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PARTICLE GEOMETRY AND OPTICAL DENSITY OF CLAY SUSPENSIONS*

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Abstract—Data on montmorillonite and illite collected by A. Kahn were further analyzed to show the relationship between particle geometry and the optical density (OD) of the clay suspensions. A correction was introduced to the calculations of the minor dimension of the montmorillonite particles which took into account the volume of water between unit layers.

The assumption of disc geometry which was used by A. Kahn in the calculations of the clay particle dimension was found to be consistent with his OD measurements, thus showing that optical measurements can be used to find an equivalent radius of montmorillonite and illite when the general geometry of the particles is the same.

INTRODUCTION

IN THE visible range the decrease in light intensity upon passing through illite and montmorillonite suspensions is due to scattering (Banin and Lahav, 1968). In dilute suspensions of these clay minerals the turbidity is related (Doty and Steiner, 1950) to the molecular weight M of the particles according to the expression:

$$\tau = \frac{HMCQ}{(1+2BMC)} \qquad (1)$$

where

τ is the turbidity $= \dfrac{2{\cdot}303 \times \text{OD}}{\text{optical path length}}$

C is the clay concentration

$H = \dfrac{32\pi^3 U_w^2 (\mathrm{d}U/\mathrm{d}C)^2}{3N\lambda^4}$

U_w is the refraction index of the solvent at wavelength λ

N is Avogadro number

$\mathrm{d}U/\mathrm{d}C$ is the refractive index increment of the suspension

B is the deviation from van't Hoff behavior, and

Q is the particle dissipation factor (Doty and Steiner, 1950).

Q characterizes the ability of the particles to dissipate light from the incident beam and it is so defined that the observed turbidity multiplied by $1/Q$ will equal the turbidity that would have been observed in the absence of interference.

The connection between Q, λ, and the major dimension D of colloid particles of several geometrical shapes has been worked out by Doty and Steiner (1950). Similar relationships can be computed for discs by using the relevant equation given by van de Hulst (1957, p. 98) in Doty and Steiner equations. However, the range of applicability of these theoretical relationships is limited to particle size $\ll \lambda/|m-1|$, m being the refractive index of the particle relative to that of the medium (van de Hulst, 1957). The error introduced in the application of these theoretical relationships increases with particle size and with m, and indeed Flory (1953) specifies $D/\lambda = 1$ as the upper limit of particle size. However, this error will be less pronounced for thin discs than for spheres.

Montmorillonite and illite particles are plate shaped with irregular geometry. Several workers (Kahn, 1959; Kelley and Shaw, 1942; Lahav and Banin, 1970; Quirk, 1968; van Olphen, 1954) assumed that the shape of these particles can be approximated by discs, an assumption which is included in the concept of equivalent or effective radius. It is the purpose of this article to test more quantitatively the "disc assumption" by a detailed study on the agreement between theory and experimental findings of OD measurements. The experimental data used here were taken from A. Kahn (1959) who compared systematically several methods, including OD measurements, in his studies of size and shape of several clay minerals.

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In his work, A. Kahn separated each of the clay minerals under study into five size fractions R_1, R_2, R_3, R_4, and R_5 where R_1 and R_5 are the biggest and smallest size fractions, respectively. The two plate-shaped clay minerals of this study, montmorillonite and illite, seem to suit our purpose because their smallest size fractions are in the range of applicability of the theoretical relationships between Q, λ and D.

RECALCULATION

Major dimension (equivalent diameter)

Electron microscopy enables one to measure directly the particle dimensions. However, owing to the multitude of geometrical shapes, all of them plates, it is difficult to express such a measurement in one number. The average surface area of the clay particles seems a desirable parameter for the population of each size fraction (see also Kelley and Shaw, 1942) but no such measurements were carried out by Kahn. The available data are of two methods: Electron Microscopy and Electro-Optical-Birefringence. Most of the values obtained by the two methods agree within a factor of about 1·7–2·1 (see Table 1). This, together with the electron microscope study and information from other workers (van Olphen, 1963) support an important assumption which is usually made: in the whole range of particle size under study the geometrical shape of the particles is basically that of plates with a large axial ratio. On the basis of this general shape, numerous variations of the detailed geometry are possible.

Minor dimensions (equivalent thickness)

Based on Electro-Optical Birefringence and viscosity measurements, A. Kahn calculated the thickness of the clay particles using the following equations:

$$\eta_r = 1 + K\phi \tag{2}$$

and

$$\frac{a}{b} = 1{\cdot}2\,K \tag{3}$$

in which η_r is the relative viscosity
ϕ is the volume fraction of the particles in the suspension
a and b are the major and minor dimensions, respectively, and
K is a constant.

