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Study of the Nature of Surfaces with Polar Molecules I. Adsorption of Lauric Acid on Aluminum Oxides and Hydroxides

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Lauric acid is adsorbed on aluminum hydroxides and oxides from solutions in nonpolar solvents, giving isotherms with a pronounced saturation character. Especially from solutions in pure *n*-pentane, a complete monolayer of lauric acid on alumina is formed at very low equilibrium concentrations.

The specific lauric acid adsorption *f* on the various hydroxides amounts to 0.43 mmole/100 m^2, on the aluminas heated above 800°C to 0.617 mmole/100 m^2. Aluminas obtained just above the decomposition temperature of the hydroxides give low values for *f*, which are attributed to steric hindrance in narrow pores. It could be shown that the lauric acid molecules adsorbed adapt themselves to the periodicity of the oxygen atoms forming the surface of the aluminas, each lauric acid molecule being bound to four oxygen atoms.

The adsorption of lauric acid provides a simple method for the determination of the surface area of aluminas in the absence of steric hindrance in narrow pores. Comparison of the lauric acid adsorption with the Brunauer-Emmett-Teller (BET) surface area will give useful information about the presence of narrow pores.

1. INTRODUCTION

Long-chained polar organic molecules are strongly adsorbed from their solutions in nonpolar solvents on the surface of aluminum oxides and hydroxides. The polar group of the organic molecules is bound firmly to the surface whereas the hydrocarbon chains will orient themselves parallel to their longitudinal direction and form a large angle with the surface.

The saturated fatty acids are particularly suited for the study of surface phenomena on the aluminas as they can be obtained in a pure form and can easily be determined quantitatively by titration with an alcoholic potassium hydroxide solution. Preliminary investigations (1) showed that the lower acids, such as butyric acid, may attack some of the aluminas by a chemical reaction which is not even limited to the surface layer. Since the solubility of the higher acids, such as stearic acid, is limited in nonpolar solvents, lauric acid was considered the best suited adsorbate.

The adsorption isotherm of lauric acid on alumina has a pronounced saturation character. A monolayer of lauric acid is formed at low equilibrium concentrations owing to the strong dipole forces; however, after the formation of this monolayer the

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surface is deprived of its polarity and further adsorption is impossible.

The surface area occupied by fatty acids when spread on water is at least 20.5 Å²/molecule (2). This value does not necessarily obtain when they are adsorbed on the surface of a solid, as the fatty acid will adapt itself to the nature of the surface. So de Boer and Vleeskens (3) found that on heated and rehydrated silica only 0.25 mmole of lauric acid is adsorbed on 100 m^2 of surface area (corresponding to about 66 Å²/molecule), whereas on a dehydrated silica surface the lauric acid adsorption is about ⅔ of this value.

The great length of the hydrocarbon chain (about 18 Å for lauric acid) can also influence the surface area occupied by a lauric acid molecule in an adsorbed layer. The volume of the amount of adsorbate, on the internal surface of a porous substance, can on no account be larger than the volume of the pores. So in narrow pores the amount of lauric acid adsorbed per unit of surface area may be less owing to steric effects, depending on the shape and the dimensions of the pores. On the external surface such a steric hindrance is not to be expected.

2. STARTING MATERIALS

Aluminum hydroxides:

PSH	Commercial gibbsite type H manufactured by Peter Spence & Co.
By and WAA	Bayerite prepared by Schmäh's method (4) at a pH of 7 and 12, respectively
BoG	Well-crystallized boehmite prepared by hydrothermal treatment of PSH at 250°C in water
BoW	Well-crystallized boehmite prepared by hydrothermal treatment of gelatinous boehmite at 250°C in water
MiBo 1 to 5	Microcrystalline boehmite prepared by hydrothermal treatment of gelatinous boehmite at various temperatures in water or in diluted NaOH solution
HS	Gelatinous boehmite prepared from aluminum triisopropoxide by hydrolysis with steam at 120°C
A	Gelatinous boehmite prepared from alum and sodium aluminate by precipitation

The aluminas were prepared from the hydroxides by heating in air until constant weight (6 to 24 hr).

