EXCHANGE EQUILIBRIA ON MONTMORILLONITE INVOLVING ORGANIC CATIONS

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ABSTRACT

Exchange equilibrium of triethylammonium cation for dimethylhydrogenatedtallow-benzylammonium cation on a montmorillonite lattice has been investigated. Quantitative measurements were made to determine the magnitude of exchange taking place in the reactions. The results of these measurements have been described in terms of a Langmuir adsorption isotherm and in terms of the law of mass action. From the law of mass action, the thermodynamic equilibrium constant was determined to be 0.56 or 0.59 depending on the method of calculation.

INTRODUCTION

In recent years, there has been considerable research on the formation of organo-clay complexes by ion exchange of various amine salts or quaternary compounds for inorganic cations on montmorillonite. Lately, it has been demonstrated that organic cations will exchange for other organic cations attached to the montmorillonite substrate (McAtee, 1962, 1963).

The nature of the exchange of triethylammonium cation for dimethyl-hydrogenatedtallowbenzylammonium cation on montmorillonite[1] lattice was investigated in the work described herein. This organo-clay is one of the major commercially available materials (Bentones[2]) that is used to gel various organic dispersants. One principal use is to form greases by its action to gel oil. In the study of the various mechanisms by which the gel structure of greases change, it was recognized that cation exchange upon the clay substrate might take place and thus produce the observed changes. The work described herein was conducted so as to substantiate the exchange mechanism and to determine the thermodynamic equilibrium constant. From the magnitude of the equilibrium constant information is learned regarding the extent of the exchange reaction. Equilibrium reactions have been described in terms of the law of mass action and also in terms of a Langmuir adsorption isotherm. These expressions were used to calculate an equilibrium constant for the exchange equilibrium on the montmorillonite substrate.

[1] Hydrogenated tallow consisted of straight chain hydrocarbon radicals, 68% C_{18}, 27% C_{16}, and 5% C_{12}, C_{14}, and C_{20}; Kirk, R. E. and Othmer, D. F., ed., Encyclopedia of Chemical Technology, Vol. 6, 1953, p. 144.

[2] Registered Trade Mark, Baroid Division, National Lead Co.

Experimental

Materials. A sample of spray dried, centrifuged Wyoming bentonite, supplied by the National Lead Company, Baroid Division, was used to prepare a two per cent suspension in water. The clay suspension was passed at 70° C. through a column of Dowex-50W-X2, which had been previously converted to the sodium form. A Versenate titration was carried out to insure that the amount of Ca^{2+} and Mg^{2+} ions remaining on the clay was less than 5 meq/100 g clay.

Dimethylhydrogenatedtallowbenzylammonium bentonite was prepared by mixing the equivalent of 100 meq/100 g clay of dimethylhydrogenatedtallowbenzylammonium chloride (hereinafter designated DMHT-B) in aqueous solution to a hot dispersion of sodium bentonite. The product was filtered, washed, and dried in air. The DMHT-B-clay complex was ground to a powder by a mortar and pestle after which 1.5 g samples were extracted with isopropanol for 150 hours. The extracted samples were dried and subjected to a standard ignition loss technique to determine the exact amount of the DMHT-B cation remaining on the clay surface (McAtee, 1959).

Triethylamine chloride was prepared by allowing distilled commercial triethylamine obtained from the Eastman Company to react with dry HCl gas. The product was recrystallized and the purity was checked by determining its melting point. A 5×10^{-3} N solution of triethylamine chloride in 80 per cent isooctane-20 per cent isopropanol was prepared.

Methods. Accurately weighed portions of the extracted DMHT-B-clay complex were mixed with increasing amounts of triethylamine chloride solution in small, 20 ml thick-walled glass bottles fitted with a solvent tight screw cap. A small insoluble plastic ball was placed in each bottle to improve mixing. Dispersion was produced by shaking the contents of the bottles in a Spex Mill/Mixer or a Burrell Wrist Action shaker until equilibrium was achieved. The equilibrium mixture was filtered in a pressure filter cell at room temperature and it was then washed several times with 80 per cent isooctane-20 per cent isopropanol solvent. The filtrate and washings were diluted to standard volume and reserved for analysis.

Residues from the above procedure were again transferred to the thick-walled bottles, shaken with 15 ml portions of 80 per cent isooctane-20 per cent isopropanol solvent for several minutes, and filtered. This step was repeated three times, and each time the filtrate was combined so that the final volume was approximately 45 ml. This was diluted to a standard volume of 50 ml and reserved for analysis.

Analysis. Filtrates from the equilibrium mixtures, as well as those obtained from the shaken residues, were analyzed spectrophotometrically for DMHT-B cation content using a Beckman DK-1 Recording Spectrophotometer. Filtrates were analyzed for chloride content by means of a potentiometric titration using a standardized silver nitrate solution.

RESULTS AND DISCUSSION

DMHT-B-clay complex. Ignition-loss experiments were conducted on samples of the DMHT-B-clay complex to determine the exact amount of organic material transferred to the clay surface. These experiments were conducted before and after the DMHT-B-clay complex was extracted. Results for the unextracted material indicated that the amount of organic material transferred to the clay was 100 meq/100 g clay ± 1 meq. The amount of DMHT-B cation remaining on the clay surface after the samples were extracted was reduced to 75 ± 1 meq/100 g clay. It was concluded that these 75 meq were exchanged onto the clay surface and not merely adsorbed physically.

