

Electrochemical Studies of Ceramic Clays

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With 2 Figures

Abstract

One of the ceramic clays known as RAJMAHAL clay was rendered into the H-clay by leaching with 0.02 N HCl and washing it free from excess of the acid. The H-clay was sieved through 120 mesh, and the clay suspension was shaken in a mechanical shaker for different intervals of time. It was observed that the p_H of the clay suspension took 8 hours to reach a constant p_H value.

The suspension was then titrated against 0.01 N NaOH solution both by conductometry and potentiometry. The points of equivalence obtained by both of these techniques were strikingly identical. There were three loops (two prominent and one suppressed) and three points of intersection in the potentiometric and conductometric curves respectively. These results have been discussed in the aspect of clay mineralogy.

Introduction

X-ray, differential thermal and optical methods have been suggested for identifying and characterizing the clay minerals in soils¹⁻³). Electrometric and viscometric methods have also been developed by MUKHERJEE et al⁴), for identification purposes. The crystalline structure of clay minerals as envisaged by PAULING⁵), GRUNNER, et al⁶)⁷) offers satisfactory explanation to the results obtained by these various methods.

During recent years considerable amount of work has been carried, out on the base-exchange capacity (b. e. c) of H-clay⁸)⁹). It was shown that the base exchange capacity (b. e. c) of H-clay was not a fixed quantity but depends on the p_H at which it was estimated, and on the nature and concentration of cations introduced into the system in making the estimation.

1) G. W. BRINDLEY, Mineralogical Society of Great Britain, Monograph. 75 (1951).

2) R. E. GRIM, Clay Mineralogy, McGraw Hill Book Co. Inc. N.Y. (1953).

3) C. E. MARSHALL, Z. Kristallogr. **10**, 3 (1935).

4) J. N. MUKHERJEE, Bull. Indian Soc. Soil. Sci. **6**, 1 (1951).

5) L. PAULING, Proc. nat. Acad. Sci. USA **16**, 578, 582 (1930).

6) J. W. GRUNNER, The Crystal Structure of kaolinite, Z. Kristallogr. **88**, 75 (1932).

7) J. W. GRUNNER, Am. Mineral. **20**, 475 (1935).

8) MITRA, Indian J. A. S., **6**, 555 (1936).

9) J. N. MUKHERJEE, MITRA u. S. MUKHERJEE, Trans. Nat. Inst. Sciences, **1**, No. 10,22 (1937); Bull. Indian Soc. of Soil Science No. 4, 41 (1942).

MARSHALL, MUKHERJEE, MITRA and co-workers have considered in detail the significance of the titration curves showing the relation between p_H and milliequivalents of added NaOH^{10-12} . They observed that the character of the clay mineral, its concentration and the base used for titration also affect the nature of the titration curves.

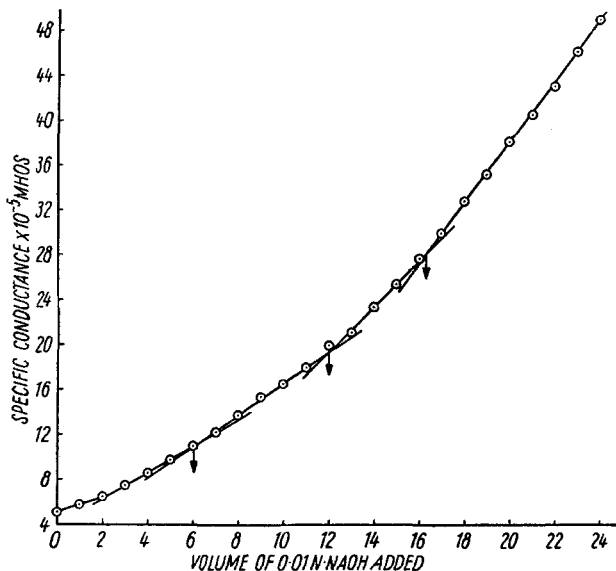


Fig. 1

B. CHATTERJEE studied the nature of clay minerals in Sakrand Soil (Sind) which was saline in character. He observed by determining its chemical composition and potentiometric titration of the H-clay that the mineralogical characteristics of the clay fraction corresponded to the illites.

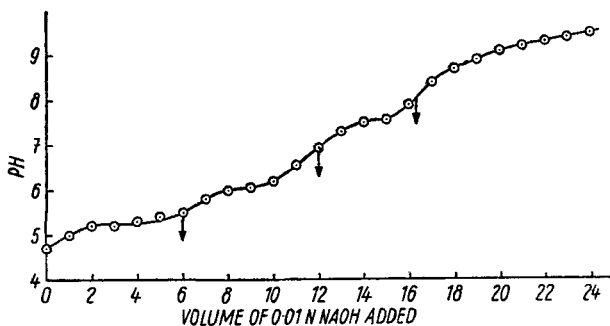


Fig. 2

¹⁰ C. E. MARSHALL, *The colloid Chemistry of the Silicate Minerals* (1949).

