

Effect of Acidification on the Adsorption Profile for Ester on Zeolite, Diatomite and Activated Carbon

¹Duke O. Orata* and ²John N. Wabomba

^{1,2}Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya.

Abstract: In this paper we report on the adsorption and catalytic properties of zeolite, diatomite and activated carbon. It is observed that, adsorption of ethyl acetate on zeolite, diatomite and charcoal is enhanced significantly on acidification, in the case of zeolite but suppressed in the case of diatomite and activated carbon. The adsorption efficiencies of zeolite, diatomite and activated charcoal are above 93% and is independent of the amount of solid used.

Infra-red spectra showed that the C=O stretching vibration of the adsorbed molecules shifted to lower frequencies compared to carbonyl band at 1700cm^{-1} observed in the spectra of pure ester. The Lewis and Bronsted acid sites on zeolite samples were also identified from the infra-red spectra of ethyl acetate adsorbed on both raw and acidified samples. Quantitative elemental analysis shows changes in the amounts of cations on increased acidification which correlates to the amount of ester adsorbed.

I. Introduction

In the recent past, the study of clay-organic interaction has been extensive and important generalizations have emerged in the understanding of the reaction mechanism¹. Clay montmorillonites such as bentonite have been effectively used as adsorbents for both organic chemicals and heavy metals. Bentonites are known for their sorptive properties, which results from their high surface area and their tendency to absorb water in the interlayer sites.^{2, 3, 4}

Quantitative analytical determinations of the amount substance adsorbed at a fixed temperature (adsorption isotherm), has facilitated/enabled studies on replacement of inorganic by organic cations. It is thus now possible to estimate the number of neutral molecules associated with each exchangeable cation. Mechanisms of interaction between adsorbed molecules and the silicate surfaces have been postulated with the help of chemical and x-ray studies.¹

It has also been proposed that, H-bonds of the type $\text{NH}\dots\text{O}$, $\text{OH}\dots\text{O}$ and also $\text{CH}\dots\text{O}$ and Van-der-Waal's forces give stability to the organic complexes.

Adsorption chemistry is key in the treatment of polluted waste streams and today efforts are being made to utilize cost effective alternative technologies that include the use of solid sorbents such as activated carbon, natural zeolites, agricultural wastes, bio-mass and clay materials in the treatment of chemically contaminated streams particularly for the developing countries.^{5, 6}

Detailed discussion on the chemistry of zeolites, diatomite and activated carbon are found in references 7-14 and references therein.

In this paper results on the kinetics of adsorption of ethyl acetate on diatomite, zeolite and activated charcoal have been presented.

II. Experimental Section

In the experiments conducted, conductivity measuring units, infrared spectroscopy and x-ray fluorescence spectrophotometer were used.

The electrochemical apparatus comprised of a direct conductivity measuring bridge PR model 9501 used in conjunction with PR model 9530 resistance box. The IR apparatus was a Pye-unicam SP3 model 300 IR spectrophotometer. The XRF spectrophotometer comprised of IBM PC fitted with an AXIL program for spectrum analysis and a QAES (75) programme for quantitative analysis.

All the chemicals used - 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.

The activated charcoal (Howse and McGeorge) Diatomaceous brick dust (May and Baker), natural zeolite (BDH) and Athi river bentonite were also used as received.

The diatomaceous brick dust has a mesh size of 60-100, particle size of 0.15-0.25mm, loss on drying not more than 0.5% at 105°C and compacted density of about 400g per litre. Zeolite 625 (standard grade) on the other hand has a mash size of BSS 14-30, wet density (apparent) 0.84g/ml, exchange capacity wet 1.8 meq/vl, max.operating temperature of 120°C and pH range of 1-14.

The Athi river bentonite has a mesh size ranging from 150 to 200, a pH of 9.2 and a cation exchange capacity (CEC) 1. 18 –1.23 mM/g and a pH of 9.2 (Orata *et al*, 1999).

III. Results and Discussion

Conductometric Determination of Amounts Of Ethyl Acetate Adsorbed On Solid Support/Host Matrix.