Lauric acid	Purest quality of BDH
n-Pentane	*n*-Pentane of technical quality was treated with some concentrated sulfuric acid, washed with water, dried, and fractionated.

3. CHOICE OF SOLVENT

An adsorbent in contact with a solution will adsorb both solute and solvent. To obtain a selective adsorption of the solute, the adsorption forces between solvent and adsorbent should be extremely low compared with those between solute and adsorbent, as the concentration of the solvent is high compared with that of the solute. Therefore, only saturated aliphatic hydrocarbons, such as *n*-pentane, will be suitable solvents for the determination of the lauric acid adsorption.

In Fig. 1 the adsorption isotherms of lauric acid on an alumina sample from solutions in different solvents are shown. It clearly appears that diethyl ether and benzene give much lower values than pentane, which has to be attributed to the competitive adsorption of solvent molecules.

Even the impurities in technical pentane (unsaturated hydrocarbons) will give low results at low equilibrium concentration. The pentane, therefore, should be purified as already described.

4. METHODS

(a) *Lauric Acid Adsorption*

A quantity of the alumina sample comprising a surface area of 100–250 m^2 is

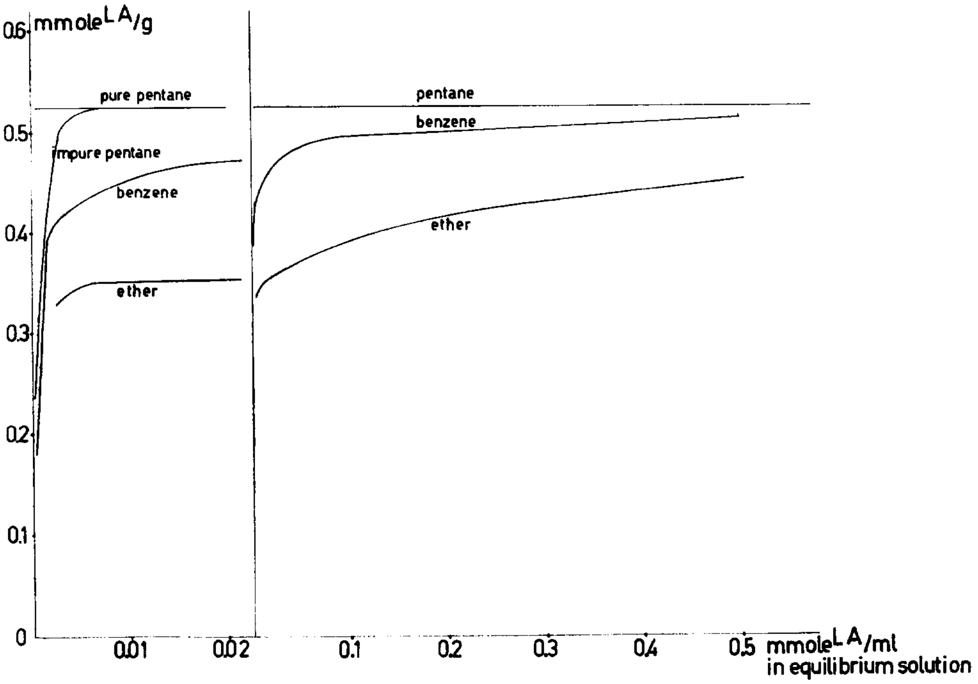

FIG. 1. Lauric acid adsorption isotherms on alumina from solutions in various solvents.

weighed in a small sealing bottle. Then 20 ml of 0.1 N lauric acid solution in pentane is added to it and the bottle sealed by fusion. After shaking for 16–24 hr in a rotator, the solid matter is allowed to settle. The bottle is carefully opened, and 10 ml of the supernatant clear liquid is pipetted off. The lauric acid is titrated with a 0.05 N alcoholic potassium hydroxide solution after the addition of 50 ml neutral ethyl alcohol.