¹¹ J. N. MUKHERJEE, R. P. MITRA, *J. Colloid Sci.* **1**, 141 (1946).

¹² J. N. MUKHERJEE, R. P. MITRA, *J. phys. Chem.* **47**, 543, 549 (1943).

In this paper, we communicate the results of the electrochemical titrations of the hydrogenated RAJMAHAL clay with a view to determine the type or types of clay mineral of which the RAJMAHAL clay may be composed.

Experimental

The clay was sieved to remove very coarse particles. About 50 gms. of the sieved clay was suspended in distilled water and the floating organic impurities were removed mechanically. Finally the H-clay was prepared by leaching with 0.02 N-HCl to ensure complete exchange of exchangeable cations with H ions. The excess of the acid was then washed out with distilled water and finally with conductivity water. The H-clay so obtained was dried and sieved through 120 mesh. 5 gms. each of the sieved clay was taken in two pyrex glass bottles fitted with glass stoppers and mixed with 50 c. c. of conductivity water and then shaken in mechanical shaker for 8 hours to reach a constant p_H value.

The suspension was then titrated against 0.01 N NaOH solution both by conductometry and potentiometry. The observed conductance after each addition was corrected for the dilution effect by multiplying it by the factor $V/50$ where 'V' c. c. is the total volume of the solution in the conductivity cell at the stage, and 50 c. c. refer to the volume originally taken. The corrected conductance thus obtained was plotted as a function of volume of the titrating solution. The equivalence point was obtained by the point of intersection of the two parts of the curve.

Observation

Table 1

Variation in p_H in the RAJMAHAL clay suspension system mixed in the ratio (1:10) for different hours of shaking

Time of shaking hours	p_H observed	Time of shaking hours	p_H observed	Time of shaking hours	p_H observed
0.5	3.8	4.0	4.5	10.0	4.7
1.0	4.1	6.0	4.6	12.0	4.7
2.0	4.3	8.0	4.7	16.0	4.7

Discussion

The potentiometric titration curve of the hydrogen clay (H-clay) against 0.01 N NaOH shows two sharp inflexion points at p_H 5.5 and 6.9, but another weak inflexion appears at p_H 8.1. These inflexion points are also confirmed by the intersections of the conductometric curve. The base exchange capacities at the first and second inflexion points are 1.2 and 2.4 miliequivalent of NaOH or in the ration 2:1. This ratio corresponds to the value of the H-kaolinite.

Table 2

Temperature = 20° C; Initial volume = 50 c. c.; Time of shaking = 8 hours; Cell constant = 0.42

Vol. of Alkali added in c. c.	Resistance in Ohms.	Specific conductivity · 10 ⁻⁵ mhos	Corrected conductance · 10 ⁻⁵ mhos	PH
0.0	8000	5.25	5.25	4.7
1.0	7450	5.64	5.75	5.0
2.0	6750	6.23	6.47	5.2
3.0	6000	7.00	7.42	5.2
4.0	5300	7.92	8.55	5.3
5.0	4700	8.93	9.83	5.4
6.0	4200	9.88	11.08	5.5
7.0	3900	10.77	12.28	5.8
8.0	3600	11.66	13.81	6.0
9.0	3300	12.73	15.37	6.1
10.0	3050	13.77	16.52	6.2
11.0	2850	14.74	17.98	6.6
12.0	2600	16.15	20.03	6.9
13.0	2500	16.80	21.16	7.3
14.0	2300	18.26	23.37	7.5
15.0	2150	19.54	25.40	7.5
16.0	2000	21.00	27.71	7.9
17.0	1880	22.13	29.94	8.4
18.0	1740	24.17	32.83	8.7
19.0	1640	25.61	35.33	8.9
20.0	1540	27.27	38.18	9.1
21.0	1470	28.57	40.57	9.2
22.0	1400	30.00	43.20	9.3
23.0	1325	31.00	46.28	9.4
24.0	1265	33.20	49.12	9.5
25.0	1200	35.00	52.50	9.7

The third point of equivalence at pH 8.1 (16.2 c. c. of 0.01 N NaOH) throws some ambiguity regarding the composition of the RAJMAHAL clay minerals, whether it is a pure kaolinite or a mixture of some other type of clay mineral. It is difficult to give a conclusive evidence of the structure without X-ray diffraction studies for which there is no facility in our laboratory, yet from the values of the base exchange capacity of the clay at the points of inflexion and their ratios at the inflexion points it appears that RAJMAHAL clay consists of kaolinites mixed with its transformation products.

The low values of the base exchange capacities obtained by us may be due to the bigger size of the grains of the particles of clay suspensions as observed by HARMON and FRAULINI¹³).

¹³) HARMON and FRAULINI, J. Amer. ceram. Soc. 19, 307 (1936).

The equilibration of the hydrogen RAJMAHAL clay has also been determined by shaking the suspensions on a mechanical shaker for different intervals of time. The observations are given in the table No. 1 which show that the perfect equilibrium is attained in the clay system after eight hours of shaking.

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