

## Bentonite Used As a Host-Matrix in the Study of Ester Hydrolysis

Duke O. Orata\* and John N. Wabomba

<sup>1,2</sup>Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya.

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**Abstract:** In this paper results obtained on the kinetics of ester adsorption on raw, acid treated and pre-heated bentonite have been presented. The infra-red profiles and the XRF spectra of the raw and acid activated bentonite have also been discussed.

The change in properties of bentonite on heating and acidification are shown to affect its adsorption characteristics. The adsorption efficiencies of bentonite are high, enhanced on acidification but diminished with pre-heating.

Infra-red spectra shows that the C=O stretching vibration of the adsorbed molecules shifted to lower frequencies compared with the carbonyl band at  $1700\text{cm}^{-1}$  in the spectra of pure esters. The Lewis and Bronsted acid sites on the raw and acidified bentonite samples were also identified from the spectra of ethyl acetate adsorbed on the raw and acidified samples.

Quantitative elemental analysis of the raw and acid treated bentonite shows changes in the amounts of cations on acidification.

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### I. Introduction

A considerable amount of work has been directed towards understanding the structure of solid surfaces. Due to lack of mobility of the particles of solids, solid surfaces are likely to be very complex in structure owing to the atoms staying where they are placed when the surface is formed. (Adams, 1941).

The study of complexes formed by clay and organic substances was initiated in the decade 1930-1940 (Raussell *et al.*, 1987). Experiments involving simple organic chemicals and pure bentonite clay soon indicated that the exchangeable, inorganic cations could be replaced by organic cations (Giesecking, 1939; Hendricks, 1944) and also that uncharged polar compounds could enter the interlayer space without cations being released, (Bradley, 1945; McEwan, 1948).

Bentonites are highly valued for their sorptive properties that stem from their tendency to absorb water in interlayer sites (Christids *et al.* 1997). It has been reported that bentonite can be used to remove cadmium and zinc ions (Gonzalez *et al.* 1994), Cu(II) (Naseem *et al.* 1999), Pb(II) (Naseem and Tahir 2001) and uranyl ions (Olguin *et al.* 1997) from aqueous solutions.

The term bentonite was first applied by Knight (1898) to a particular highly colloidal plastic clay found near Fort Benton in the cretaceous beds of Wyoming. Today however, the term is used frequently for clays with these properties without reference to a particular mode of origin.

Bentonite varies in colour from white to grey, yellow, green, blue, black but is perhaps most often yellow or yellowish green (Grim, 1953). It has a characteristic waxy appearance when freshly dug and on exposure to air it often develops a characteristic Jigsaw puzzle set of fractures accompanying the shrinking on drying.

Bentonite is a montmorillonite clay with principal intercalated cations being alkaline earth ions and alkali metal ions and a fixed amount of other components like Al, Fe and  $\text{SiO}_2$  (Theng, 1974). With regard to exchangeable cations most bentonites that have been described carry  $\text{Ca}^{++}$  as the most abundant ion (Grim, 1974), only a few are known which carry  $\text{Na}^+$  as the dominant ion and of these the Wyoming bentonite is the main example. A few bentonites have been reported that carry  $\text{H}^+$  or  $\text{K}^+$  as the dominant ions.  $\text{Mg}^{++}$  is frequently present as an exchangeable ion in relatively small amounts and this is the case when  $\text{Ca}^{++}$  is the dominant ion (Kerr *et al.*, 1936; Ross *et al.*, 1945).

Due to the fact that the layer lattice structure in bentonite is expandable, the ions and large molecules can penetrate between the sheets resulting in increased basal spacing. The ability of large organic molecules to penetrate and orient themselves along the plane of the silicate sheet has been reported (Theng, 1974).

In Kenya bentonite (Ca montmorillonite) is found at Amboseli, Athi River and in Nanyuki (Pulfrey *et al.* 1972). At Athi River, Ca Montmorillonite is found as Grey green clay at shallow beds as a matrix to gypsum modules.

## II. Experimental Section

All chemicals ethyl acetate (BDH), butyl acetate (BDH) amyl acetate (BDH) sulphuric acid (Kobian) sodium hydroxide (May and Baker) calcium chloride (Kobian) hydrochloric acid (Gowa chemicals) and methyl orange (Hopkin and Williams) were used as received without further purification. Athi-river bentonite was also used as received.

Athi river bentonite is a montmorillonite with a mesh size ranging from 150 to 200, cation exchange capacity (CEC) 1.18–1.23 m/g and a pH of 9.2 (Orata *et al.*, 1999).

In the experiments, three methods of analysis namely, conductivity (for electrical analysis), infrared spectroscopy (for structural analysis) and x-ray fluorescence (for elemental composition) were used. The electrochemical apparatus comprised of a direct conductivity measuring bridge of a PR model 950 I used in conjunction with PR model 9530 resistance box. The IR apparatus comprised of the Pye unicam SP3 model 300 IR spectrophotometer. The XRF apparatus on the other hand comprised of IBM PC fitted with an AXIL program for spectrum analysis and a QAES (75) programme for quantitative analysis.

