Sedimentation Volume and Viscosity of Pure Clay Minerals and their Mixtures as Influenced by the Addition of Quaternary Ammonium Compounds

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In view of the high adsorbability of quaternary ammonium compounds by the colloidal clays the interaction between them as been studied in considerable details particularly in relation to: (I)adsorption, (ii) stability of the colloidal clays, (iii) electrochemical and electrokinetic proprties, (iv) sedimentation volume, and (v) viscosity changes.

Large-size alkyl quaternary ammonium molecules are absorbed as such in addition to those that enter by exchange reactions. The smaller quaternary cations behave in the same way as the inorganic cations.

The sedimentation volume of the clay minerals attains a maximum value (MSV) at a concentration of quaternary ammonium compounds equivalent to 75-80% of the base change capacity of the clay. Further addition after the maximum leads to charge-reversal as shown by the zeta potential measurements. At this point the flocculated mass begins to deflocculate. The value of MSV follow the order: montmorillonite> illite> mica> kaolinite. For a binary mixture of kaolinite and montmorillonite, MSV is proportional to the content of montmorillonite.

The viscosity of aqueous clay suspensions increases on the addition of quaternary ammonium compounds reaching a maximum corresponding to nearly 80% b.e-c.. The possibility of separation of binary mixtures of clay minerals based on the above observations has been indicated.

A knowledge of the precise nature and content of the clay mineral is of considerable importance to soil studies. Almost all of the conventional methods of identification and characterisation of the clay minerals have their limitations and without the combination of two or more methods a definite inference can hardly be made. A new chapter has recently been developed in the studies of clay minerals based on the interaction of organic compounds with the clay minerals[1].

Sedimentation volume is one of the characteristic properties distinguishing stable from flocculated suspensions and has therefore been measured in great detail along with others such as pH, zeta potential and viscosity of clay sols in order to follow the nature and extent of interaction of clays and their mixtures with quaternary ammonium compounds. In a stable suspension, where sedimentation is slow, the sediment is likely to be very dense. A flocculated system, on the contrary, sediments more rapidly owing to aggregate formation, and the sediment is usually bulky[2]. This essentially means that sedimentation volume depends on the rate of sedimentation, which is also determined by particle size of the suspension. Thus, coarse particles may be too heavy to allow any loose

1. Grim, R. E., "Clay Mineralogy", McGraw Hill Book Co. Inc., N.Y. (1963).
2. Kruyt, H. R., "Colloid Science", Elsevier Publishing Co., 1952.

packing, and with very fine colloidal particles sedimentation of the stable system may be often slow.

The influence of stability upon the sedimentation volume has already been recognised and applied to soil colloid by Ehrenberg[3]. Kruyt and Troelstra[4] used the sedimentation volume to distinguish between several grades of stability of negative AgI sols in presence of K^+, Ba^{++}, Al^{+++} and Ag^+. Very little work along this line has been done using organic electrolytes.

The importance of determining the volumes of the flocs obtained by the addition of any electrolyte to different clays and clay mineral mixtures has also been recognised by Wiklander and Anderson[5].

EXPERIMENTAL

0.5 to 1μ fractions were separated from clay minerals containing kaolinite, montmorillonite and illite and were treated with H_2O_2 to destroy the organic matter, if any. Mica suspension was that of coarse particles obtained by grinding and sieving through 100 mesh sieve. The suspensions were converted to H forms by electrodialysis. The base exchange capacity was determined by N. $BaCl_2$-Ba $(OH)_2$ method[6]. Binary mixtures were prepared in the laboratory from the samples described in Table I. The b.e.c. values are also recorded in the Table I.