(i) Ethyl acetate adsorbed on zeolite

In the set of experiments to be discussed the key objective was to study the effect of solid support/host matrix (zeolite, bentonite, activated carbon and diatomite) on the hydrolysis of esters. Samples of zeolite weighing 1.0g, 2.0g, 3.0g, 4.0g and 5g were accurately measured in triplicate. Equal amounts of distilled water (wt/wt) were added to the zeolite -ethyl acetate mixture to generate a thin slurry. The slurry was left to stand for 12 hours before the volumes of the solutions were made upto 50mls.

After 12 hours one set of the resultant solutions was filtered using the Watmann no.1 filter paper with a diameter of 125 mm. The filtrate temperature was kept constant 25°C and hydrolyzed by equal volumes of 0.0025M NaOH solution.

Conductivity measurements were made, with the time of mixing being the zero point of the reaction. The process was repeated with the other 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 for the solutions were matched to those obtained from the hydrolysis of varying concentrations of ester with 0.0025M NaOH. The results obtained are shown in Table 1 below

Table 1: Amount (%) of ethyl acetate adsorbed on natural zeolite

TIME INTERVAL (hrs)	MASS OF ZEOLITE				
	1.0g	2.0g	3.0g	4.0g	5.0g
12	99.65	99.94	99.85	99.80	99.65
24	99.70	99.95	99.90	99.81	99.70
36	99.66	99.96	99.86	99.78	99.65

(ii) Ethyl acetate adsorbed in, Diatomite and Activated Carbon

The procedure for the adsorption of ethyl acetate on diatomite and activated carbon and the subsequent hydrolysis is similar to that described in (i). The hydrolysis of the non-adsorbed ethyl acetate in the filtered solutions was monitored by observing the changes in electrical conductance during the reaction process. The reaction temperature was maintained at 25°C. The data obtained was analyzed and the results presented as percentages shown in Tables 2 and 3 respectively.

Table 2: % Ethyl acetate adsorbed on diatomite

TIME INTERVAL	MASS OF DIATOMITE				
	1.0g	2.0g	3.0g	4.0g	5.0g
12 hours	99.51	99.55	99.58	99.63	99.64
24 hours	99.45	99.46	99.53	99.53	99.63
36 hours	99.40	99.43	99.50	99.55	99.60

Table 3: % Ethyl acetate adsorbed on activated carbon

TIME INTERVAL	MASS OF ACTIVATED CARBON				
	1.0g	2.0g	3.0g	4.0g	5.0g
12 hours	99.93	99.84	99.45	99.57	98.83
24 hours	99.90	99.58	99.48	99.15	98.45
36 hours	99.87	99.55	99.57	99.00	98.10

The results show that all the three solid supports considered i.e. zeolite, diatomite and activate carbon are excellent adsorbents of ethyl acetate. Well over 98% of the ethyl acetate remained adsorbed on the different quantities of the solids used throughout the time of study. It is however, important to note that, the threshold for effective adsorption peaks at 1.0g of the solid host matrix. This can be remotely considered as the adsorption saturation point as no significant changes are observed for the higher masses.

In the case of diatomite we observe slight increase in the amount of ethyl acetate adsorbed with increasing amount of diatomite. While for activated carbon and zeolite we observe a decrease in the amount of ester adsorbed as the amount of solid host matrix is increased. The effect is however more pronounced in activated carbon than in zeolite.

When similar experiments were repeated but now in a solution of 0.04M Ethyl acetate in 50mls of solution, maximum ester adsorption was obtained in the case of 1.0gm of activated charcoal, 2.0gms of zeolite and 5.0gms of diatomite.

(iii) Ethyl acetate adsorbed on acid-activated zeolite, diatomite and activated charcoal.

Several samples of acid activated zeolite, diatomite and charcoal were prepared by mixing the solids 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 150⁰ C for 24 hrs. After drying, the slurry was washed repeatedly with hot distilled water and the solid residue dried again in the oven at 90⁰C 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 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 25⁰C.

Conductivity measurements were made as already described. The percentages of ethyl acetate adsorbed as shown in Figure 1 below.

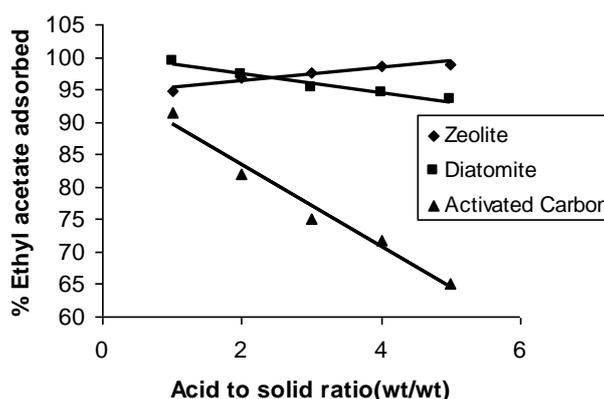


Figure 1: Graph of (%) ethyl acetate adsorbed versus acid:solid ratio for the different solid supports.