## III. Results and Discussion

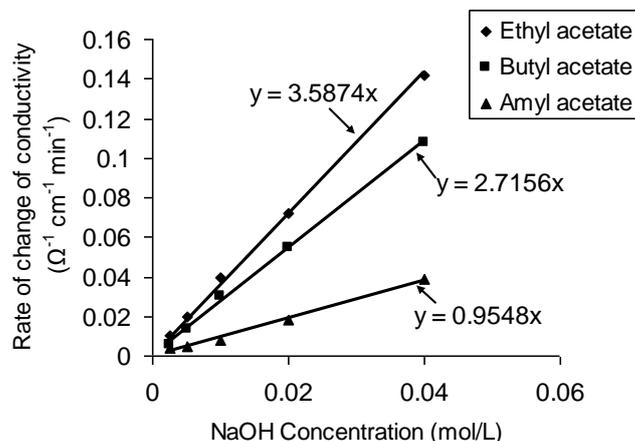
### (i) Effect of Change of Sodium Hydroxide on the Rate Of Ester Hydrolysis

In this experiment the effect of change in the concentration of NaOH on the rate of hydrolysis of three different esters was studied. The three esters studied were ethyl acetate, butyl acetate and amyl acetate.

0.4M solutions of ethyl acetate, butyl acetate and amyl acetate were freshly prepared and used in the experiments. Also 0.04M, 0.02M, 0.01M, 0.05M and 0.0025M solutions of NaOH were prepared and used each in turn to hydrolyze the esters.

The rates of hydrolysis were conductometrically determined by observing the changes in electrical conductance with time. The experiments were carried out in a constant temperature water bath maintained at 25°C.

The rates of change in conductivity for the three different esters with NaOH concentration are shown in Figure 1.



**Figure 1: Graph of rate of change of conductivity against NaOH concentration for ethyl acetate, butyl acetate and amyl acetate.**

The results show that there is incremental increase in the rate of ester hydrolysis with NaOH concentration. We propose that the slope is a measure of the efficiency of the kinetic process. Therefore, in this case the ratio of the efficiencies are 3.59: 2.72: 1.00 for Ethyl acetate: Butyl acetate: Amyl acetate respectively. These differences in the reaction rates can be attributed to steric effects resulting from molecular sizes of the different esters.

The order of the saponification reaction and the velocity constants were determined by fitting the data obtained into the three equations for first order, second order and for third order kinetics.

In all the cases it was observed that the second order rate equation gave the most concordant constant value for the velocity constant (k). This implies that hydrolysis of esters by NaOH follows second order kinetics with rates depending on both the concentration of the ester and that of the base. The average rate constant (k) for the hydrolysis of the esters were found to be 0.04654, 0.05565 and 0.03586 for ethyl acetate, butyl acetate and amyl acetate respectively.

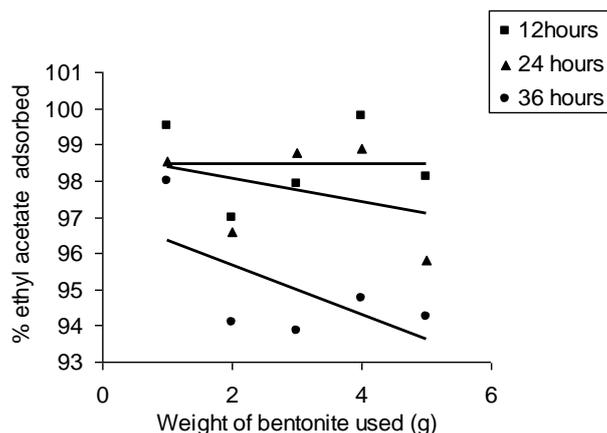
**(ii) Conductometric Determination Of Amounts Of Ethyl Acetate Adsorbed On Bentonite**

In this experiments the key objective was to study the effect of weight of the host matrix/ or solid support on the hydrolysis of ester. 1.0g, 2.0g, 3.0g, 4.0g and 5.0 gm samples of bentonite were accurately weighed in triplicate. Equal amounts of distilled water (wt/wt) were added to the bentonite-ethyl acetate mixture to generate a thin slurry. The preparations/ or slurry were left to stand for 12 hours before the volumes of the solutions were made up to 50mls.

After 12 hours the resultant solutions were filtered using the Watmann no.1 filter papers with a diameter of 125 mm. The filtrates were then kept in a constant temperature water bath maintained at 25°C and hydrolyzed by equal volumes of 0.0025M NaOH solution.