(*b*) *BET Surface Area*

The specific surface areas were calculated from low-temperature nitrogen adsorption measurements with the BET equation [see, for instance, reference (5)]. The molecular surface area of the nitrogen molecule was taken as 16.25 Å^2 (calculated from the density of liquid nitrogen).

5. ADSORPTION ON HEATED SAMPLES

The results of the lauric acid adsorption on the heated samples are given in Table 1. It appears that the specific lauric acid adsorption f (expressed as mmoles of lauric acid per 100 m^2 of surface area) strongly depends on the heating temperature and the nature of the sample. The lowest and most diverging values are found for aluminas obtained from crystalline hydroxides heated just above their decomposition temperature, where the internal surface area has been formed.

Steric effects appear to be responsible for these low values of f. The mean pore width $\bar{d}$—defined $2V_p/S$, where V_p is the pore volume and S the BET surface area (5)—is very low, sometimes even lower than 10 Å, so that appreciable steric hindrance and consequently low values for f can be expected. These phenomena will be the subject of one of the following papers.

At increasing temperatures of pretreatment, f increases and converges to a constant value of 0.617 mmole/100 m^2 at heating temperatures above 800°C independent of the starting material (Fig. 2).

6. ADSORPTION ON THE HYDROXIDE

The results of the lauric acid adsorption on the hydroxide (previously dried at 120°C) are given in Table 2.

The mean value of the specific lauric

TABLE 1[a]

ADSORPTION OF LAURIC ACID OF ALUMINUM OXIDES

Temp. (°C)	*S* (m^2/g Al$_2$O$_3$)	*LA* (mmole/g Al$_2$O$_3$)	*f* (mmole/100 m^2)	*S* (m^2/g Al$_2$O$_3$)	*LA* (mmole/g Al$_2$O$_3$)	*f* (mmole/100 m^2)	*S* (m^2/g Al$_2$O$_3$)	*LA* (mmole/g Al$_2$O$_3$)	*f* (mmole/100 m^2)
		PSH			WAA				
540	169	0.756	0.447	237	1.016	0.429			
620	134	0.680	0.507	185	0.904	0.489			
720	97	0.591	0.609	138	0.766	0.555			
820	78	0.481	0.617	103	0.628	0.610			
920	29	0.206[b]	0.710[b]	84	0.515	0.613			
980	19	0.165[b]	0.868[b]	70	0.420	0.600			
		By			BoG			A	
250	489	0.998	0.204	—	—	—	—	—	—
450	412	1.003	0.243	17.1	0.055	0.321	417	2.28	0.55
500	—	—	—	65.3	0.211	0.323	—	—	—
580	245	1.126	0.460	65.7	0.219	0.333	355	2.02	0.57
750	134	0.768	0.573	19.1	0.116	0.608	280	1.64	0.59
850	103	0.635	0.617	16.8	0.106	0.631	236	1.45	0.614
		HS							
800	182	1.117	0.613						
900	141	0.886	0.628						

[a] From reference (6).

[b] These figures are high, because some of the Na$_2$O content of the sample (0.26%) became free as a result of sintering and reacted with lauric acid.