ϕ was calculated from the clay concentration and density but the contribution of the water associated with the clay particles was neglected. This practice seems justified in the case of illite but not in that of montmorillonite.

The swelling of Na–montmorillonite studied by X-ray diffraction methods (Norrish, 1954; Norrish and Quirk, 1954; Posner and Quirk, 1964) has indicated that in water solutions of low electrolyte concentrations the particles exist as single unit layers or platelets. In several other studies (Lahav and Banin, 1968) such a complete dispersion was not always obtained. As discussed earlier by Lahav and Banin (1968), optical and negative adsorption studies show that the dispersibility of Na–montmorillonite is greatly dependent on the method of preparation of the clay suspension. Thus particles containing several unit layers can exist in suspension presumably as metastable forms. Mering (1946) also concluded from X-ray study that crystalline swelling of Na–montmorillonite ceased at 20 Å. Though his record is probably to be interpreted as failure to observe a definite diffraction line up to the low angle cut-off of the camera (Norrish and Quirk, 1954), it should be noted that Mering had dried his clay before causing it to swell by water. This treatment might have induced the association of unit layers to form bigger particles (Lahav and Banin, 1968).

The data of A. Kahn (1959) which will be used here, indicate that whereas the small size fraction of Na–montmorillonite, R_5, R_4, and R_3, were almost completely dispersed, the other size fractions contained particles with considerable thickness. In view of the fact that the purity of all the size fractions was checked and found satisfactory, this indicates that for unknown reasons the clay particles were not completely dispersed into single unit layers. This problem will be further discussed later on. Thus it is necessary to calculate again the values of ϕ taking into account the contribution of the water layers inside the particles. When the thickness of the particle is near 10 Å (i.e. that of a single unit layer), the contribution of the outer first layer or layers of adsorbed water should also be taken into account in the calculation of ϕ. Though the exact thickness of this layer is not known for the time being, we assume that it is one molecular layer thick, i.e. 3 Å on each side of the clay particle. The contribution of this layer can be neglected when the particles are several unit layers thick.

From Tables 4 and 5 in Kahn's article and by comparison to the data in another article (Kahn, 1958)*, it was found that in the OD measurements the clay concentration in both the illite and montmorillonite suspensions was 500 ppm. The density

*No other information is available. Personal communication with Dr. A. Kahn.

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Table 1. Dimensions and optical density of the montmorillonite and illite. EOB = electro-optical-birefringence. EM = electron microscopy.

Clay mineral	Fraction	Major dimension (a) E.O.B.	Major dimension (a) E.M.	Major dimension (a) EOB/EM	Minor dimension (b) EOB	Minor dimension (b) Corrected EOB	Axial ratio Not corrected	Axial ratio Corrected	Optical density of suspension λ = 4000 Å	Optical density of suspension λ = 5010 Å	Optical density of suspension λ = 6310 Å	No. of unit layers for eq. [4]
Montmorillonite	R_1	24,600	13,800	1·78	146	271	168	91	0·575	0·439	0·33	15·2
	R_2	20,600	10,800	1·91	88	160	234	129	0·23	0·120	0·09	9·18
	R_3	7600	6800	1·12	28	44	271	174	0·118	0·053	0·031	2·86
	R_4	5900	3200	1·84	22	31	268	190	0·0435	0·021	0·0132	2·18
	R_5	4900	2800	1·75	18	25	272	193	0·040	0·0185		1·93
Illite	R_1	7400	4800	1·54	720		10·3		1·41	0·98	0·515	1
	R_2	5200	3000	1·73	346		15·0		0·67	0·33	0·190	1
	R_3	4200	2000	2·10	172		24·4		0·39	0·162	0·078	1
	R_3	3800	1200	3·17	324		11·7		0·107	0·042	0·024	1
	R_5	3600	1000	3·60	68		52·9		0·212	0·086	0·044	1

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used by Kahn was 2·83 and 2·69 g/cm³ for illite and montmorillonite, respectively. ϕ for montmorillonite was recalculated by equations (2) and (3) assuming thickness of 9·4 Å and 9·0 Å to a unit layer and water layer, respectively (van Olphen, 1963). The number of unit layer, n, in a particle was calculated accordingly (Table 1). In illite ϕ was not recalculated and the number of unit layers in a particle was calculated for a c-spacing of 10·1 Å (Grim, 1968).