TABLE I

Description of samples	Source	Clay Minerals*	b.e.c. of 0.5-1μ size fraction (m.e/100g)
1. Aqua-gel (Aq. M.)—An American product from bentonite	Assam Oil Co. (India) Ltd.	Montmorillonite	109.5
2. Rajmahal Kaolin (R. K.)	Calcutta Mineral Supply	Kaolinite	5.7
3. Fithian Illite	Illinois, U. S. A.	Illite	34.1
4. Mica	Indian Sheet Mica	Muscovite (-100 mesh)	11.4

*On the basis of x-ray examination, D. T. A., and lattice composition.

The following reagents used in the present investigation were further purified by either repeated crystallization or distillation. The names and abbreviations used of the quaternary compounds are stated below:

CTAB— Cetyl trimethyl ammonium bromide (Eastman Kodak Co.)
CEDAB—Cetyl ethyl dimethyl ammonium bromide (Eastman Kodak Co.)
CPB— Cetyl pyridinum bromide (City Chemical Corporation, New York)
PTAI—Phenyl trimethyl ammonium iodide (BDH)
TMAB—Tetramethyl ammonium bromide (Eastman Kodak Co.)

3. Ehrenberg, P., "Die Boden Kolloide", 3rd Ed. Dresden, 1922.
4. Kruyt, H. R., and Troelstra, Kolloid Chem. Beihefte, 1943, 54, 225.
5. Wiklander, L., and Anderson, E. K., Acta Agriculturae Scandinavica., 1953, 5, 2.
6. Mitra, R. P., Mukherjee, S. K. and Bagchi, S. N., Indian J. Agric. Sci., 1940, 10, 3030.

TMAOH—Tetramethyl ammonium hydroxide (Eastman Kodak Co.)

CTAOH—Cetyl trimethyl ammonium hydroxide (prepared from bromide by exchanging in a column of Amberlite I.R.A.110 in the OH-form.

Standard solutions of the bromide and iodide reagents were prepared from vacuum-dry samples and standardised by estimation of the C content and/or conductometric titration with $AgNO_3$. The hydroxides were analysed by titration with standard acid. 10 ml of the well dispersed hydrogen clay (1.0%) was taken in each of a series of graduated cylinders of equal dimensions, and different amounts of the quaternary compounds were added. The total volume was made up to 20 ml with water. The mixtures were thoroughly shaken and allowed to stand undisturbed for 24 hours. After this the sedimentation volume was read off, at the same time noting merely the state of flocculation and deflocculation. The results obtained with montmorillonite-CTAB system are given in Table II, as typical of these measurements.

TABLE II

Sedimentation volume of a binary mixture of class: R.K. *AqM=1:2, with CTAB. Clay concentration —0.5%. Total volume-20 ml.

m.e.% CTAB	S. V. (ml) after 24 hours
1. 0	0.5
2. 5	6.5
3. 20	10.6
4. 40	11.0
5. 55	13.0
6. 75	13.0
7. 100	6.4
8. 171	6.4
9. 228	6.4

2&3: partial slow coagulation; 4 & 5: rapid coagulation; 6: Rapid coagulation with slight dispersion; 7,8 & 9: dispersion increases gradually. *See Table I.

For the measurement of cataphoretic speed, and hence of zeta potential 20 ml 0.1% clay suspension and 20 ml of the electrolyte were mixed and allowed to shake for 6 hours in a mechanical shaker. The measurement was done at room temperature taking the usual precautions in a flat rectangular type of cell used by Freundlich and Abramson.[7]

For viscometric studies equal volumes of H-clay (1.0%) and aqueous solutions of the organic reactants in varying concentrations were taken in stoppered Jena bottles and the mixtures were allowed to equilibrate for 24 hours. The viscosity of the mixtures was then determined at 30°C ± 0.5 with the Ostwald viscometer.

The experimental data on the above measurements are graphically presented in Figs. 1 to 7.