Plots of ethyl acetate adsorbed versus the acid : solid ratio yields linear graphs for the different solid host matrices used.

For zeolite it was observed that there is an almost direct linear relationship between the amount of ethyl acetate adsorbed and the acid : solid ratio. The situation is however different for diatomite and activated carbon whereby the amount of ethyl acetate adsorbed is inversely proportional to the acid : solid ratio. The ethyl acetate adsorbed decreases with the increase in the acid : solid ratio. This implies that the ability of zeolite to adsorb ethyl acetate can be enhanced when higher acid ratios are used .

For diatomite and charcoal, adsorption abilities are significantly reduced on acidification. The rate of decrease in the amount of ethyl acetate adsorbed versus the acid to solid ratio is greater in the case of activated charcoal as compared to diatomite.

In the case of activated carbon, for every increase by one unit of acid in the acid : solid ratio, the ability to adsorb ethyl acetate diminishes by an average of 7.02 % . The decline in diatomite is about 1.53% for every increase by one unit of acid in the acid to solid ratio. On the other hand there is no significant increase in the % ethyl acetate adsorbed versus the acid : solid ratio in the case of zeolite. We propose that, the observed effect of acidification on the adsorption profile of the ester on the solid host matrices, is a function of the population of 'adsorbable' active protons on the solid host matrix, with the latter depending on the nature of the solid support.

(iv) X.R.F analysis of the raw and acid activated solid samples

X-ray fluorescence analysis was used to determine the elemental composition of raw and acid activated zeolite diatomite, and activated charcoal. The acidified samples of zeolite diatomite and activated carbon were prepared by mixing the solid support with conc. sulphuric acid at a predetermined acid to clay ratios(wt/wt) i.e sample A1 (1:1), sample A3 (3:1) and sample A5 (5:1). The source of radiation was ¹⁰⁹Cd. 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 pallets 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 didn't exceed 2%.

The results obtained from pressed pellets made of the raw and acid activated zeolite, diatomite and activated carbon are as shown in Tables 4-6 below.

Table 4: Elemental composition of raw and acidified charcoal.

ELEMENT	% METAL CONCENTRATION			
	Raw	A1	A3	A5
K	1.14	—	0.26	0.12
Ca	1.69	0.25	0.1	0.17
Mn	0.12	0.01	0.014	0.015
Fe	0.0628	0.02	0.044	0.0663
Ni	—	—	—	—
Cu	0.0012	0.0052	0.0021	0.004
Zn	0.001	0.0027	0.0025	0.0065

Table 5: Elemental composition of raw and acidified diatomite

ELEMENT	% METAL CONCENTRATION			
	Raw	A1	A3	A5
K	1.4	0.73	0.88	1.25
Ca	1.3	0.61	0.6	0.68
Mn	0.0219	—	0.026	—
Fe	1.64	0.73	0.8	0.97
Ni	0.0062	0.0052	0.0079	—
Cu	0.0077	0.0043	0.0044	0.0021
Zn	0.0135	0.0074	0.0096	0.0068

Table 6: Elemental composition of raw and acidified zeolite

ELEMENT	% METAL CONCENTRATION			
	Raw	A1	A3	A5
K	3.81	3.15	3.56	4.94
Ca	0.60	0.35	0.34	0.30
Mn	0.0264	0.0101	—	0.015
Fe	10.80	9.49	10.52	13.5
Ni	—	—	—	—
Cu	0.0013	0.0039	—	—
Zn	0.0103	0.0084	0.0074	0.009

The data obtained in the indicate that in all the cases studied the metal extraction increased with the acid : solid ratio. When we consider the extraction of calcium cations

(Ca^{++}), we observe that the greatest extraction of about 50%, occurs for the case of sample A1. Not much extraction was recorded at the higher acid : solid ratios. Potassium ion (K^+) on the other hand which also like Ca^{++} occupy the inter -layer region of the clay montmorillonite shows quite a different trend from Ca^{++} . K^+ in all the cases except for activated carbon shows a slight drop of about 17% (in the case of zeolite and diatomite) for sample A1 then steadily picks up with the increase in the acid :zeolite. 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.

