

## Heats of Adsorption of Aliphatic Alcohols on $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 25–200°C. II. Variations with Chain Length

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**ABSTRACT:** The adsorption of the first five members of the aliphatic alcohol series on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has been studied at 25–200°C by means of a heat-flow Calvet microcalorimeter (moderately high temperature). At very low coverage and at 25°C, the values of the differential heats of adsorption of the different alcohols were very high (250–200 kJ/mol) and were apparently independent of the chain length. However, at average coverage, the chain length of the alcohol began to influence both the values and the trends in the differential heats of adsorption of the various alcohols on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Finally, at high coverage, it was found that the incorporation of each additional –CH<sub>2</sub>– group in the homologous series led to a decrease in both the integral heat of adsorption and the amount of alcohol adsorbed according to the series MeOH > EtOH > 1-PrOH > 1-BuOH > 1-PeOH. Increasing the temperature led to an increasing dependence of the differential heat on the chain length of the alcohol.

In addition, from measurements of the thermokinetic parameters for the heat emission peaks for the adsorbed alcohols, it has been deduced that all five aliphatic alcohols studied adsorb on to an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface in an open-chain perpendicular fashion.

## INTRODUCTION

This paper describes further studies of the adsorption of the first five members of the aliphatic alcohol series on to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> over the temperature range 25–200°C in order to understand more fully the gas–solid interactions which occur through the use of adsorption microcalorimetry. In a previous work (Rossi and Rossi 1996) we reported on a study of the influence of the experimental temperature on variations in the heats of adsorption and the amounts of alcohol adsorbed on to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In the present work, the variations in the heats of adsorption (both integral and differential) and in the amounts of the various alcohols adsorbed on to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> have been studied in terms of the hydrocarbon chain length or molecular weight for the first five members of the homologous series of aliphatic alcohols.

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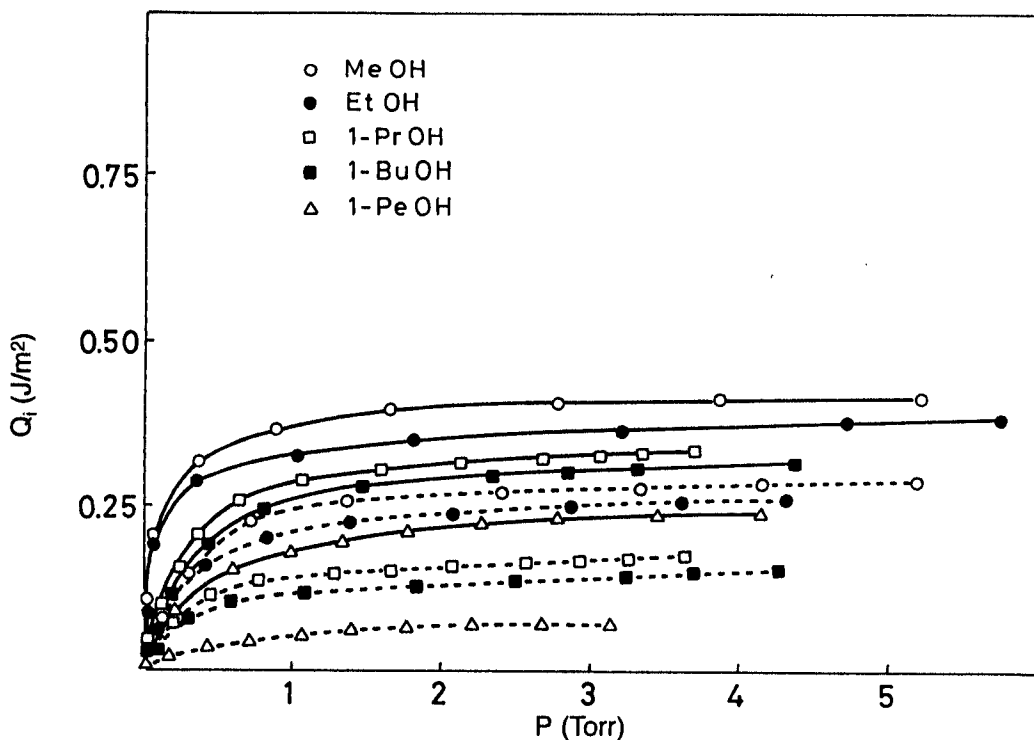
## EXPERIMENTAL

### Materials

The sample of alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) employed and the different alcohols used were the same as those described in a previous work (Rossi and Rossi 1996). For simplicity, these alcohols are denoted throughout the text as MeOH (methanol), EtOH (ethanol), 1-PrOH (propan-1-ol), 1-BuOH (butan-1-ol) and 1-PeOH (pentan-1-ol). The pretreatment of the alumina samples and the activation conditions employed at various temperatures and pressures prior to their use in adsorption experiments were the same as described previously.