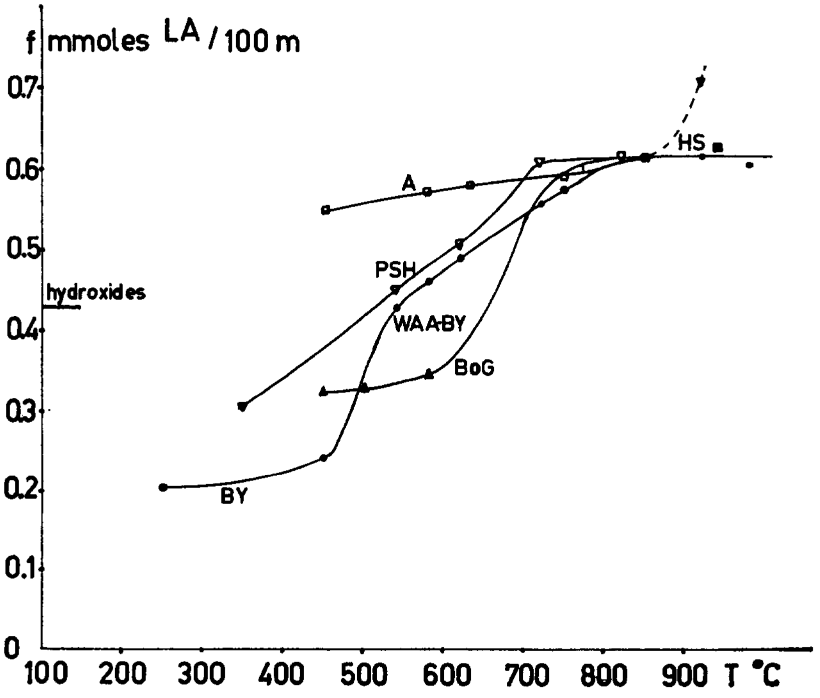

FIG. 2. Specific lauric acid adsorption *f* on aluminas.

TABLE 2[a]
ADSORPTION OF LAURIC ACID ON ALUMINUM HYDROXIDES

Sample	S_{BET} (m^2/g Al$_2$O$_3$)	LA (mmole/g Al$_2$O$_3$)	f (mmole/100 m^2)	S_{geom} (m^2/g Al$_2$O$_3$)
By	6.0	0.025	0.42	—
WAA	35.6	0.156	0.439	—
BoG	1.3	0.005	0.4	—
BoW	64	0.272	0.426	68
MiBo 1	158	0.659	0.418	—
MiBo 2	100	0.420	0.420	98
MiBo 3	68	0.296	0.436	75
MiBo 4	225	1.122	0.441	—
MiBo 5	201	0.870	0.434	—
HS	416	1.70	0.409	—
A	609	2.57–3.20[b]	0.42–0.53[b]	—

[a] From reference (6).

[b] The lauric acid adsorption of this very reactive sample of gelatinous boehmite could hardly be determined; within a short time the whole mass gelatinized. Scattered results were obtained after centrifuging.

acid adsorption f on these samples is 0.43 mmole/100 m^2, notably lower than on the aluminas heated above 800°C. This low figure cannot be attributed to steric hindrance in narrow pores, since, by determining the geometrical surface area S_{geom} of three samples of microcrystalline boehmite from a number of electron micrographs, a good agreement was obtained between S_{geom} and S_{BET}. This indicates that the particles do not possess an internal surface area; hence the particles themselves are not porous.

Lauric acid adsorption is weaker on an aluminum hydroxide surface than on an aluminum oxide surface. This also follows from the shape of the isotherms. Whereas already at very low concentrations of lauric acid in the equilibrium solution a complete monolayer is formed on the oxides (Fig. 1), a much more sloping character is found for the hydroxides (Fig. 3).