The reaction process was conductometrically monitored using a Phillips model 9501 conductivity meter. The time of mixing marked the start of the reaction. The process was repeated with the other two sets of solutions after 24 hours and 36 hours respectively

To determine the concentration of the non-adsorbed ester, the slopes of the plot of conductivity versus time obtained for the 12, 24 and 36 hour sample filtrate were mapped to those obtained from the hydrolysis of varying concentrations of ester with 0.0025M NaOH. The results obtained are shown in figure 2 below



**Figure 2: Graph of % ethyl acetate adsorbed on varying amounts of bentonite after 12, 24 and 36 hrs time intervals.**

The above results indicate that in all the cases concentration of the non-adsorbed ethyl acetate in solution increased with time. This shows that desorption of ethyl acetate from bentonite takes place progressively when the adsorbed ethyl acetate is left in contact with the solution for long.

We further observe from the results that, there is no linear relationship between the amount of ethyl acetate adsorbed and the weight of bentonite used. It is apparent that 1.0g bentonite sample recorded the highest amount of adsorbed bentonite.

This implies that in the case of bentonite, adsorption of ester is not an extensive property, hence it is probably more economical to use smaller amounts of bentonite to adsorb ethyl acetate since it adsorbs more ester more consistently than when larger amounts of bentonite are used.

**(iii) Amyl Acetate And Butyl Acetate Adsorption On Bentonite**

The procedure described in (ii) above for ethyl acetate was repeated with amyl acetate and butyl acetate respectively. From the conductivity data, results were computed and the amounts of amyl acetate and butyl acetate adsorbed on bentonite expressed in percentages as shown in Tables (i) and (ii) respectively.

**Table (I): % Butyl Acetate Adsorbed On Bentonite.**

Time interval	Mass of bentonite				
	1g	2g	3g	4g	5g
12 hours	99.55	96.8	97.25	98.55	96.5
24 hours	97.13	99.25	98.10	97.35	93.5
36 hours	97.8	94.83	94.35	92.10	92.15

**Table (ii): % Amyl Acetate Adsorbed On Bentonite.**

Time interval	Mass of bentonite				
	1g	2g	3g	4g	5g
12 hours	99.25	92.7	93.93	90.50	91.88
24 hours	99.62	96.88	93.68	95.45	90.00
36 hours	98.19	96.13	90.48	90.05	90.93

From the results above, it is clear that there is no direct relationship between the amount of ester adsorbed and the weight of bentonite used. However it is worth noting that well over 90% of the total ester initially adsorbed in both cases, remained adsorbed on bentonite throughout the 36 hour time interval considered. At this point, it is also important to note that in more than half of the experiments conducted with the different weights of bentonite, the amount of ester desorbed within the first 12 hours was found to be greater than that desorbed after 24 hours and less compared to that desorbed after 36 hours.

This indicates that for butyl and amyl acetate, the adsorption/desorption processes are in a state of dynamic equilibrium where-by the esters desorb into the solution (probably at the saturation point for the solid-liquid interphase).

We propose that the adsorption/ desorption equilibrium is strongly entropy driven. This can attributed to the fact that on adsorption of ester molecules on the host matrix/ bentonite the entropy is significantly reduced, but at the saturation point desorption is favoured entropically.

It is also possible that ‘Donnan’ like potentials are developed at the solid liquid interface and this probably also has a rudimentary effect on the ester adsorption/desorption kinetics.

Once again, we observe that after the 36 hours time interval 1.0 gram bentonite was found to retain the greatest amount of the esters initially adsorbed while the 4.0 g and 5.0g samples retained the least. This again points to the fact that as the amount of bentonite increases, its effectiveness to adsorb the ester decreases. Thus for optimum adsorption 1 gram or less of bentonite should be used to adsorb the 0.04M ester equivalents in 50mls of solution.

**(iv) Ethyl Acetate Adsorbed In Pre-Heated Bentonite**

In this experiment the objective was to establish whether there is thermal degradation in the adsorption properties of bentonite.

Three separate samples of bentonite weighing 20gms each were placed on clean, dry watch glasses. The samples were spread out on the watch glasses to facilitate uniform heating in an oven set at 150°C for 24 hrs.

On removal and after cooling, the bentonite samples were mixed and homogenized on a crucible. From heat treated sample, three sets of smaller samples weighing 1.0g, 2.0g ,3.0g ,4.0g and 5.0gms were prepared and placed in conical flasks. To each sample 0.2ml of the 10.22M ethyl acetate solution were added followed by distilled water whose weight in each case was equal to the weight of the bentonite used. This was necessary to generate thin slurry. The preparations were left to stand for 12 hrs for adsorption to take place after which 50ml solutions were made from each sample using triply de-ionised water.

The resultant solutions of the three sets of samples were left to stand for different varying lengths of time i.e. for 12, 24 and 36 hours respectively before filtering.

The filtrates were then hydrolyzed by equal volumes of 0.0025M NaOH in a constant temperature water bath maintained at 25°C. The progress of the reaction was monitored using a Phillips PR model 950I conductivity bridge.

The conductance data obtained was analyzed for the non-adsorbed ester and the results subtracted from the total ester used in each case in order to ascertain the amount of ester adsorbed. The ethyl acetate adsorbed was expressed in percentages as shown in table (iii) below.