### Microcalorimetric apparatus

The microcalorimetric assembly (Calvet microcalorimeter, moderately high temperature) and its connection to a volumetric Pyrex ramp was the same as described previously (Rossi and Rossi 1996). Measurements of the calorimetric peak areas and the volumetric isotherms which give the total integral heat ( $Q_i$ ) and total adsorption, respectively, as a function of pressure have already been reported (Rossi and Rossi 1996). In addition, the differential heat of adsorption ( $q_{diff}$ ) obtained by differentiation of the integral function with respect to the amount of the various alcohols adsorbed ( $n_a$ ) has already been discussed (Rossi and Rossi 1996; Rossi *et al.* 1990).



**Figure 1.** Calorimetric isotherms for five aliphatic alcohols adsorbed on to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (continuous line corresponds to data measured at 25°C and dashed line to data measured at 200°C).

## RESULTS AND DISCUSSION

Figure 1 shows the calorimetric isotherms for the adsorption of the five aliphatic alcohols on  $\alpha$ - $\text{Al}_2\text{O}_3$  at 25°C and 200°C, respectively (the continuous line corresponding to 25°C and the dashed line to 200°C). For the sake of convenience, we have not reported the calorimetric isotherms for the alcohols at 50, 100 and 150°C since the trends observed were similar to those at 25°C and 200°C. In addition and in all cases, the values of the integral heats were found to fall as the temperature increased in the range 25°C  $\rightarrow$  200°C. This effect is similar to that described in our previous work (Rossi and Rossi 1996) where we pointed out that the integral heats of the five alcohols studied all diminished as the temperature increased from 25°C to 200°C. At both these temperatures, the additional of a further  $-\text{CH}_2-$  group to each alcohol leads to a decrease in the integral heat (Figure 1). In addition, the integral heats exchanged irreversibly and those exchanged reversibly per unit surface area of the adsorbent decreased with increasing molecular weight in the series  $\text{MeOH} > \text{EtOH} > 1\text{-PrOH} > 1\text{-BuOH} > 1\text{-PeOH}$ . This trend is very similar to that observed for the adsorption of four aliphatic alcohols on a controlled-pore glass (Jednacak-Biscan and Pravdic 1980).

In Figure 2 the corresponding trend for  $Q_i/\text{M.W.}$  (where M.W. is the molecular weight of the alcohol) is shown for the five alcohols studied as a function of the number of carbon atoms contained. This ratio decreases at all temperatures as the chain length of the alcohols adsorbed increases. The value of this ratio may be related to the number of active sites on the  $\alpha$ - $\text{Al}_2\text{O}_3$  surface at which the strongly adsorbed molecules are attached. The decrease in this ratio as a

