

THE ADSORPTION OF WATER BY CLAYS

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ABSTRACT: Following the work of Davis & Worrall (1971) the adsorption of glucose from aqueous solution on sodium kaolinite has been re-examined. Colorimetric and radiochemical methods were used for glucose assay. Adsorption is very small and is probably positive.

INTRODUCTION

In a recent paper* with the above title, Davis & Worrall (1971) presented data demonstrating that glucose is negatively adsorbed from aqueous solution onto a china clay, a ball clay and a fuller's earth. Such negative adsorption was relatively large. Using a simple model in which it is assumed that the glucose molecules are excluded from a water layer of uniform thickness t around each clay particle, values of t were found to range from 33 Å to 143 Å for those homoionic forms of china clay and of ball clay which were investigated. With fuller's earth, values of t ranged from 6 Å to 14 Å. It was suggested that the 'adsorbed water' on the kaolinites was made up of an inner, rigidly bonded layer some 15 Å thick, and an outer layer up to 200 Å thick existing as 'flickering clusters'. An alternative interpretation in terms of the exchangeable cations reducing the solubility of the glucose close to the clay-water interface ('salting-out') (Mortland, 1970) was not considered. There are only a limited number of publications describing the adsorption of glucose and other sugars onto clay minerals (Holzapfel, Engel & Rudzinski, 1951), chiefly montmorillonites (Clapp, Olness & Hoffmann, 1968; Greenland, 1956a, b; Mitra & Panda, 1957; Mitra, Misra & Panda, 1957). In general, adsorption of glucose was found to be small and positive although the nature of the correction applied by Greenland (1956b) for solvent adsorption is not clear. In some works, the montmorillonite-sugar complex has been examined by X-ray diffraction (Clapp *et al.*, 1968; Greenland, 1956a). The formation of such a complex does not necessarily relate to the adsorption equilibrium in solution (Hoffmann & Brindley, 1961).

Certainly when judged by current ideas (Graham, 1964; Martin, 1961) on structured or ordered water close to solid surfaces and including silicate surfaces, the values of t suggested by Davis & Worrall (1971) are very large. For example,

* Read at a meeting of the Clay Minerals Group of the Mineralogical Society, in Cambridge, March 1970.

recent slow-neutron scattering experiments using hydrated lithium-vermiculites have shown (Olejnik, Stirling & White, 1971) that structure is induced in the interlamellar water but only within a very short distance from the silicate surface, about 1–2 molecular layers. Because of this and because of parallel work on the cellulose-kaolinite interaction* we re-examined the adsorption of glucose from aqueous solution onto kaolinite.

EXPERIMENTAL WORK

The kaolinite was from the same batch as that used in a previous study (Bidwell, Jepson & Toms, 1970). It contained less than 2 wt % mica as the only other detectable mineral present and had been extracted from a selected stope sample by elutriation with water. The required particle size fraction (nominally 100 wt % below 5 μm e.s.d. with 80 wt % less than 2 μm e.s.d.) had been achieved using a hydro-cyclone. The reasons for using this somewhat tedious preparative route are argued in the original paper. The kaolinite (nitrogen area, 8.8 $\text{m}^2 \text{g}^{-1}$) was converted to the sodium form by repeated washing with M NaCl at pH 6.5 followed by distilled water until the rinsings were free from Cl^- ion. The clay was then dried overnight at 80°C.

Analar D-glucose (B.D.H. Ltd.) was used without further purification. Adsorption measurements were made at 25°C and at pH 6.5; clay solids contents of 10 wt % and 20 wt % were investigated. The experimental technique was to add the dried clay to the glucose solution and then stir for 16 h. In the experiments at 10 wt %, the suspension was then left to stand for 2 h after which a sample of the clear supernatant was withdrawn for analysis. In the experiments at 20 wt %, the suspension was centrifuged in a sealed tube for 1 h and then returned to the thermostat for a further 1 h before withdrawing a sample for analysis. Experiments were made using sterile equipment and materials in order to minimize loss of glucose through microbiol degradation.