**Table (Iii): % Ethyl Acetate Adsorbed On Pre-Heated Bentonite**

Time interval	AMOUNT OF PRE-HEATED BENTONITE USED				
	1g	2g	3g	4g	5g
12 hours	99.63	97.13	95.13	93.00	91.18
24 hours	99.13	97.13	95.00	92.50	89.25
36 hours	99.38	97.25	94.50	92.13	89.63

From the above results it is clear that there exists an inverse linear relationship between the amount of pre-heated bentonite used and its ability to adsorb ethyl acetate. This is true for all the time intervals considered i.e. 12, 24 and 36 hours respectively. The amount of ester adsorbed did not however vary considerably with time for equal weights of bentonite used. The difference in the amount of ethyl acetate adsorbed on the same weight of preheated bentonite for the 3 time intervals considered never exceeded 1%.

It is also worth noting that the ability of preheated bentonite to adsorb ethyl acetate declines by an average of 2% for each unit increase in the amount of bentonite. This suggests that better/maximum adsorption of ethyl acetate by pre-heated bentonite can be achieved when slightly less than 1.0gm of preheated bentonite is used to adsorb 0.04M ethyl acetate in 50mls of solution.

This also further suggests that bonding of organic molecules to the cations or their ingress into the bentonite matrix is mediated by a bridging water molecule, although even direct cation-organic interaction is possible with special treatment, such as preheating the clay to dehydrate the cation.

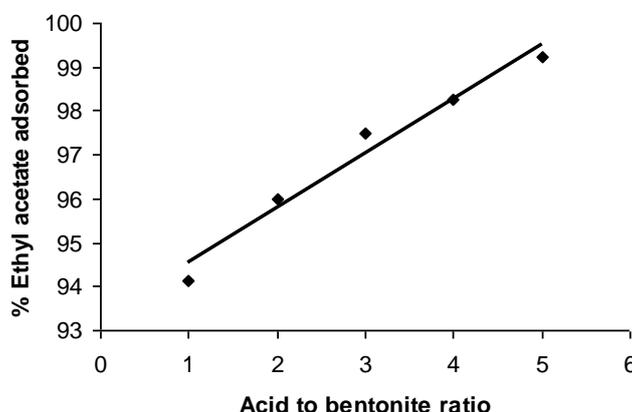
**(v) Ethyl Acetate Adsorbed On Acid Activated Bentonite.**

Several samples of bentonite were prepared by mixing the bentonite with Sulphuric acid at a pre-determined acid : solid ratio (wt/wt) i.e sample A(1:1), sample B (2:1), sample C (3:1), sample D (4:1) and sample E (5:1) for each solid.

The resulting slurry from the mixture was dried at 150<sup>0</sup> C for 24 hrs. After drying, the slurry was thoroughly washed three times with hot distilled water and the solid residue dried again in the oven at 90<sup>0</sup>C for 24 hrs. The samples A,B,C,D and E were used in the adsorption experiments involving ethyl acetate and were also subjected to IR and XRF analysis.

1.5 gms from each of the dried samples A B C D and E were taken and placed into separate flasks. To each flask containing the sample, 0.2 mls of the 10.22 M ethyl acetate solution were added followed by 1.5mls of distilled water to generate a thin a slurry. The slurry was left to stand for 12 hrs to allow for ethyl acetate adsorption to take place before the volume was made to 50ml. The resultant solutions in the flasks were then left to stand for 36 hrs, filtered and the filtrates hydrolyzed by the 0.0025 M NaOH at 25<sup>0</sup>C. The reaction was monitored conductometrically and the data obtained were analysed and the results presented as percentages of ethyl acetate adsorbed.

A plot of ethyl acetate adsorbed versus the acid : solid ratio yields a linear graph for bentonite as shown in figure 3 below.



**Figure 3: Graph of ethyl acetate adsorbed versus acid: bentonite ratio.**

It was observed that there is linear relationship between the amount of ethyl acetate adsorbed and the acid : solid ratio. This implies that the ability of bentonite to adsorb ethyl acetate can be enhanced when higher acid ratios are used .

**(vi) X.R.F Analysis Of The Raw And Acid Activated Bentonite**

X-ray fluorescence analysis was used to determine the elemental composition of raw and acid activated bentonite. The acidified samples of bentonite were prepared by mixing them with sulphuric acid at a predetermined acid to bentonite ratios(wt/wt) i.e sample A1 (1:1), sample A3 (3:1) and sample A5 (5:1). The source of radiation was <sup>109</sup> Cd. Pellet formation procedure was adopted for the sample preparation. Manual pulverization of the sample in an agate mortar helped reduce particle size to less than 50 microns. Thin pellets diluted with pure starch powder were used in the sample analysis.

In each case the sample was well spread on an area which covers the opening of the source, i.e. the measurements were performed in the same geometry as calibration procedure.