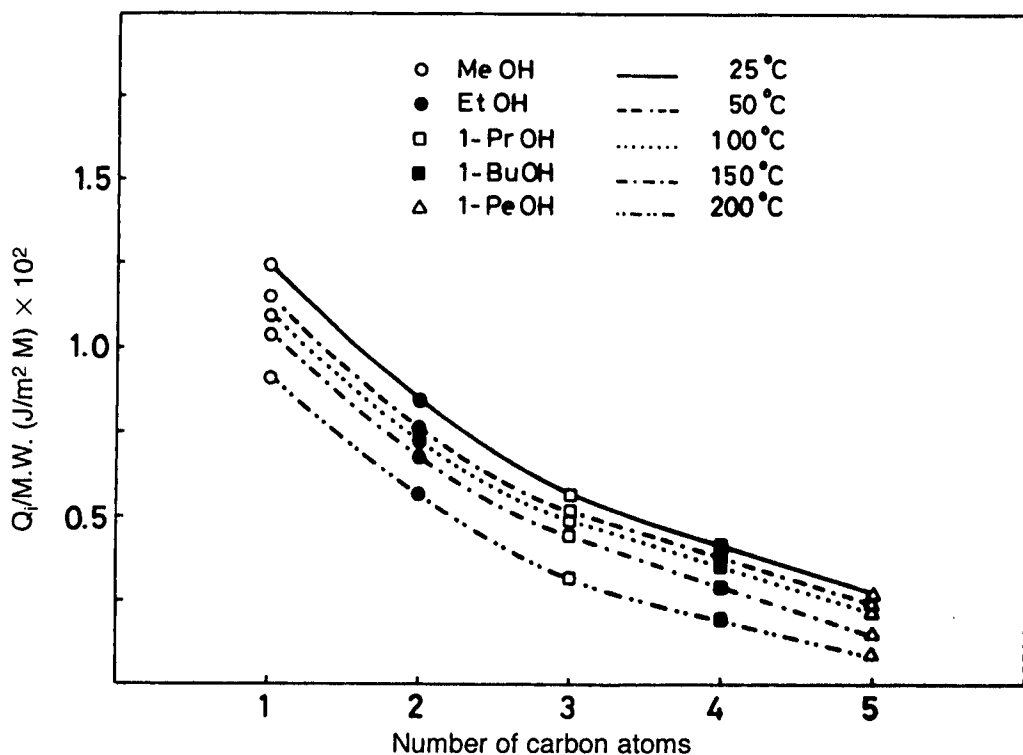


Figure 2. Variation in the integral heat of adsorption/molecular weight ratio for five aliphatic alcohols adsorbed on to  $\alpha$ - $\text{Al}_2\text{O}_3$  as a function of the number of carbon atoms in the alcohol for various temperatures.

function of the molecular weight of the alcohol may be related to the molecular areas of the alcohols concerned. Thus, the molecular area of methanol is without doubt smaller than that of the other alcohols and, in particular, the area of adsorbent covered by 1-PeOH is larger than that covered by the smaller methanol molecules [ $\sigma_a = 21.9 \text{ \AA}$  for methanol and  $\sigma_s = 38.8 \text{ \AA}$  for 1-pentanol — average  $\sigma$  values calculated from adsorption measurements (McClellan and Harnsberger 1967)].

Figure 3 shows the volumetric isotherms for the adsorption of the five aliphatic alcohols on to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 25°C and 200°C (the continuous line refers to 25°C and the dashed line to 200°C). In the interests of clarity we have again omitted the analogous volumetric isotherms for the same alcohols measured at temperatures of 50, 100 and 150°C, since they fall within the range of values covered by those at 25°C and 200°C. As far as the data depicted in Figure 3 are concerned, it should first be noted that, at higher pressures, all the isotherms are characterized by a plateau which is virtually horizontal, and consequently they may be classified as type I indicating almost complete monolayer coverage with no multilayer adsorption (Gregg and Sing 1982). Secondly, the amounts of the five alcohols either irreversibly or reversibly adsorbed on to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> decreased as the molecular weights of the alcohols increase at all the experimental temperatures studied. The extent of such decrease is very similar at all temperatures, in accordance with the range previously described.

This range is similar to that reported by Barto *et al.* (1966) with respect to the adsorption of four aliphatic alcohols on two different samples of alumina and by Jones and Wade (1968) for the