Optical density (OD) *measurements*

Equation (1) was used to calculate Q from values of τ obtained from Kahn's OD measurements. It was also necessary to know H, C, M and B. τ was found from Kahn's figures 4 and 5 with the help of an epidioscope (magnification about 10 times). C was found to be 500 ppm in both illite and montmorillonite as explained above. B was assumed to equal zero (see Lahav and Banin, 1970). The molecular weight of a *unit layer* in a particle was found from the equivalent diameter D, the area of a unit cell (45·8 Å²) and the molecular weight of a unit cell.

The molecular weight of a unit cell of Na–montmorillonite is 734 (van Olphen, 1963) whereas that of Na–illite is 839 (Grim, 1968). The molecular weight of an illite particle, M, was found by multiplying the molecular weight of a *unit layer* by the number of unit layer, n, in a particle. In the calculations of the molecular weight of the montmorillonite particles the contribution of the water layers was taken into account as explained above. Six H_2O molecules were assumed per unit cell (Grim, 1968) and three molecular layers were assumed in each water layer.

In the calculation of H the presence of water layers was taken into account (Banin and Lahav, 1968) in (dU/dC) as follows:

$$\frac{dU}{dC} = \frac{n}{n(\rho+1)-1}(U_c - U_w) \qquad (4)$$

where U_c is the refractive index of the clay and the other variables were explained above. Since no separate measurement was made to determine U_c for the clays under study, and because there are differences between clay minerals of the same group (Grim, 1968), the choice of U_c is somewhat arbitrary. The value of U_c for the two clay minerals under study was taken as 1·55 (Banin and Lahav, 1968).

Since the illite particles are considered as crystals, the value of n assigned to them in equation (4) was 1. In montmorillonite, however, n is the number of unit layers in a particle which can be looked at as "quasi crystal" (Quirk, 1968). The data used in these calculations are given in Table 1.

In Fig. 1, Q is plotted as a function of D/λ, D being the equivalent diameter of the clay discs, taken from electro-optical-birefringence and viscosity measurements. The relationships between Q and D/λ were calculated according to Doty and Steiner (1950) by introducing the proper expression given by van de Hulst (1957) for randomly oriented discs (p. 98). A computer program was used for this purpose. Though the theoretical relationships between Q and D/λ are applicable to values of D/λ not much greater than 1 (solid line), it is interesting to note the reasonable agreement between the calculated curve and the experimental measurements in the whole range of D/λ under study*.

It should be noted that the good agreement between the theory and the experimental data of the two clays cannot be obtained when the major dimension of the particles is taken from Electron-Microscopy measurements. This might be expected since the axial ratio of the particles was calculated from viscosity and electro-optical birefringence data in which the "disc assumption" was also used. Therefore, the concept of equivalent radius of a disc should be used in the context of the assumptions included in the experimental methods.

EVALUATION

Both illite and montmorillonite particles are plate shaped with the major dimension much bigger than the minor dimension. Therefore, if the assumption of "equivalent disc" is valid, it should be applicable to the two clay minerals. Figure 1 shows that this is the case when the specific properties of the clays, such as n, ρ, or M, are taken properly into account.

It is interesting to note that the axial ratios, though bigger than 10 in all the size fractions of the two clays under study, vary greatly from about 10–190. This variability has no effect on Q when its effect on H is taken into account, as is expected from the theory (Doty and Steiner, 1950). However, for each geometrical shape there is a unique relation between Q and D/λ and in the different size fractions under study the experimental relationship represents a weight average of the relevant properties of all the particles.

The data from A. Kahn which have been used here indicate that the Na–montmorillonite under study did not disperse completely into single unit layers. If one neglects completely the electro-optical-birefringence and viscosity measurements