The poor extraction of Calcium at higher acid : solid ratios can be attributed to the Ca^{2+} ions binding partially on the degraded clay structure. This can be attributed 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 Segor and Orata.¹⁶ (1999). Iron (Fe) shows a sharp drop of 45% for sample A1 then picks up steadily with an average of 18% in all the cases when the acid :solid ratio is increased by 2 units.

The case of steady increase in K^+ ion concentration with increase in the acid : clay ratio for zeolite compares well with the increase in the amount of ethyl acetate adsorbed on the acidified clays considered earlier (see Figure 1). 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.

Thus, it is possible that, K^+ ions in the interlayer spaces plays a very important role in the adsorption of ethyl acetate by zeolite. Similarly, the decrease in K^+ ions concentration with the increasing acid : carbon ratio correlates well with the decrease in the amount of ethyl acetate adsorbed in activated carbon.

(v) Infra – red spectroscopic analysis of esters adsorbed in raw and acidified zeolite, diatomite and activated carbon.

The infra red spectra of ethyl acetate in its pure state and when adsorbed in raw and acid activated zeolite, diatomite and activated carbon were obtained. The pure ester was first dried for 24 hours using anhydrous calcium chloride before being analysed.

3.0mls of the ester were separately mixed with 2g of the solid 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 40⁰ 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 2 – 8.

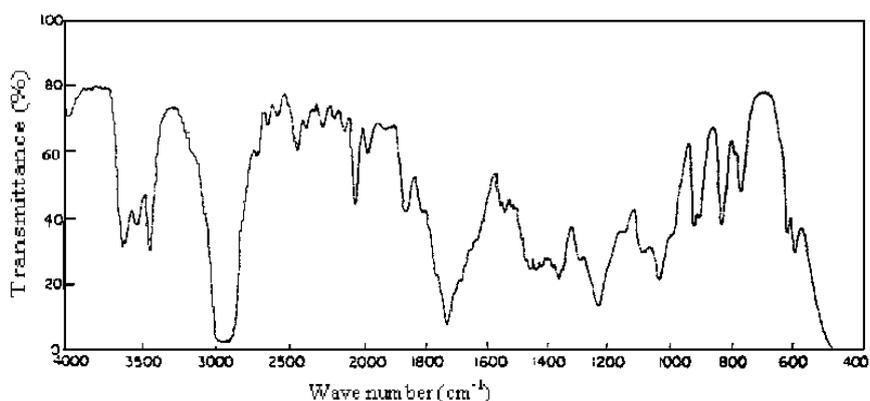


Figure 2: IR spectra of ethyl acetate.

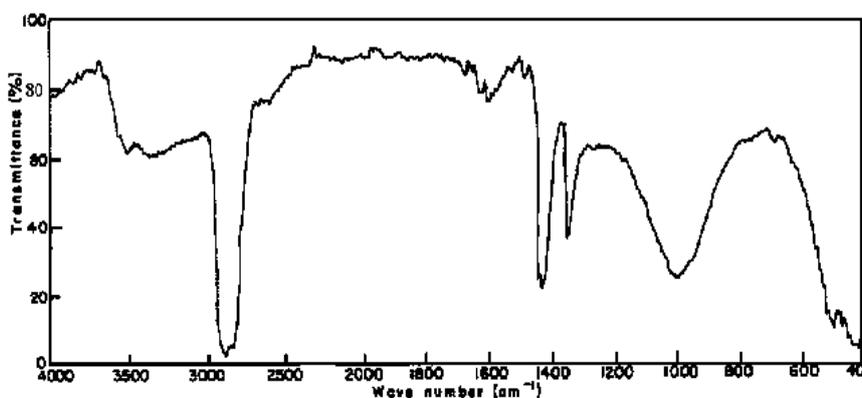


Figure 3: IR spectra of ethyl acetate adsorbed on raw zeolite.