A set of 3 pellets was pressed out of each diluted sample mixture and results of complete analysis computed. Reproducibility of the results was achieved with overall accuracy obtained within 4%. Statistical errors did not exceed 2%.

The results obtained from pressed pellets made of the raw and acid activated bentonite are as shown in table (vi) below.

**Table (iv) Elemental composition of raw and acidified Bentonite**

% Metal ion concentration				
Element	Raw	A1	A3	A5
K	0.85	0.98	1.22	1.26
Ca	3.17	2.19	0.48	0.47
Mn	0.056	—	—	—
Fe	6.0	1.58	0.112	0.26
Ni	—	—	—	—
Cu	0.0034	0.0024	—	—
Zn	0.012	0.0036	—	0.0015

The data obtained indicate that the metal extraction increased with the acid : bentonite ratio. Table (vi) shows a steady increase in potassium ion ( $K^+$ ) concentration when bentonite is subjected to higher acid ratios. On average an increase of about 19% was observed for every increase in acid:bentonite ratio of 2 units. The case was however different for calcium a divalent cation. An initial drop of 31% was observed for sample A1. When the acid:bentonite ratio was increased to 3:1 (i.e. sample A3) a further drop of 53% in  $Ca^{++}$  ion concentration was noted. There was however no further significant decrease in the amount of  $Ca^{++}$  ions with increased acidification. Other cations; manganese, iron, nickel, copper and zinc were leached on increased acidification.

In general when we consider the extraction of calcium cations ( $Ca^{++}$ ), it was observe that the greatest extraction of about 50%, occurs for the case of sample A1. Not much extraction was recorded at the higher acid : bentonite ratios. Pottassium ion ( $K^+$ ) on the other hand which also like  $Ca^{++}$  occupy the inter -layer region of the clay shows quite a different trend from  $Ca^{++}$ .  $K^+$  steadily picks up with the increase in the acid - to - bentonite. The increase in the inter - layer  $K^+$  concentration is not quite clear and can be attributed to several factors ranging from impurity to its preferential retention as the other monovalent and divalent cations are leached by the acid. This explanation remains purely speculative.

The poor extraction of Calcium at higher acid : bentonite ratios can be attributed to the  $Ca^{2+}$  ions binding partially on the degraded clay structure. Fijal et.al (1975) attributed this to the attachment of  $Ca^{2+}$  ions to centres of negative charge found in certain regions of the tetrahedral layers thus capable of bonding strongly with the  $Ca^{2+}$  ions. The metal extraction pattern for Fe, an octahedral ion is quite different from that of Calcium. This is in line with the observations made by Orata and Segor (1999). Iron (Fe) shows a sharp drop of 45% for sample A1 then continues with a downward trend in all the cases when the acid : solid ratio is increased by 2 units.

The increase in  $K^+$  ion concentration with increase in the acid:clay ratio for bentonite compares well with the increase in the amount of ethyl acetate adsorbed on the acidified clays considered earlier as can be seen in table (v) and Figure 3 above. This observation is supported by the fact that uncharged (polar) organic molecules are adsorbed essentially by replacement of the interlayer water whose proportions are in turn affected by the interlayer cations.

It is thus possible that  $K^+$  ions in the interlayer spaces plays a very important role in the adsorption of ethyl acetate by bentonite.

#### **(vii) Infra – Red Spectroscopic Analysis Of Esters Adsorbed In Raw And Acidified Bentonite.**

The infra red spectra of three esters, i.e., ethyl acetate, butyl acetate and amyl acetate in their pure state and when adsorbed in raw bentonite were obtained. The pure esters were first dried for 24 hours using anhydrous calcium chloride before being analysed 3mls of each ester were separately mixed with 2g of raw bentonite and left to dry for 24 hrs. In order to ensure that the mixtures were completely dry, the dried samples were put in the oven set at  $40^{\circ}C$  for 30 minutes. Small pieces from each dry sample were uniformly ground in nujol to generate a thin clear film which was subsequently smeared and pressed in sodium chloride disks for infra red analysis. The spectra obtained are shown in Figures 4 - 10 below.