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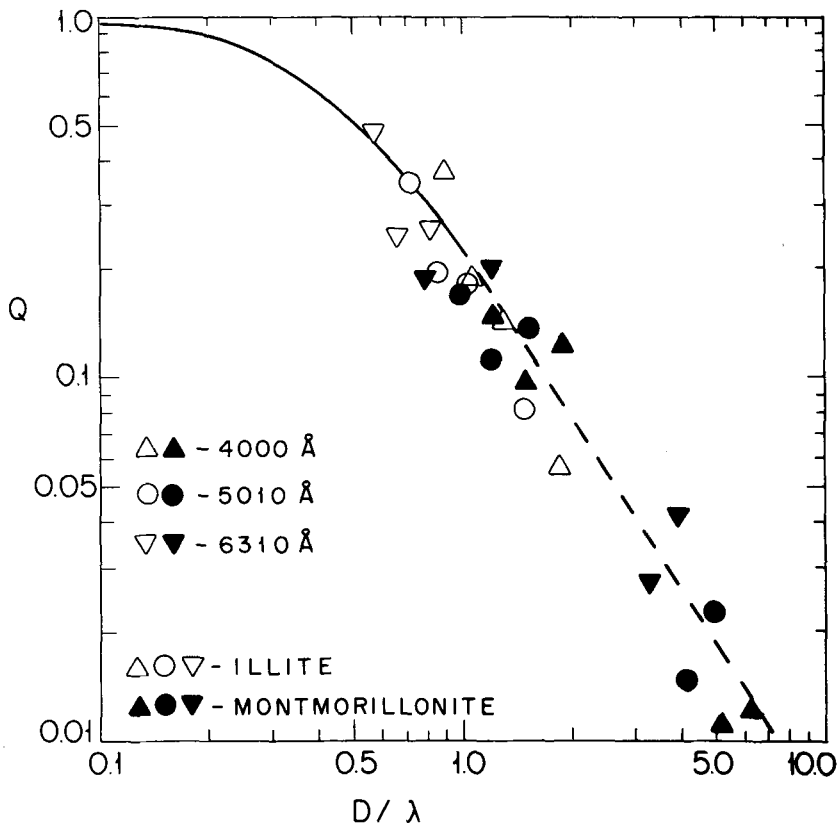


Fig. 1. Q as a function of D/λ for the illite and montmorillonite at three wavelengths.

and calculates Q in equation (1) assuming $n = 1$ and taking into account only the major dimension of the particles from the electron microscope study, this gives very high values of Q for all the size fractions except for R_5. Another possibility is that the coarse fraction of montmorillonite, namely R_1 and R_2, contains impurities of other minerals. The effect of such impurities is not expected to be too high since the purity of each clay sample was checked by means of X-ray diffraction and all the samples were considered to be satisfactory (Kahn, 1950).

The experimental points in Fig. 1 cover a range of D/λ values of one order of magnitude, i.e. from about 0·6 to about 6. The theory used here is strictly applicable up to D/λ values in the vicinity of about 1. The reasonably good agreement between the experimental data of both illite and montmorillonite with the theory indicates that the error introduced by working with large D/λ values is not very big.

In summary, it seems that even though the interpretation of the data obtained by viscosity, electro-optical-birefringence and optical methods is based on certain simplifying assumptions, the results of these measurements are consistent with each other and give good approximation of the dimensions of plate shaped clay particles. They can be used for purposes of comparative or particle size distribution studies.

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Résumé – Les données sur la montmorillonite et l'illite rassemblées par A. Kahn ont été analysées plus en détail afin de montrer la relation existant entre la géométrie des particules et la densité optique (O.D.) des suspensions d'argile. On a introduit une correction dans les calculs de la plus petite dimension des particules de montmorillonite, qui tient compte du volume de l'eau entre les feuillets élémentaires.

L'hypothèse de la forme en disque qui avait été utilisée par A. Kahn dans les calculs de dimension de la particule d'argile s'est révélée en accord avec ses mesures de O.D. ce qui démontre donc que les déterminations optiques peuvent être utilisées pour trouver un rayon équivalent de la montmorillonite et de l'illite quand la géométrie générale des particules est la même.

Kurzreferat – Die durch A. Kahn gesammelten Messwerte an Montmorillonit und Illit wurden weiter analysiert um die Beziehungen zwischen der Teilchengeometrie und der optischen Dichte (OD) der Tonsuspensionen aufzuzeigen. Es wurde eine Korrektur der Berechnungen der kleinen Dimension der Montmorillonityeilchen eingeführt, die das Volumen von Wasser zwischen den Einheitsschichten berücksichtigt.

Es wurde festgestellt, dass die von A. Kahn in den Berechnungen der Tonteilchendimension verwendete Annahme der Scheibengeometrie mit seinen optischen Dichtemessungen vereinbar ist, womit gezeigt wird, dass optische Messungen verwendet werden können um einen äquivalenten Radius von Montmorillonit und Illit zu finden wenn die allgemeine Geometrie der Teilchen die gleiche ist.

Резюме — Были подвергнуты анализу собранные А. Каном данные о монтмориллоните и иллите для выяснения соотношения между геометрией частиц и оптической плотностью (ОП) глинистой суспензии. Введена поправка в вычислениях малых размеров частиц монтмориллонита с учетом объема воды между единичными слоями. Показано, что допущение о дисковидной форме, которое использовал А. Кан при вычислении размера глинистой частицы, согласуется с его измерениями ОП; это указывает на возможность использовать оптические измерения для определения эквивалентного радиуса частиц монтмориллонита и иллита при одинаковой геометрии частиц.

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