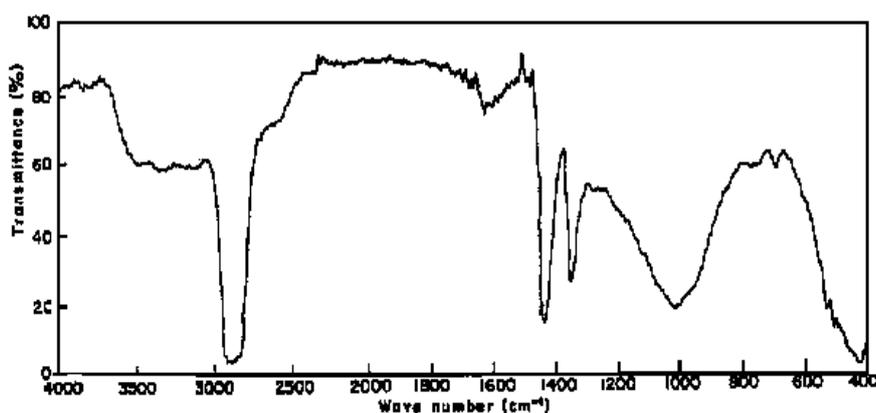


Figure 4: IR spectra of ethyl acetate adsorbed on acid activated zeolite.

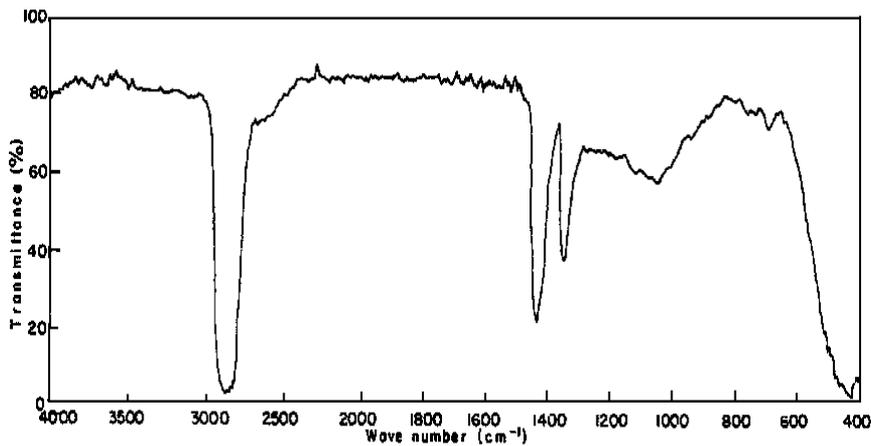


Figure 5: IR spectra of ethyl acetate adsorbed on raw diatomite.

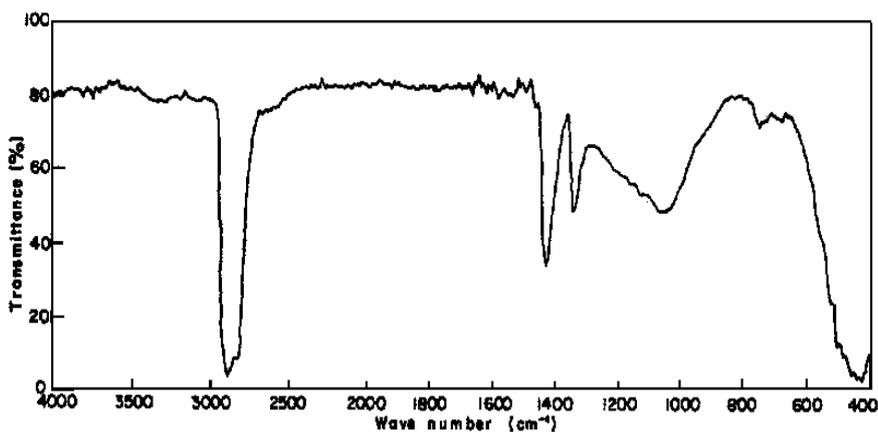


Figure 6: IR spectra of ethyl acetate adsorbed on acid activated diatomite.