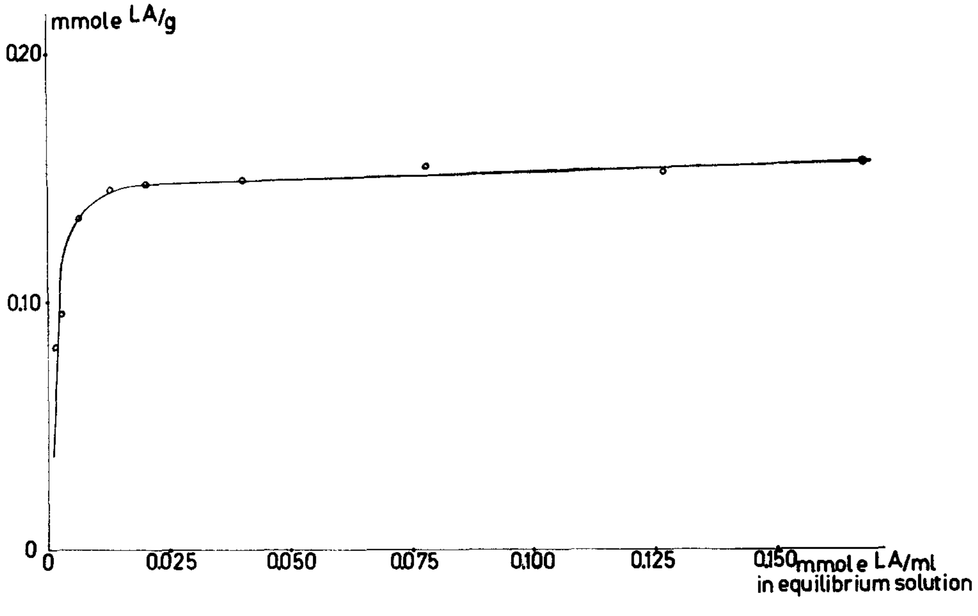

FIG. 3. Lauric acid adsorption isotherm on aluminum hydroxide WAA.

7. The Surface Covering of Alumina by Lauric Acid

It is not very probable that the packing of the adsorbed lauric acid molecules will obtain the same density on a crystalline polar surface as in a monolayer of lauric acid on a water surface. It may be expected that the lauric acid because of its strong selective adsorption, will adapt itself to the surface structure of the adsorbent.

All aluminas obtained between the decomposition temperature of the hydroxides and 1000°C have structures based on a nearly closest-packed cubic oxygen sublattice and are closely related to that of spinel-type γ-Al_2O_3. We may, consequently, assume that the surface of the aluminas is formed by planes with more or less simple indices of this oxygen sublattice.

At relative low temperatures, these planes are given by the pseudomorphosis relations between the original hydroxide and the appropriate alumina; at higher temperatures, however, when an appreciable sinter-