In some experiments, the glucose was isotopically labelled with D-glucose- ^{14}C (unspecifically labelled; freeze-dried; Radiochemical Centre, Amersham) and amounts determined by scintillation counting. In other experiments, the glucose was determined colorimetrically by the Folin (1929, 1930) method. Solution amounts were determined by weight rather than by volume to reduce errors; solution compositions are accordingly expressed as weight fractions of glucose. In calculating the amounts of glucose adsorbed, a correction was made for the presence of a small amount of water, about 0.1 wt %, on the nominally dry clay.

EXPERIMENTAL ERRORS

The amount of glucose adsorbed is given by

$$a = \frac{y}{x}(c_i - c_f) \quad (1)$$

where c_i and c_f are the starting and final glucose weight fractions respectively and

* The anhydrous form of D-glucose is the basic unit of the cellulose chain.

x is the weight of clay added to a weight y of solution. Neglecting errors in x and y we have

$$\delta a = \frac{y}{x} \{(\delta c_i)^2 + (\delta c_f)^2\}^{\frac{1}{2}}, \quad (2)$$

and for small a so that $c_i \sim c_f$, (2) becomes

$$\delta a \sim \sqrt{2} \frac{y}{x} \delta c_f \quad (3)$$

Writing

$$\delta c_f = \alpha c_f \quad (4)$$

where α is a factor we have

$$\delta a = \alpha \sqrt{2} \frac{y}{x} c_f \quad (5)$$

which is the required relation.

For the radiochemical measurements the counts were such that $\alpha = 0.01$ (standard error). The precision was not as good in the spectrophotometric work. As judged by calibration plots of absorbance versus concentration, α was around 0.03 (standard error). Other things being equal then, the values of $\delta a/a$ for the spectrophotometric measurements will be about three times greater than those for the radiochemical measurements.

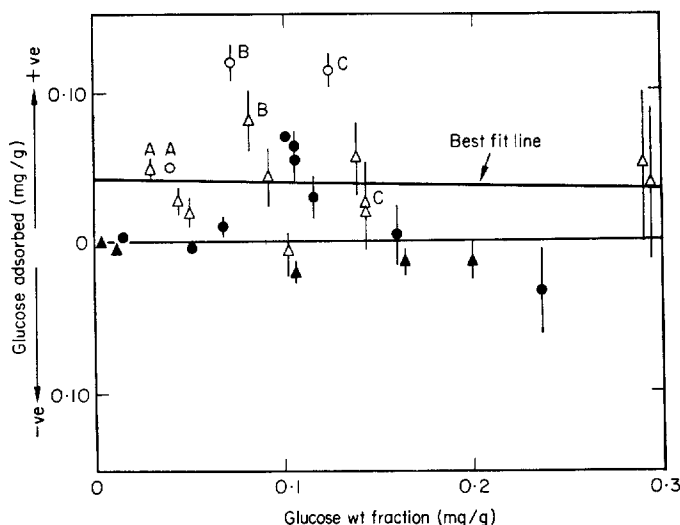


FIG. 1. Adsorption of glucose on Na-kaolinite at 25°C. The pairs of points, A, B and C are referred to in the text. This work: Δ , colorimetric, 10 wt %; \bullet , radiochemical, 10 wt %; \circ , radiochemical, 20 wt %. Davies & Worrall (1971): \blacktriangle , colorimetric, 25 wt %.

EXPERIMENTAL RESULTS

The results are shown in Fig. 1 as glucose adsorbed versus glucose in solution. The vertical bars centred on each experimental point are calculated from eqn. (5). The standard errors in a are large because a represents a difference between two comparable quantities. Taking an example, with $y/x = 4$ and $c_t = 10^{-4}$ then for $\alpha = 0.01$ we have $\delta a = 5.6 \times 10^{-6}$. A typical value of a would be 4×10^{-5} giving $\delta a/a = 0.16$ or 16%. With $c_t = 3 \times 10^{-4}$ and the other values unchanged, $\delta a/a$ would become 0.48 or 48%. The relative errors in the values of c_t are much less (1% or 3% depending on the choice of α) and are not shown.

Three pairs of experimental points in Fig. 1 are distinguished by the letters A, B and C. Each pair represents a combined measurement in which c_t was determined both radiochemically and colorimetrically in the same adsorption experiment. We have calculated the results obtained by Davis & Worrall (1971) for their Na-china clay in terms of glucose adsorption and their values are also shown in Fig. 1. Errors in a have been calculated assuming α of eqn. (4) to be 0.01 although we would regard this as optimistic from our own experience with the colorimetric method.