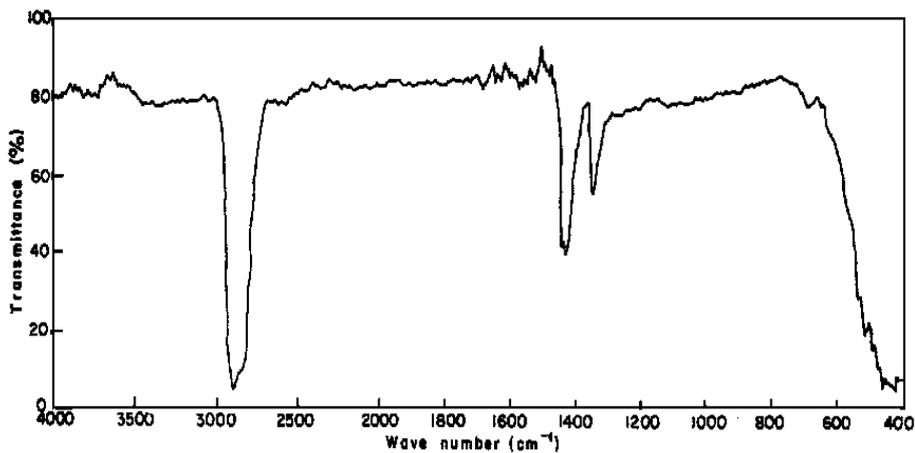


Figure 7: IR spectra of ethyl acetate adsorbed on raw charcoal.

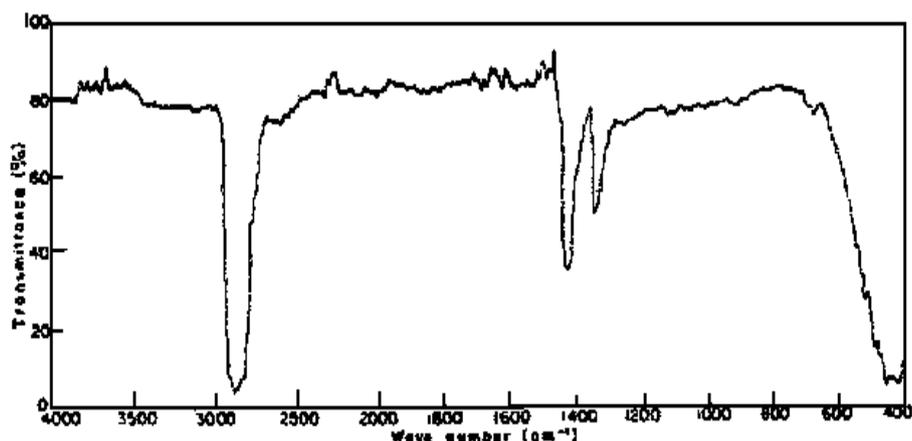
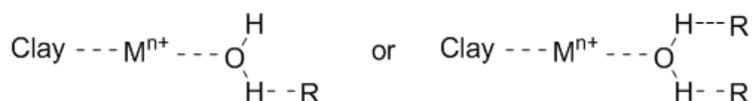
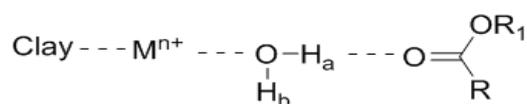


Figure 8: IR spectra of ethyl acetate adsorbed on acid activated charcoal.

The infra red spectra of the zeolite- ester complexes pressed in Sodium Chloride disks showed that the C = O stretching vibration of the adsorbed molecules shifted to a lower frequency at ≈ 1590 and 1640 cm^{-1} (see Figs. 3 and 4) compared with the carbonyl band at 1700 cm^{-1} in the spectra of pure ester (see Fig. 2,). 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 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 zeolite. The existence of association via water bridges was first demonstrated for pyridine adsorbed on montmorillonite¹⁷ 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 montmorillonite – 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 cm^{-1} to 1620 cm^{-1} the OH_a bond is also shifted to a slightly higher position.

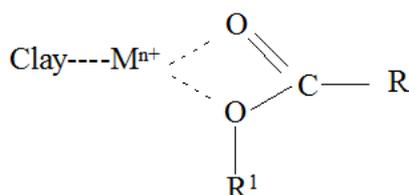
Observations for the existence of Bronsted and Lewis acid sites were made with the raw and acid activated zeolite (see in Fig. 3 and 4.). The spectra can be interpreted as showing evidence of the chemisorption of ethyl acetate at both aprotic and protic sites. The band at $\approx 1450\text{ cm}^{-1}$ can be considered diagnostic for the Lewis site and that at $\approx 1550\text{ cm}^{-1}$ for the Bronsted site. 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. Fe^{3+} for Si^{4+} in the tetrahedral layer.