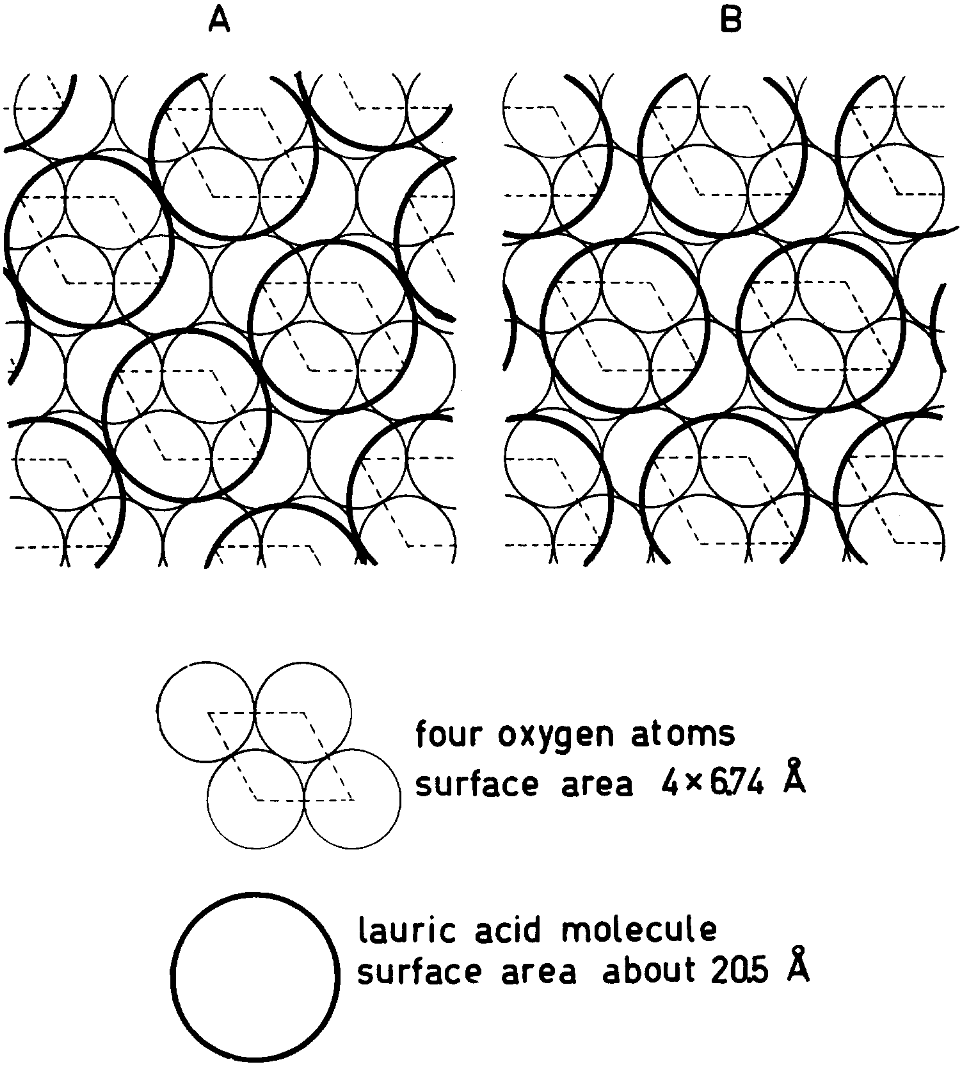

Fig. 4. Two stacking arrangements of lauric acid adsorbed on an alumina surface formed by oxygen atoms.

ing and consequently material transport has occurred, the most stable plane (i.e., the octahedral plane of the cubic oxygen lattice) will be the most abundant plane in the surface. One oxygen atom in this plane will occupy a surface area of 6.74 Å². A lauric acid molecule, when spread on water, will occupy a surface area of at least 20.5 Å² (2). By using these figures, two possible stacking arrangements of lauric acid can be found, which follow the periodicity of the oxygen surface. They are shown in Fig. 4. It appears that one lauric acid molecule in both cases will occupy the surface area of four oxygen atoms or 27.0 Å².

The experimental value of the specific lauric acid adsorption (0.617 mmole/100 m²) is equivalent to a molecular surface area of lauric acid of 26.9 Å², which is in excellent agreement with the figure calculated in the foregoing.

8. SURFACE AREA DETERMINATION FROM LAURIC ACID ADSORPTION

If steric hindrance in narrow pores is known to be absent, the adsorption measurements of lauric acid can be used for the determination of the specific surface area of an alumina sample. The procedure given above is relatively simple and does not require any complicated apparatus.

The specific surface area of an alumina sample is found by multiplication of the number of mmoles of lauric acid adsorbed by 162 (in the case of oxides) or by 232 (in the case of hydroxides). On the other hand, comparison of lauric acid adsorption with the BET surface area will give indications for the possible presence of narrow pores.

REFERENCES

1. HOUBEN, G. M. M., Thesis, Delft, p. 85 (1951).
2. ADAM, N. K., "The Physics and Chemistry of Surfaces." Clarendon Press, Oxford, 1930.
3. DE BOER, J. H., AND VLEESKENS, J. M., *Koninkl. Ned. Akad. Wetenschap., Proc.* **B61,** 2 (1958).
4. SCHMÄH, H., *Z. Naturforsch.* **1,** 323 (1946).
5. HERMANS, M. E. A., AND LIPPENS, B. C., *Powder Met.,* No. 7, 66 (1961).
6. MEIJS, W. H., Thesis, Delft, p. 41 (1961); LIPPENS, B. C., Thesis, Delft, chap. V, (1961).