RESULTS AND DISCUSSION

It has already been demonstrated[6] that the amount of total acid liberated from H-clay is much less than the amount of organic compound adsorbed as calculated from the

7. Abramson, H., J. Gen. Physiol, 1929, 12, 459.

8. Chakravarti, S. K., J. Indian. Soc. Soil Sci., 1957, 5, 85.

carbon content. The simultaneous adsorption of bromide ion by the clays suggests that some salt molecules as such are also adsorbed.
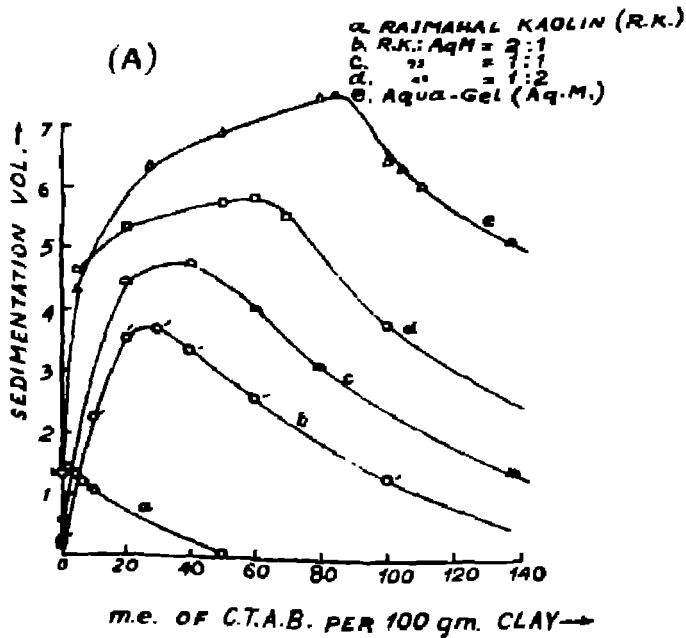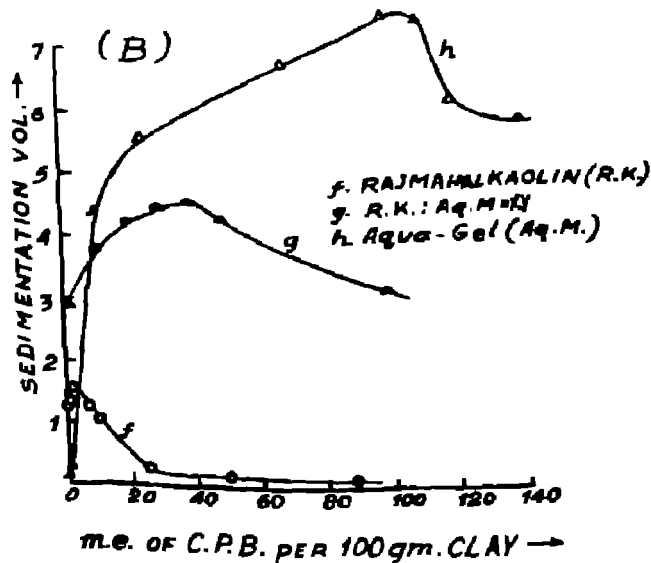

FIG. 1A.

FIG. 1B.

It will be observed from Figs. 1A, 1B that the sedimentation volume attains a maximum value at a concentration corresponding to about 75-80% of the b.e.c. of the clay

