biphase catalysis that uses the onium ions with four bulky alkyl groups attached on the nitrogen or phosphine. The organo hectorite undergoes a different mechanistic process and results in a faster catalytic reaction. Polar aprotic solvents such as DMF or THF are used typically for homogeneous reactions. These solvents have strong solvation for metal cations but weak affinity for anionic nucleophiles. They can reduce the shielding of electrons in anions and strengthen the nucleophilicity of the anionic reactants. However, these kinds of chemicals are usually expensive and difficult to remove after reaction and may present environmental problems in large scale operation.

Triphase catalysts not only have the advantage of catalyst recycling, but sometimes provide various selectivities for chemical reaction, regiochemistry, or even stereochemistry. Polystyrene supported onium salts proceed by a mechanistic process similar to that of biphase catalysis. This may result in analogous products to those obtained by using these two materials as the phase transfer catalysts. For example, the O-alkylation product (Figure 7) predominates in the alkylation reaction of benzyl bromide and naphthoxide when ether polymer supported or free onium salts are used as catalysts since the alkylation reaction[61,64] occurs at the organic environment. With organo hectorite the reactions proceed in the aqueous instead of the organic phase, so the C-alkylation product predominates in this catalytic alkylation reaction. Also, when the cationic

surfactant hexadecyltrimethyl ammonium bromide is used as the micellar catalyst for the cyanization of n-bromoalkanol or 1-bromoalkane, the former reactant is much more reactive than the latter. However, as the cationic surfactant is intercalated into the hectorite interlayer and used as the triphase catalyst for the same cyanization reactions, the reactivities of both reactants are comparable. The reactant, n-bromoalkanol can change the micelle structure in micellar catalysis but 1-bromoalkane can not. However, neither of the two reactants can alter the mechanistic structure of organo hectorite triphase catalysis. Clay supported or free chiral ammonium such as the (-)-benzylquininium ion can be also used as chiral catalysts for asymmetric synthesis reactions. Very interestingly, these two materials always tend to produce the predominate enantiomeric products with opposite configuration. In borohydride reduction reactions of alkylphenylketone[125,126], epoxidation of chalcone[127] and Michael thio-addition of 2-cyclohexenone[128,129], the major enantiomeric products that results from the two chiral catalysts have opposite configurations. The orientations of the onium ion are different on hectorite and in liquid solution, leading to a different spatial constraint and resulting in opposite configurational enantiomers. Moreover, clay-supported and free chiral onium ions proceed, via asymmetric synthesis reactions in two different liquid phases. Organic hectorite proceeds by phase transfer catalysis reactions in aqueous environment but free onium ions carry out the analogous reactions in the organic phase. The difference of reaction environment may also provide a different selectivity in the asymmetric synthesis.

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