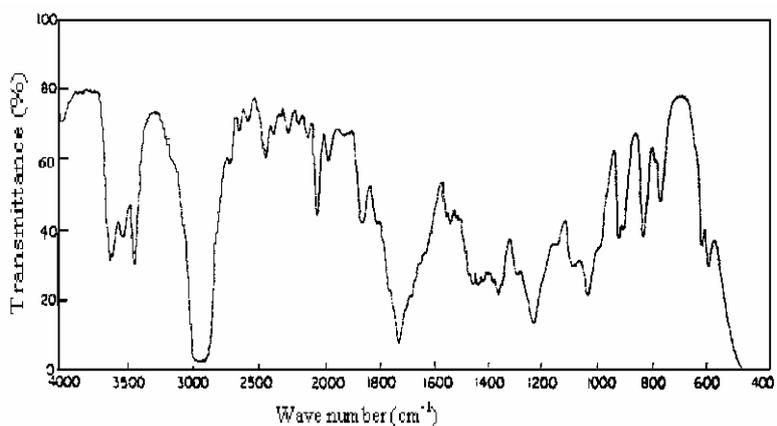


Figure 4: IR spectra of ethyl acetate

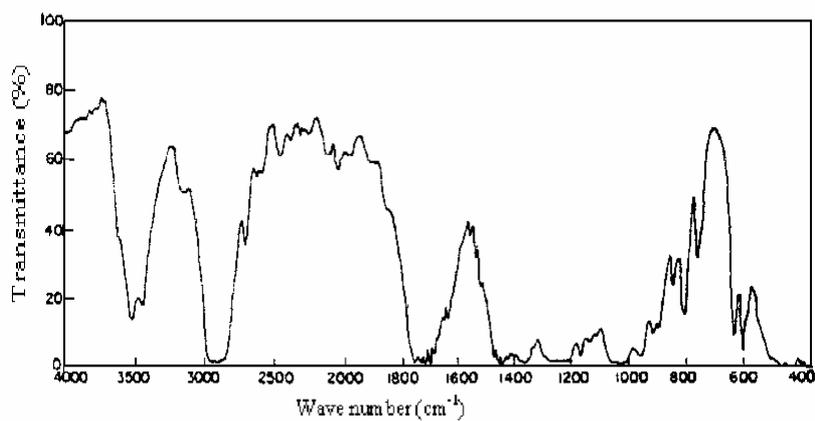


Figure 5: IR spectra of amyl acetate

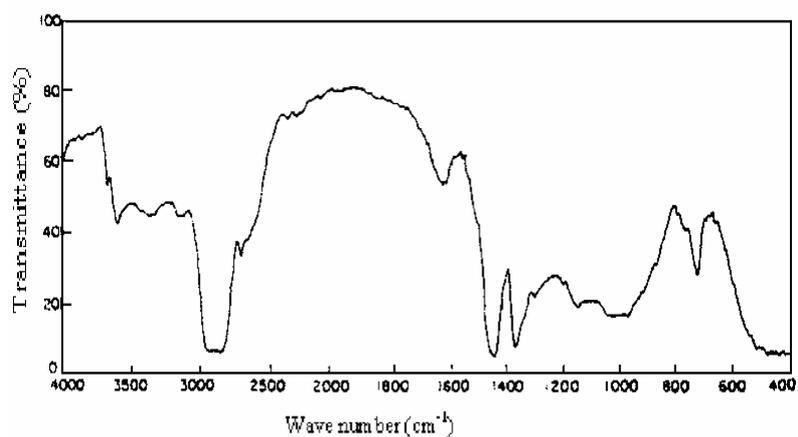


Figure 6: IR spectra of raw bentonite.

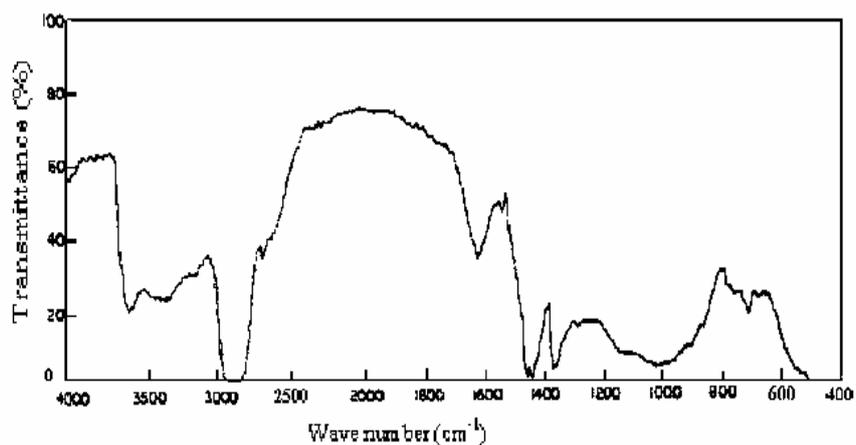


Figure 7: IR spectra of butyl acetate adsorbed on raw bentonite.