Si^{4+} is affected on acidifying the montmorillonite since acidification leads to the presence of protons on the matrix, thus increased Bronsted acidity. This is in agreement with the observations made by Segor and Orata¹⁶ (1999) and Mokaya et. al.¹⁸ (1992).

In the case of ethyl acetate adsorbed in acidified diatomite and activated charcoal (see Fig. 6 and 8) and in raw diatomite and raw activated charcoal, (see Fig. 5 and 7), it is interesting to note that the infra red spectra did not show the characteristic C = O stretching band near 1700 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 $>CH_2 - CH_3$ stretching were observed at $\approx 2850\text{ cm}^{-1}$ and at 2960 cm^{-1} . One strong band was also observed at $\approx 1000\text{ cm}^{-1}$ and 1300 cm^{-1} corresponding to C – O stretch in all the cases except for the raw and acidified charcoal (see fig.7 and 8). This can be attributed to either polymerization or solid 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.¹⁹

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/charcoal by adsorption forces.

IV. Conclusion

The three solid supports considered - zeolite, diatomite and activated carbon exhibit have excellent adsorption properties for esters.

The results presented indicate that adsorption kinetics of ethyl acetate can be altered significantly by changing the chemical properties of zeolite, diatomite and activated charcoal.

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

The XRF analysis indicate that metal extraction increases with increase in acid-to-solid ratio.

References

- [1]. Rausell-colon J.A and Serratos. J.M (1987). Reactions of clays with organic substances; in chemistry of clay and clay minerals, Longman Scientific and technical publications. pp., 371-382.
- [2]. Christids, G.E., Scott, P.W., and Dunham, A.C., (1997) Appl. Clay Sci. 12, 329-347.
- [3]. Naseem, R., Ikram, M., and Tahir, S.S., (1999) Adsorption Sci. Technol. 17(5), 431-440.
- [4]. Naseem, R. and Tahir, S.S., (2001) Water Res. 35(16), 3982-3986.
- [5]. Bailey, S.E., Olin, T.J., Bricka, R.M. and Adrian, D.D. (1999) Water Res. 33, 2469-2479.
- [6]. Volesky, B., and Holan, Z.R. (1995) Biotechnol. Prog. 11, 235-250.
- [7]. Sand L. B and Mumpton F. A. (1976) Natural Zeolites; Occurrence, properties and use pergamon press U.K., pp. 1-27.
- [8]. Lenntech (2006) Water Treatment and Air Purification; Substance Removal by Zeolites. Rotterdamseweg, Delft, Netherlands. www.lenntech.com/zeolites-removal., pp. 1-3.
- [9]. Robinson, S. M., Kent, T. E. & Arnold, W. D. (1995) in **Natural Zeolites** Occurrence, Properties, Use, eds. Ming, D. W. & Mumpton, F. A. (Int. Comm. Nat. Zeolites, Brockport, NY), pp. 579-586
- [10]. Donat R., Erdem E., and Karapinar N. (2004). The Removal of Heavy Metal Cations by Natural Zeolites. Colloids And Interface Science 280. 309-314.
- [11]. Deeson A.F.L (1973) The collectors encyclopedia of rocks and minerals, clarckson N. Potter inc/publishers Great Britain.
- [12]. Hockey. J.A (1965) chemistry and industry 2. 57.
- [13]. Raymond E.K (1950) Encyclopedia of chemical technology 5, 33-37.
- [14]. Wolfgang G. Ed. (1986) Ullman's Encyclopaedia of industrial chemistry 5th ed. A7, 109 -132.
- [15]. IUPAC (1972) Mannual of Definitions, Terminology and symbols in colloid and surface industry.
- [16]. Orata. D and Segor F. (1999) Bentonite as a template for electrosynthesis of thyroxine; Catalysis Letters, 58,157-162.
- [17]. Farmer . V.C and Mortland. M.M (1966) Infrared study of the coordination of pyridine and water to exchangeable Cations in Montmorillonite and Saponite J. Chem. Soc., A, 344-351.
- [18]. Mokaya R. and Jones. W. (1992) in Ion exchange processes advances and applications., pp., 244-252.
- [19]. Bailey. G.W and White. J.L (1970) Adsorption of pesticides in soil Residue Rev 32, 29-92.