Determination of equilibrium conditions. Three important reaction conditions were investigated. First, the time required to reach equilibrium was measured as a function of the shaking time of the mixture of reactants. This was determined to be four minutes using a Spex Mill/Mixer or 15 minutes using a Burrell Wrist Action Shaker.

A second condition studied was the effect of changing the amount of the solid sample of DMHT-B-clay complex used in each reaction run. It was concluded that sample size could vary from 100 mg to 300 mg without affecting the results.

The third condition examined was that of changing the initial concentration of the triethylammonium chloride solution added to the DMHT-B-clay complex. It was concluded that concentration had little or no effect on the extent of exchange of the ions over a ten-fold range from 1×10^{-3} N to 1×10^{-2} N.

Presentation of data. Before conducting any exchange reactions, the DMHT-B-clay complex was washed with isooctane-isopropanol solvent to remove impurities which would contaminate the spectra. A series of exchange reactions was carried out using from 10 meq triethylamine chloride (TREAC)/100 g DMHT-B-clay complex to 800 meq TREAC/ 100 g DMHT-B-clay complex. These reactions were conducted at a uniform concentration of 5×10^{-3} N TREAC.

Ultraviolet analyses of the DMHT-B cations were carried out to determine the degree of exchange which occurred in the reaction. Analyses

consisted of two parts. The first determinations represented spectropho-
tometric results of the reaction filtrates which contained exchanged
DMHT-B cations, unreacted TREAC cations, and chloride anions.

The second group of analyses were for the DMHT-B cation present in
the filtrates from washings of the residues. The DMHT-B present was
that which was readsorbed into the clay after exchange by TREAC had
occurred.

Analysis for the chloride ion corroborated the ultraviolet data obtained
by DMHT-B analyses. Analyses consisted of two separate titrations. The
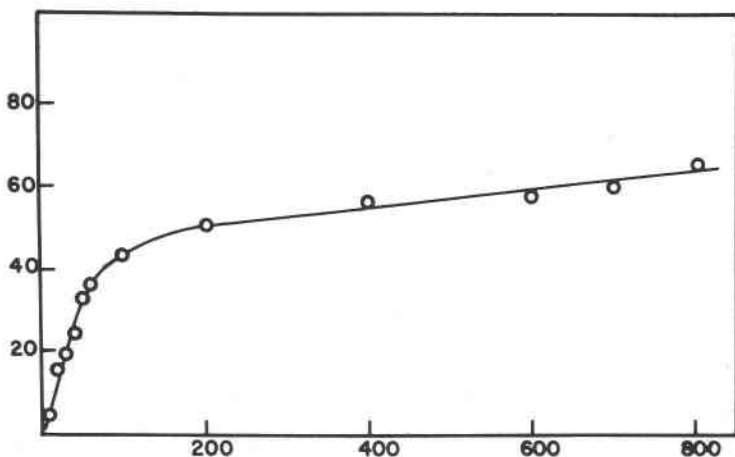first titration was of the chloride ion in the reaction filtrates used for the

FIG. 1. Exchange of triethylamine (TREAC) cation for dimethylhydrogenatedtallow-
benzylammonium (DMHT-B) cation on montmorillonite.

ordinate: DMHT-B displaced (meq/100 g clay)
abscissa: TREAC added (meq/100 g clay)

ultraviolet analysis of DMHT-B cations. Similar chloride analyses were
conducted on extraction filtrates from the residues.

Comparison of the DMHT-B exchanged with the unadsorbed chloride
ion showed that DMHT-B cation values are normally less than the corre-
sponding chloride anion values. Since the reaction filtrate contained ex-
cess unreacted TREAC cations as well as exchanged DMHT-B cations,
it was expected that chloride ion values should exceed the DMHT-B
values. A comparison of total DMHT-B cation with total chloride anion
(the sum of the determinations in both instances) showed close agree-
ment.

A plot of the exchanged DMHT-B quantities versus the added amount
of TREAC resembled a typical Langmuir adsorption isotherm as shown

in Fig. 1. The Langmuir equation, modified to fit the exchange terms, is given as follows:

$$D^+ = kqT/(1 + kT) \qquad (1)$$

where D^+ is equal to DMHT-B displaced (meq/100 g clay complex), k is a constant dependent upon the nature of the exchanging species with units of 1/(meq/100 g clay complex), q is the actual exchange capacity of the clay with units of (meq/100 g clay complex), and T is the TREAC added to the DMHT-B-clay complex with units of (meq/100 g clay complex).