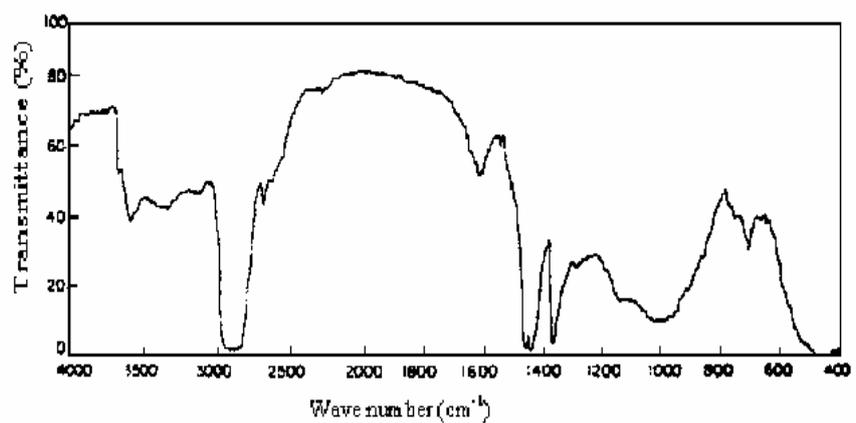


Figure 8: IR spectra of amyl acetate adsorbed on raw bentonite

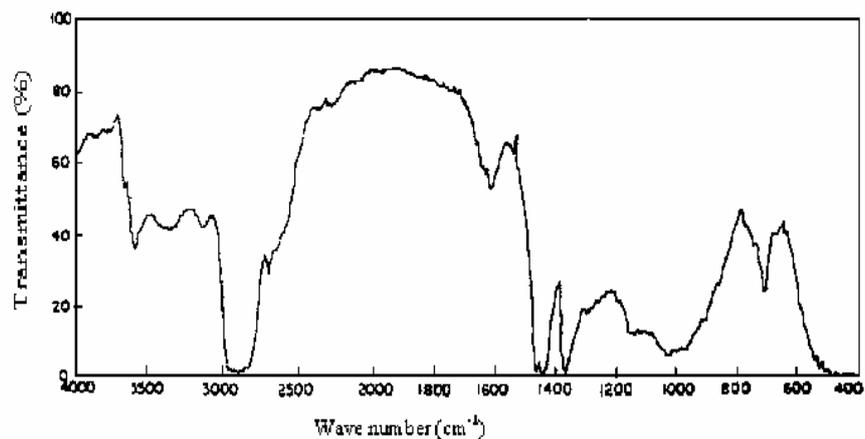


Figure 9: IR spectra of ethyl acetate adsorbed on raw bentonite.

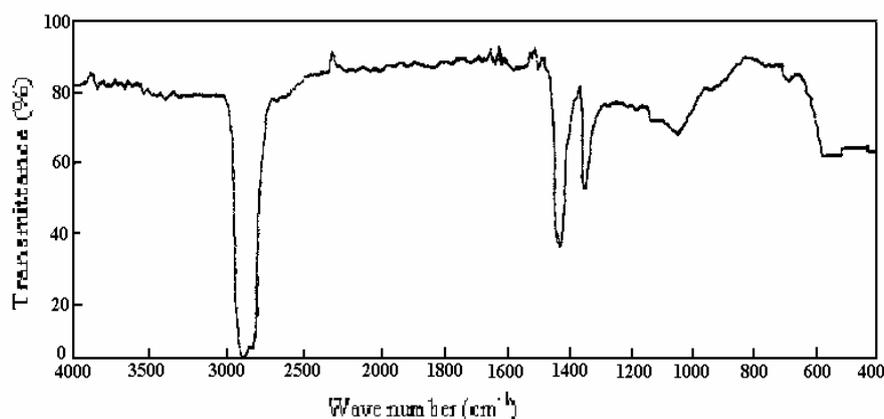
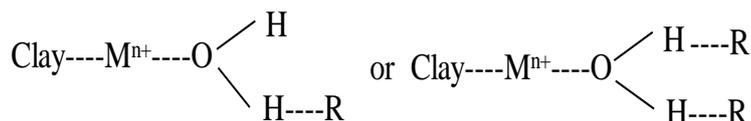


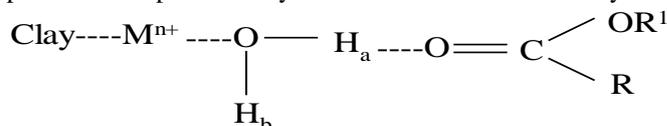
Figure 10: IR spectra of ethyl acetate adsorbed on acid activated bentonite

The infra red spectra of the complexes pressed in Sodium Chloride disks showed that the C = O stretching vibration of the adsorbed molecules shifted to a lower frequency at  $\approx 1590$  and  $1640\text{ cm}^{-1}$  (Figures 7, 8 and 9) compared with the carbonyl band at  $1700\text{ cm}^{-1}$  in the spectra of pure liquids (see Figures 4, 5). This observations together with a change in relative absorbance values of  $\approx 3590\text{ cm}^{-1}$  (free hydroxyl) and  $\approx 3380\text{ cm}^{-1}$  (bonded hydroxyl) bands of the raw bentonite (Figure 6) suggest that the carbonyl group of the esters is hydrogen bonded to hydroxyl of the silicate layer. It is, however, difficult to postulate any particular mechanism of bonding. We propose that, the esters interacts through its carbonyl group either with the inter layer cation or forms a hydrogen bond with water molecule co-ordinated to the cation depending on the polarity of the cation and the hydration status of the clay.