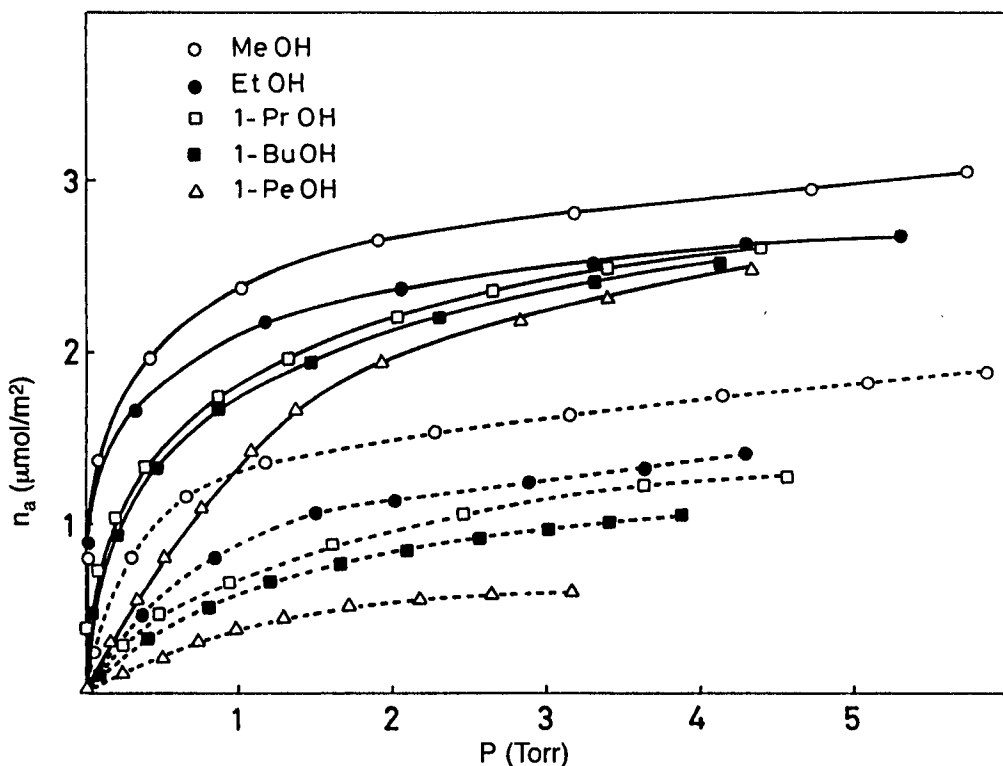
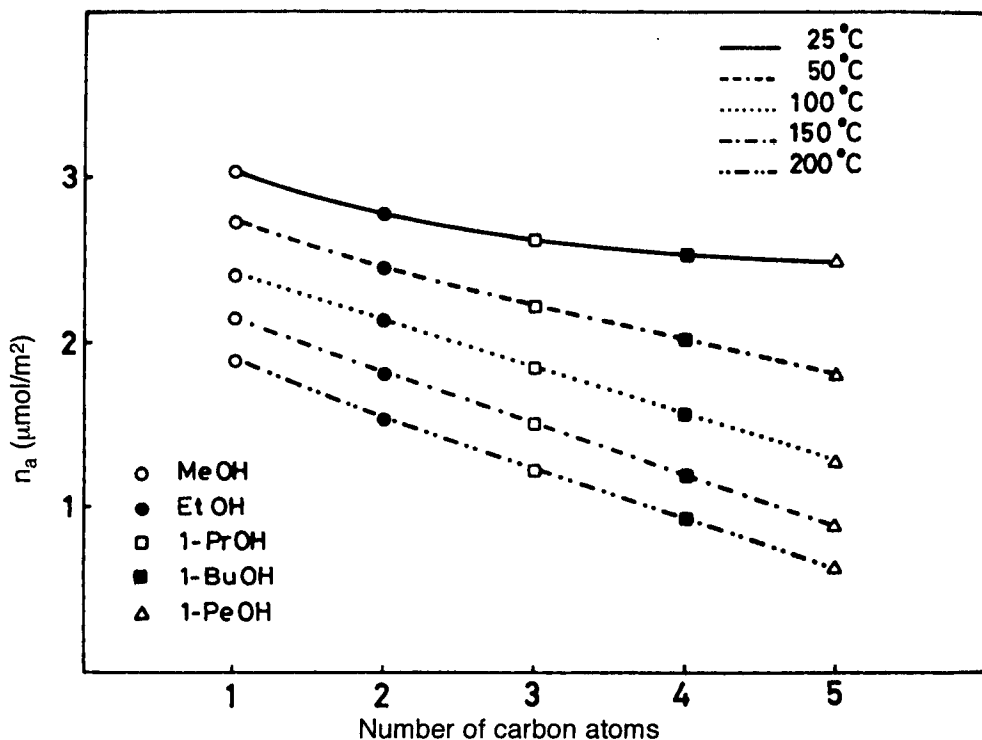


Figure 3. Volumetric isotherms for five aliphatic alcohols adsorbed on to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (continuous line corresponds to data measured at 25°C and dashed line to data measured at 200°C).

adsorption of the same aliphatic alcohols on porous Vycor. Such a trend may be related qualitatively to the molecular areas of the various alcohols, which suggests that the alcohols are attached to the  $\alpha$ - $\text{Al}_2\text{O}_3$  surface via their aliphatic chains (Barto *et al.* 1966). For completeness, we show in Figure 4 the variation in the total amounts of the five adsorbed alcohols as a function of the chain length or the number of carbon atoms at different experimental temperatures. In all cases, the amounts adsorbed on  $\alpha$ - $\text{Al}_2\text{O}_3$  decrease according to the molecular weights of the various alcohols at all temperatures studied.