The ascending portion of the curves corresponds to the gradual replacement of the hydrogen ion by the large organic cations and to the simultaneous diminution of the zeta potential caused by a suppression of the ionic atmosphere. The descending portion of the curves corresponds to charge-reversal as shown by the zeta potential measurement also (Fig. 2). Consequently deflocculation takes place on further addition of the quaternary compounds after the maximum.
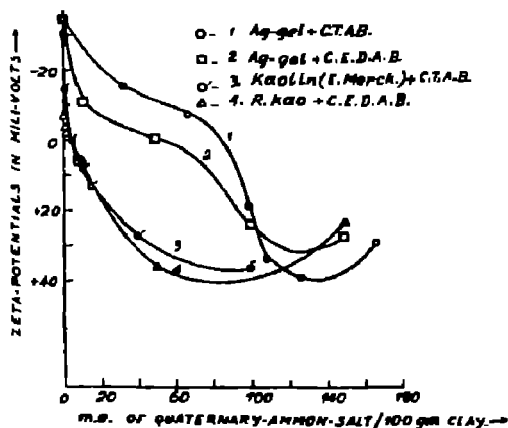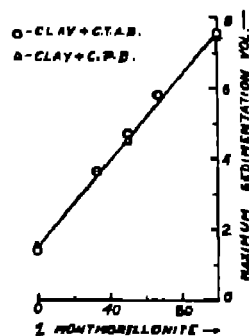

FIG. 2.

FIG. 3.

The reversal of zeta potential can only be explained by a consideration of the variation of the potential in the double layer. This variation must be caused by a strong adsorbability of the ions in question or of the products of their hydrolysis. In the case of the quaternary cations the strong adsorbability is probably the more predominant factor. The adsorbed layer must bear a higher charge than is present on the wall, so that in the outer part of the double layer the charge (and the potential) must be reversed in order to maintain electroneutrality. The strong adsorbability of these cations is also evident from the conductance measurement as well as the carbon content[9,10].

The linear plot of the maximum sedimentation volumes against percentage montmorillonite (Fig. 3) clearly shows that it is possible to determine the proportions of a binary mixture from these groups. A similar correlation between b.e.c. and viscosity of binary mixtures and the proportion of each has been already been reported[11,12,13].

The above results strongly suggest that by working at or near the maximum difference in sedimentation volume or zeta potentials, the two components may be separated more or less completely from their mixtures. A separation of the component clay minerals from the binary mixture based on the above principles has been successfully carried out[14].

The variation of sedimentation volume with the addition of alkyl ammonium hydroxides to the clay minerals is depicted in Fig. 4. The difference in the behaviour of TMAOH

9. Chakravarti, S. K. Ibid, 1959, 7, 27.
10. Chakravarti, S. K. Science and Culture, 1956, 22, 170.
11. Chakravarti, S. K.—J. Indian Soc. Soil. Sci., 1954, 22, 127.
12. Chakravarti, S. K.—Ibid, 1958, 6, 239.
13. Chakravarti, S. K.—Ibid, 1957, 5, 65.
14. Chakravarti, S. K.—(Unpublished work) D. Phil. Thesis, Calcutta University, 1959.

and CTAOH is particularly clear from the graphs 3 and 4, and 2 and 5. It was previously shown that TMA behaves, owing to its small size, like the inorganic cations[s], whereas the larger organic cations are more specific in their interactions. Thus, the particles show charge reversal with CTAOH which is adsorbed in excess of the b.e.o., whereas no such charge reversal is observed with TMAOH. PTAI interacts in a similar manner to TMAOH except that the interaction is slightly stronger towards higher additions, possibly owing to the presence of the iodide ion, which has got a stronger flocculating power (cf. curves 3 and 7).
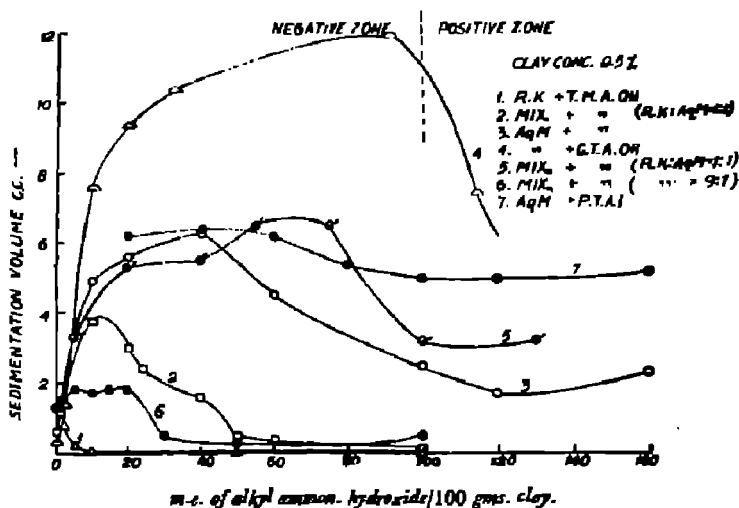

FIG. 4.