The existence of association via water bridges was first demonstrated for pyridine adsorbed on montimonillonite (Farmer et al, 1966) and has been shown to occur in many other systems since then. Water bridges are of the types:-



The first type of complex can be represented by the montmonillonite – ester system as:-



The evidence for the formation of the above structures is provided by the decrease in the vibration frequency of the C = O stretch i.e from  $1700\text{ cm}^{-1}$  to  $1620\text{ cm}^{-1}$  the  $\text{OH}_a$  bond is also shifted to a slightly higher position.

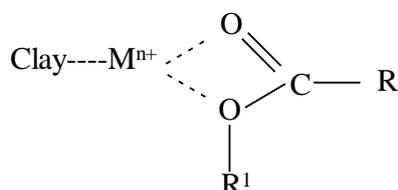
The Lewis and Bronsted acid sites on the raw and acid activated bentonite sample were also identified from the infra red spectra of ethyl acetate adsorbed in the raw and acidified samples. The spectra obtained are shown in Figures 9 and 10. In general ethyl acetate on a Lewis acid site will absorb at  $\approx 1450$  and  $1620\text{ cm}^{-1}$  whereas that adsorbed on a Bronsted acid site will absorb at  $\approx 1520\text{ cm}^{-1}$ . A band at  $\approx 1490\text{ cm}^{-1}$  suggests ester on both Lewis and Bronsted acid sites.

From the spectra (Fig. 6, 9 and 10) it is clear that the acidified bentonite sample has a higher proportion of Lewis acid sites. This is in agreement with the observations made by Orata and Segor (1999) and Mokaya et al (1992). The observation can be attributed to the fact that during metal extraction from tetrahedral layer, we are reducing the number of acid sites capable of undergoing isomorphous substitution i.e.  $\text{Fe}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral layer.  $\text{Si}^{4+}$  is affected on acidifying the montmonillonite since acidification leads to the presence of protons on the Matrix, thus increased Bronsted acidity.

In the case of ethyl acetate adsorbed in acidified bentonite (Figure. 10), it is interesting to note that the infra red spectra did not show the characteristic C = O stretching band near  $1700\text{ cm}^{-1}$  but a strong hydroxyl (bending contribution) was observed at  $\approx 1260\text{ cm}^{-1}$  and  $\approx 1410\text{ cm}^{-1}$ . Similarly strong bands corresponding to  $-\text{CH}_2-$   $-\text{CH}_3$  stretching were observed at  $\approx 2850\text{ cm}^{-1}$  and at  $2960\text{ cm}^{-1}$ . One strong band was also observed at

$\approx 1000\text{ cm}^{-1}$  and  $1300\text{ cm}^{-1}$  corresponding to C – O stretch. This can be attributed to either polymerization or clay catalysed hydrolysis of the ester into alcohol (ethanol) and other products. It might also be due to direct co-ordination to the exchangeable cation. Evidence for co-ordination is obtained from infra red spectra above showing the perturbation of characteristic vibrations of the sorbate molecules (of ethyl acetate) and the effect of the polarizing power of the cation on the displacement of the characteristic absorption frequencies.

In such a case then the complex formed by direct coordination might be of the type.



Direct coordination to the exchangeable cations has been recognized in complexes of montmorillonite with a wide variety of organic compounds such as alcohols and ketones, aliphatic and aromatic amines, nitrites and many other compounds used as pesticides. (Bailey et al, 1970)

Consequently only limited amounts of the ester can be linked by the methods described above and when amounts in excess are found present in the interlayer space, they probably are products of hydrolysis of the ester and are merely retained on the clay by adsorption forces.

#### IV. Conclusions

The results presented in this paper indicate that hydrolysis of esters by NaOH follow second order kinetics with rates depending on both the concentrations of the ester and that of the base.

It was also observed that adsorption properties of esters (especially ethyl acetate) can be altered significantly by changing the physical and chemical properties of bentonite.

Infra-red spectra showed that the C=O stretching vibration of the adsorbed molecules shifted to lower frequencies compared with the carbonyl band at  $1700\text{cm}^{-1}$  in the spectra of pure liquids. This observation points to the fact that the carbonyl group of the ester is hydrogen bonded to hydroxyl of the silicate layer. The Lewis and Bronsted acid sites on the raw and acidified bentonite samples were also identified from the infra-red spectra of ethyl acetate adsorbed in the raw and acidified samples.

XRF analysis showed that metal extraction increased with increase in acid-to-bentonite ratio. The steady increase in the inter-layer potassium ions from the initial drop can be attributed to impurities and or its preferential retention as other monovalent and divalent interlayer cations are leached by acid. The increase in potassium ion concentration with increased acidification compares well with improvement in the adsorption abilities of acidified bentonite. It can therefore be concluded that potassium ions play an important role in the adsorption of esters by bentonite.

The fact that clay minerals are cheap, have flexible adsorption properties, higher chemical stability and have potentials as catalysts and/or catalyst supports, it is worthwhile that their properties in conjunction with other organic compounds be investigated further. This could lead to improved understanding of industrial catalysis especially in the fields of purification, synthesis and pollution control.

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