**Figure 4.** Variation in the total amount of five aliphatic alcohols adsorbed on to  $\alpha$ - $\text{Al}_2\text{O}_3$  at various temperatures as a function of the number of carbon atoms in the alcohol concerned.

Figures 5, 6 and 7 show the trend in the differential heats of adsorption of the five aliphatic alcohols on to  $\alpha$ - $\text{Al}_2\text{O}_3$  at 25, 100 and 200°C, respectively. The corresponding variations at 50°C and 150°C have been omitted since they were very similar to those at 25°C and 100°C, respectively. Starting with the discussion of the adsorption data at 25°C depicted in Figure 5, we note that the values of the differential heats may be divided into three regions:

- (a) At very low coverage (ca.  $q_{\text{diff}} > 200$  kJ/mol), the values correspond to the irreversible interaction of the homologous alcohols with the strongest active sites (Lewis acid sites) on the  $\alpha$ - $\text{Al}_2\text{O}_3$  surface and are not affected by the molecular weights of the various adsorbed alcohols. On such dehydroxylated sites, the alcohols are chemisorbed dissociatively to form alkoxy and hydroxy groups.

- (b) At average coverage (ca.  $200 \text{ kJ/mol} < q_{\text{diff}} < 130 \text{ kJ/mol}$ ), the values correspond to reversible interactions with less strong active sites (the principal predominant process being the coordination of undissociated alcohol). Within this range, the trend observed for the differential heats of MeOH appears to differ from those for the other aliphatic alcohols where the absolute value of the differential heat decreases and the slope of the curve increases as the molecular weight of the alcohol increases. It is possible that the surface of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is covered more uniformly by methanol vapour under these conditions, since its molecular area is smaller than those of the other homologous alcohols studied (Jednacak-Biscan and Pravdic 1980).
- (c) At high coverage (ca.  $q_{\text{diff}} < 130 \text{ kJ/mol}$ ), which corresponds to the region where hydrogen-bond type interactions occur and when  $n_a$  is ca.  $2 \mu\text{mol/m}^2$ , the differential heats of adsorption of the five alcohols studied follow the order  $\text{MeOH} > \text{EtOH} > 1\text{-PrOH} > 1\text{-BuOH} > 1\text{-PeOH}$ . If, during the process of adsorption, the homologous alcohols are attached to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface with the hydrocarbon chain perpendicular to that surface, their molecular interactions should decrease as their steric hindrance increases.