Since most adsorption isotherms show a sharp rise in a followed by a plateau or near plateau we fitted our own experimental data to

$$a = k_1 c_t + k_2 \quad (6)$$

to give the line shown in Fig. 1. The correlation coefficient was however only 0.1 suggesting this approach to be unprofitable. A simpler assessment is to note that 21 of the 24 experimental values of a are positive.

DISCUSSION

The major conclusion to be drawn from the present work is that the adsorption of glucose from aqueous solution on kaolinite is very small. For example, an adsorption of 0.5 mg/g ($a = 5 \times 10^{-6}$) is equivalent to a statistical coverage of rather less than 0.002 glucose molecules per 100 Å². Although simple mensuration suggests that adsorption is positive (21/24 probability) some additional uncertainty must still exist. Thus whilst our error analysis gives values generally sufficient to account for the observed scatter of the experimental data from a smooth relation, there still remains the possibility of a small systematic error. Such an error could transform a genuine negative adsorption into a false positive adsorption. We differ from Davis & Worrall (1971) in their conclusion that adsorption is negative at least up to glucose concentration of around 0.2 mg/g; in our view the experimental techniques (including those of glucose determination) do not have sufficient precision. Accordingly speculations on ordered water become tenuous.

The small adsorption is consistent with the lack of any specific forces (Mortland, 1970; Greenland, 1970) between the glucose molecule and the clay surfaces. Glucose is only weakly dissociated (Thamsen, 1952) with an acid dissociation constant, pK , of 12 at 25°C. Furthermore, thermodynamic measurements on the glucose-water system show the glucose to be strongly solvated (Taylor & Rowlinson, 1955). There

is strong hydrogen bonding between the glucose molecule and its surrounding water molecules, an association which is more stable than that between the water molecules themselves. It is interesting that methylated glucose, presumably being more weakly solvated, is adsorbed on montmorillonite to a far greater extent (Greenland, 1956b) than is glucose itself.

REFERENCES

- BIDWELL J.I., JEPSON W.B. & TOMS G.L. (1970) *Clay Miner.* **8**, 445.
CLAPP C.E., OLNESS A.E. & HOFFMANN D.J. (1968) *Trans. 9th. int. Congr. Soil Sci.* **1**, 627. (J.W. Holmes, editor). Elsevier, New York.
DAVIS G.A. & WORRALL W.E. (1971) *Trans. Bri. Ceram. Soc.* **70**, 71.
FOLIN O. (1929) *J. biol. Chem.* **82**, 83.
FOLIN O. (1930) *J. biol. Chem.* **86**, 173.
GRAHAM J. (1964) *Rev. pure appl. Chem.* **14**, 81.
GREENLAND D.J. (1956a) *J. Soil Sci.* **7**, 319.
GREENLAND D.J. (1956b) *J. Soil Sci.* **7**, 329.
GREENLAND D.J. (1970) *S.C.I. Monogr.* No. 37, p. 79.
HOFFMANN R.W. & BRINDLEY G.W. (1961) *Am. Miner.* **46**, 450.
HOLZAPFEL L., ENGEL W. & RUDZINSKI R. (1951) *Gummi-u. Asbestztg*, **4**, 200.
MARTIN R.T. (1961) *Clays Clay Miner.* **9**, 678.
MITRA S.P., MISRA S.G. & PANDA N. (1957) *Proc. natn. Acad. Sci. India* **26A**, Pt. 1, 72.
MITRA S.P. & PANDA N. (1957) *Proc. natn. Acad. Sci. India* **26A**, Pt. 1, 67.
MORTLAND M.M. (1970) *Adv. Agron.* **22**, 75.
OLEJNIK S., STIRLING G.C. & WHITE J.W. (1971) *Special Discussion of the Faraday Society: Thin Liquid Films and Boundary Layers* (F. C. Tomkins, Editor), p. 194. Academic Press, London.
TAYLOR J.B. & ROWLINSON J.S. (1955) *Trans. Faraday Soc.* **51**, 1183.
THAMSEN J. (1952) *Acta chem. scand.* **6**, 270.