An examination of the curves 1 to 4 in Fig. 7 reveals that the viscosity and sedimentation volumes of clay minerals interacting with CTAOH increase to a maximum value corresponding to nearly 80% b.e.c.

Slabough and Culbertson[15] studied the interaction of bentonite and organic amine, diamine and amino acids by viscometric and cataphoretic speed measurements. They observed that as the laminae become more populated with organic groups, the micelles become less hydrated and there is a consequent shrinkage of the particle, thereby the viscosity of the colloidal suspension is reduced. It was observed that as H$^+$ ions are neutralised the viscosity reaches a minimum and then passes abruptly to a maximum corresponding to approximately 100% neutralisation of the mineral. Beyond this point an excess of amine had apparently no effect upon the viscosity of the system. Similar depression in viscosity has also been observed by Chakravarti[18] with clay minerals and their mixtures when treated with inorganic bases.

But similar arguments do not seem to apply to the results obtained in the present investigation with large quaternary ammonium compounds. Fig. 7 shows that viscosity of kaolinite and kaolinite mixtures (with montmorillonite) passes through a minimum on the addition of CTAOH, which occurs at about 10% of b.e.c. of the clays; a similar minimum is observed at 3.3% of b.e.c. of illite on the addition of CTAB. Beyond these concentration the viscosity increases up to nearly the base saturation point followed by a

15. Slabough, W. H. and Culbertson, J. L., *J. Phys. Chem.*, 1951, 55, 1151.

decrease afterwards. Binary mixtures of kaolinite and montmorillonite show two maxima in the viscosity curves, the first corresponds to the b.e.c. of kaolinite and the second to the average b.e.c. of the mixtures. Unlike kaolinite and illite, montmorillonite shows no minimum in viscosity curve with CTAOH, but the viscosity increases up to the b.e.c. and afterwards diminishes. At still higher concentration of the base the viscosity tends to rise again.

Similar variations in viscosity as well as sedimentation volume of kaolinite, mica and illite may be noticed from the graphs in Figs. 5A, 5B and 6, respectively. The difference in the features of the above viscosity curves with those obtained by Slabaugh et al. using amines, diamines and amino acids and by Chakravarti[15] using inorganic cations may be explained in the following way:
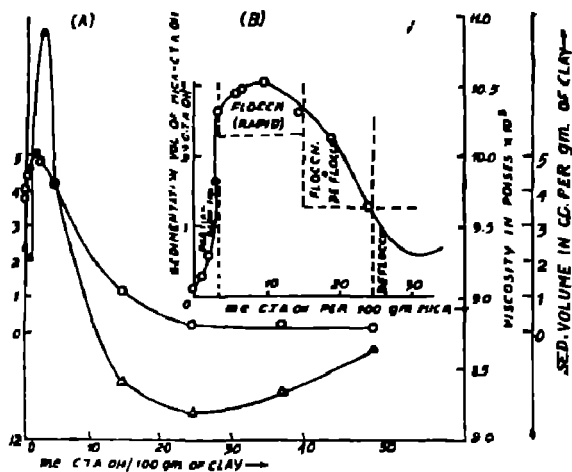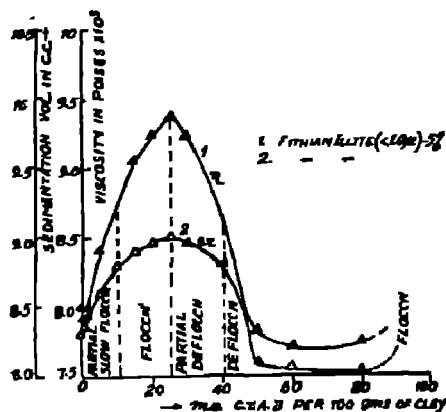

FIG. 5.