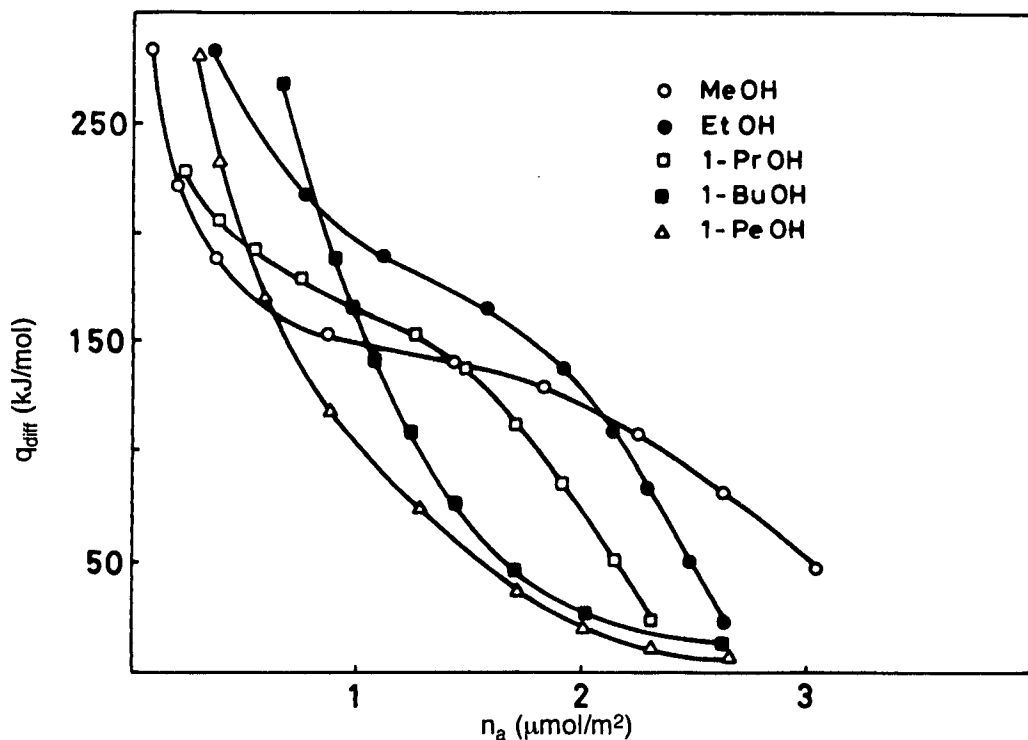


Figure 5. Differential heats of adsorption of five aliphatic alcohols adsorbed on to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 25°C.

We may conclude, therefore, that the adsorption of the series of homologous alcohols on to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface is autophobic in character, with a strongly oriented first layer.

On considering Figure 6, it appears that the trends in the differential heats of adsorption of the

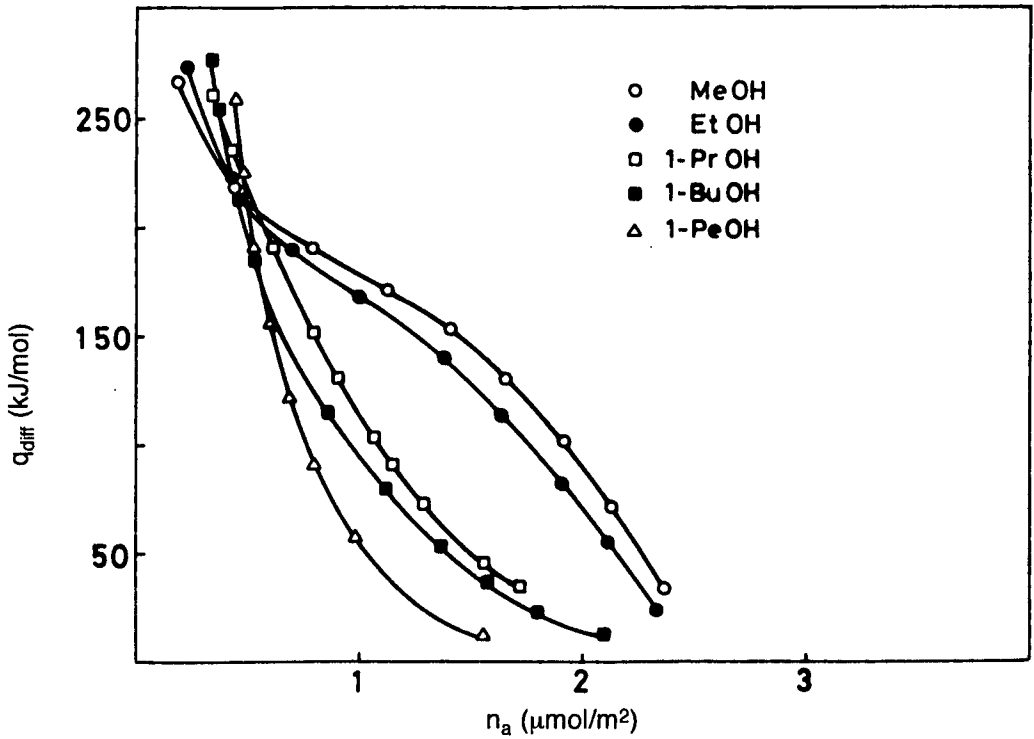


Figure 6. Differential heats of adsorption of five aliphatic alcohols adsorbed on to  $\alpha\text{-Al}_2\text{O}_3$  at  $100^\circ\text{C}$ .

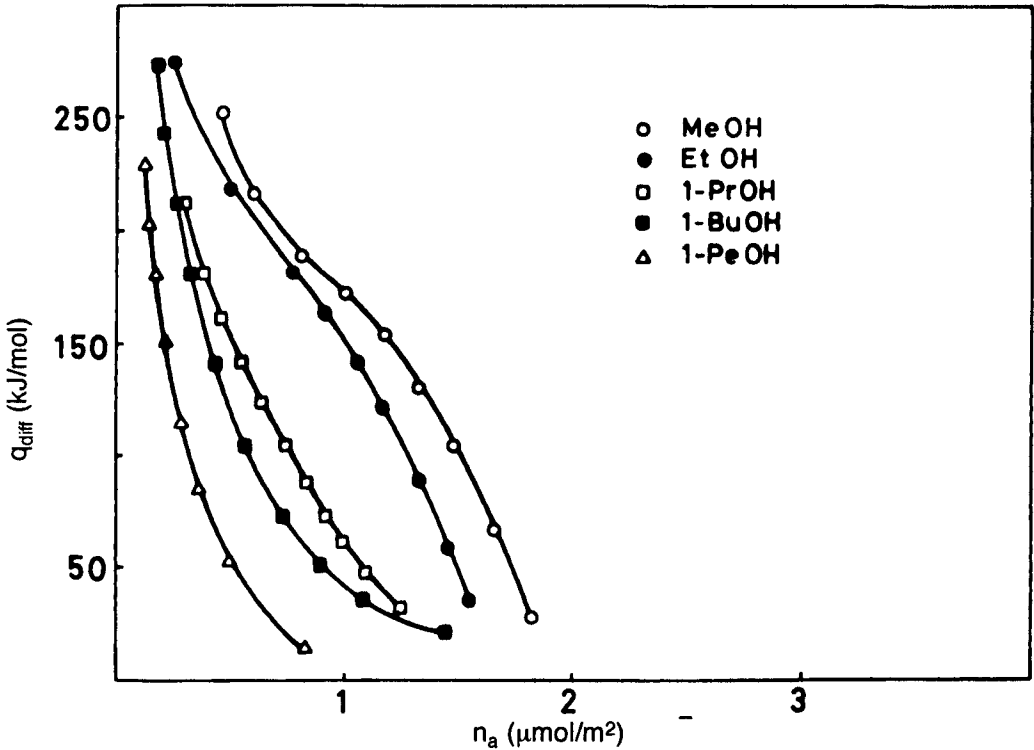
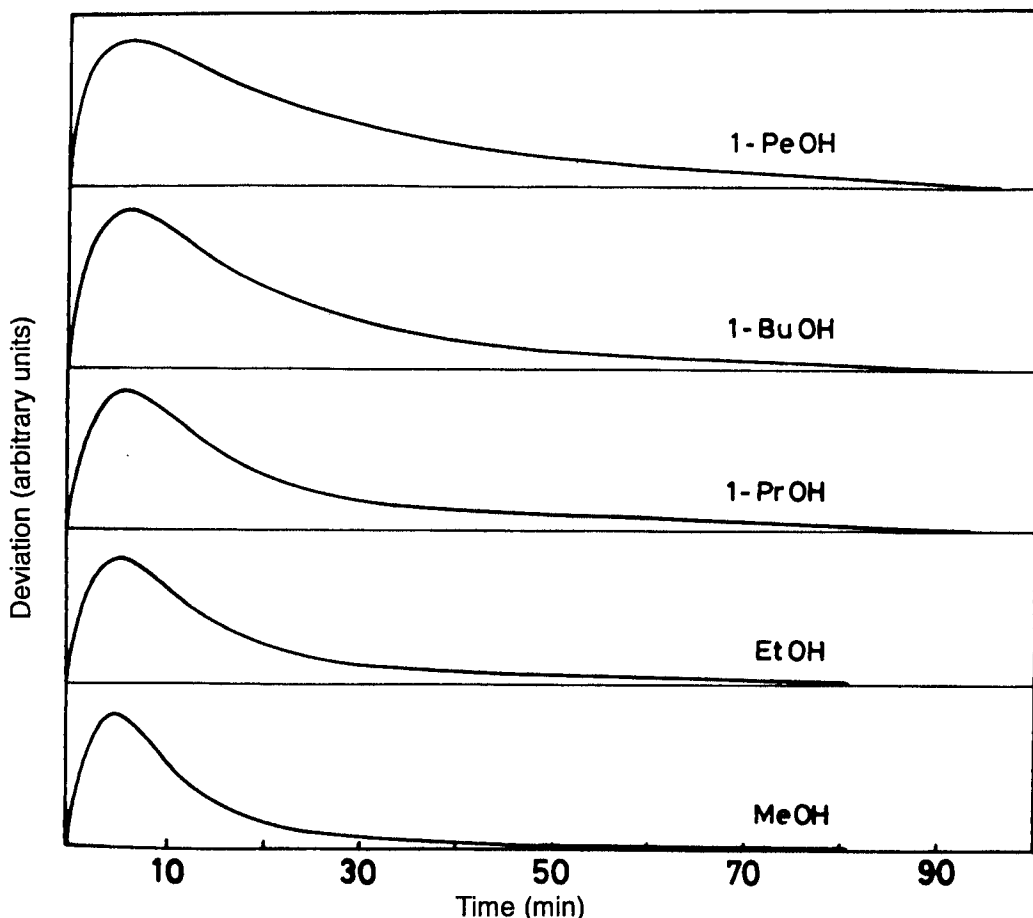