FIG. 6.

All the experiments carried out on the interaction of clay minerals with the large organic compounds (also compare Chakravarti[8] and Figs. 5 and 6) show considerable sensitivity of the reactions. Almost in each case the concentration of the electrolyte for the first visible coagulations of the colloid is very small compared to the total exchange capacity. The sedimentation volume is the sum total of the volumes of the aggregates produced as a result of flocculation. The latter causes rapid settling but the sediment is bulky because the particles preserve the haphazard positions in which they touched each other for the first time. A large number of water molecules are thereby enmeshed between the particles constituting the aggregates. Thus, the volume of the aggregates will be larger than the sum of the volumes of the individual particles. Viscosity of a suspension being a function of the "active volume" of the dispersed phase will increase with the addition of electrolytes up to that corresponding to the exchange capacity. Beyond the exchange capacity, owing to charge-reversal, the total volume of the dispersed phase diminishes and the viscosity also decreases. At still higher concentrations, however, the viscosity increases once again as flocculation occurs in the zone of positive charge (cf. Figs. 5-7).

Fig. 7 also shows that the b.e.c.'s corresponding to the second maximum in the curves for mixtures compared with the single maximum of the pure clays are seen to bear a linear relationship with the composition of the mixtures. A similar correlation was observed in the case of binary mixtures of pure clay minerals using inorganic bases[12].
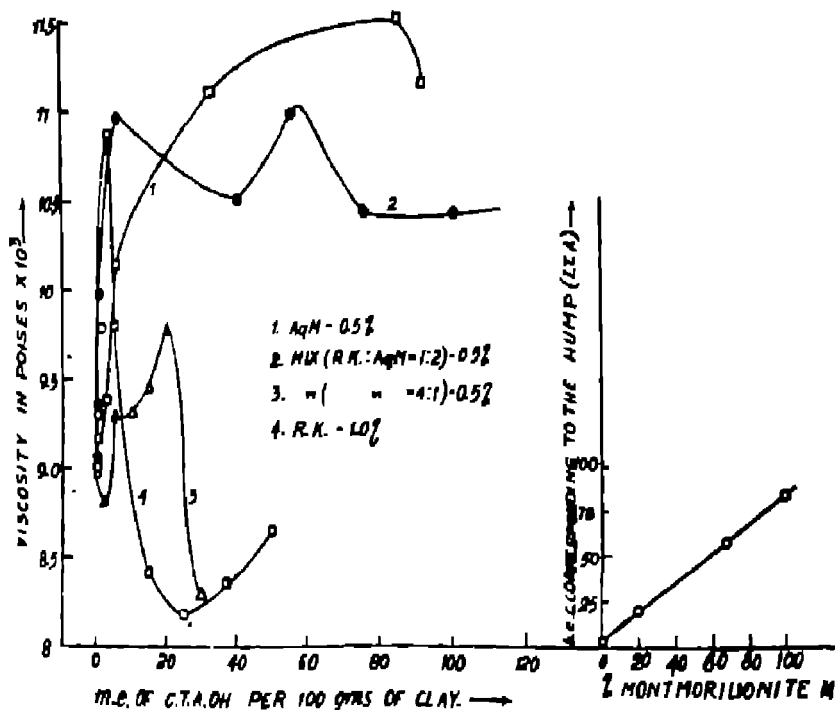

FIG. 7.

The exact state of flocculation and deflocculation and their relationships with sedimentation volume are summarised in table 2 for CTAB. Similar results have been obtained with the other clay-organic systems.

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