Figure 7. Differential heats of adsorption of five aliphatic alcohols adsorbed on to  $\alpha\text{-Al}_2\text{O}_3$  at  $200^\circ\text{C}$ .

five alcohols at 100°C appear to be different from that at 25°C (Figure 5). All the curves appear to be steeper and the three regions described above seem to decrease in range, particularly that relating to reversible interactions on less strong active sites whose range decreases as the molecular weight of the alcohol adsorbed increases. In addition, the trends in the differential heats for MeOH and EtOH appear to become similar, while the same phenomenon appears to occur for 1-PrOH, 1-BuOH and 1-PeOH.

At higher temperatures (200°C, see Figure 7), the trends in the differential heats of the five aliphatic alcohols adsorbed on  $\alpha\text{-Al}_2\text{O}_3$  again seem to become steeper. However, they decrease towards values which are lower than the heats of vaporization of the alcohols concerned (Rossi and Rossi 1996) and the slopes of the curves become much steeper with increasing molecular weight of the alcohol. The values of the differential heats extend over the range ca. 250–15 kJ/mol (corresponding to surface saturation) when plotted on the same scale as used for Figures 5 and 6. The order depicted in Figure 7 suggests that the longer the chain length of the alcohol, the lower the value of the differential heat of adsorption. This probably arises from the steric hindrance encountered by the molecules of the adsorbed alcohol when the molecular weight increases, the lateral interactions between the molecules decreasing and thereby lowering the value of the differential heat of adsorption.



**Figure 8.** Heat emission peaks for five aliphatic alcohols adsorbed on to  $\alpha\text{-Al}_2\text{O}_3$  at 25°C measured at the same equilibrium pressure (< 0.2 Torr).



## Thermokinetics

Figure 8 depicts the five heat emission peaks obtained at 25°C for the homologous series of alcohols studied at the same equilibrium pressure (ca.  $P_{\text{equil}} < 0.2$  Torr). All the peaks have the same rounded shape with an asymptotic approach to the base line value. The three thermokinetic parameters ( $t_{\text{max}}$ , time for maximum peak attainment;  $t_{1/2}$ , time for half deviation; and  $t_0$ , time for return to the base line) all show the same type of development with increasing numbers of carbon atoms in the five alcohols adsorbed (Fubini 1979). The values of these parameters increase as the chain length of the aliphatic alcohol increases. This proportionality between the thermokinetic data and the chain length suggests that the same chemisorption mechanism applies for the adsorption of all the members of the homologous series of aliphatic on to  $\alpha\text{-Al}_2\text{O}_3$ .

## CONCLUSIONS

The five aliphatic alcohols studied may be used as molecular probes in the vapour phase to investigate the surface of  $\alpha\text{-Al}_2\text{O}_3$ . Nevertheless, microcalorimetry of adsorbed methanol provides a better measure of the acid strength distribution of the  $\alpha\text{-Al}_2\text{O}_3$  surface since its molecular area is less than that of the higher alcohols. In addition, as the carbon chain length increases, the adsorption of the various alcohols becomes more autophobic in character with a strongly oriented first layer.

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