If the data follow such an equation, then a plot of T/D^+ versus T should be a straight line. This can be determined from the following relation:

$$T/D^+ = 1/kq + T/q \qquad (2)$$

The result of such a plot is shown in Figure 2. The best straight line was
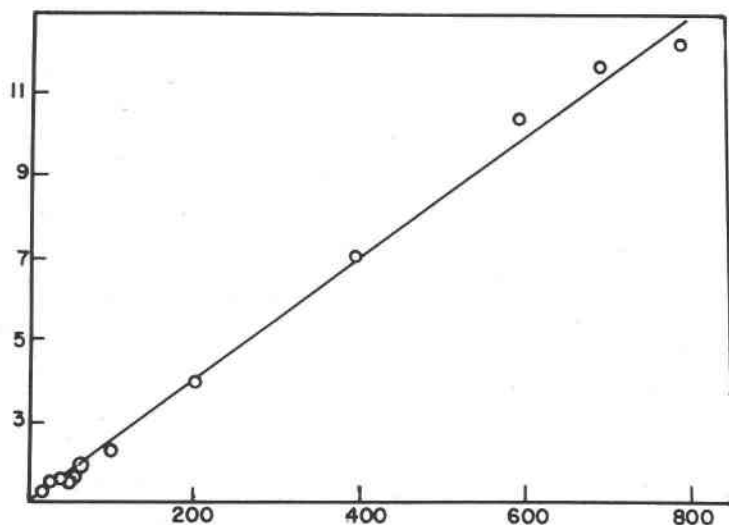

Fig. 2. Langmuir type isotherm for the exchange of triethylamine (TREAC) cation for dimethylhydrogenatedtallowbenzylammonium (DMHT-B) cation on montmorillonite.

ordinate: TREAC added/DMHT-B displaced
abscissa: TREAC added (meq/100 g clay)

determined for the curve by using the method of least squares utilizing all of the experimental data obtained.

According to the equation of this curve, the slope of the line is $1/q$. This is calculated to be 1.46×10^{-2} and its reciprocal, q, which gives the

actual exchange capacity, is calculated to be 69 meq/100 g clay complex. This exchange capacity value represented about 92 per cent of the experimentally measured value of 75 meq/100 g clay obtained by ignition of DMHT-B-clay complex. The difference may be due to the different types of exchange sites on the clay such as those on the basal surfaces as opposed to those on broken edges. If so, this difference suggests that the cations on edges may be held by forces of somewhat greater magnitude than those held by basal sites.

The value of the intercept, $1/kq$, is calculated to be 1.13, making the value of k equal 1.28×10^{-2}. Theoretically the intercept must be equal to one or greater since the intercept equals T/D^+ and D^+ (the amount of the DMHT-B displaced) cannot be greater than T (the amount of TREAC added).

Mass action relationship. Exchange equilibria are often expressed in terms of the law of mass action. The exchange carried out in this work can be represented in the following manner:

$$DM + T^+ \rightleftarrows TM + D^+ \tag{3}$$

where M refers to montmorillonite substrate, D^+ refers to DMHT-B cation, and T^+ refers to TREAC cation. For such a reaction, the thermodynamic equilibrium constant can be written:

$$K = \frac{a_{TM}a_{D^+}}{a_{DM}a_{T^+}} \tag{4}$$

where a refers to activities and subscripts indicate various components.

In order to express the thermodynamic equilibrium constant in terms of measurable quantities, a selectivity coefficient (k_c) can be defined as:

$$k_c = \frac{(m_{D^+})(N_{TM})}{(m_{T^+})(N_{DM})} \tag{5}$$

where m refers to molality of the species in solution and N refers to the mole fraction of the species in the solid phase.

Following the development by Argersinger and Davidson (1952) the relation between the equilibrium constant and the selectivity coefficient is given as follows:

$$\ln K = \int_0^1 \ln k_c dN_{TM} \tag{6}$$

In order to make use of equation (6) with the data obtained, several assumptions must be made. First, the reacted DMHT-B-clay complex must be treated as a solid solution; that is, all of the components of the solid phase form completely miscible mixtures with one another. This assumption is almost universally accepted in ion exchange reactions

(Boyd *et al.*, 1947). Another assumption is that solvent effects are small and, therefore, can be neglected. In the range of concentration studied (10^{-3}N), this assumption is justified, especially in view of the experimental accuracy. The third assumption is that of subsituting normalities for molarities. Again, this is justifiable in the concentration range under study.

Two further assumptions pertain to the activities of the constituents involved in the reaction. The ratio of the activity coefficients of the ionic species in solution approaches unity and is constant at constant ionic strength. The validity of this assumption depends upon the concentration. While it may be argued that the value is not unity at the concentrations used in this study, the ratio will be constant so long as the ionic strength remains constant. A final assumption is that changes in electrolyte sorption on the clay complex would not affect to an appreciable extent the activity coefficients of the clay complex.

Using these approximations in equation (6), a plot of log k_c versus N_{TM} was made and is shown in Fig. 3. Values used for the calculation of log k_c were taken from the curve in Fig. 1. As shown by equation (6), the area under the curve in Fig. 3 represents the equilibrium constant. The curve was integrated graphically by means of counting the squares and it yielded a value of -0.23 for the log K. The thermodynamic equilibrium constant, K, was calculated to be 5.9×10^{-1}.

The limitations in a log k_c versus mole fraction plot using an exchange curve are manifest at the very low and very high values of the mole fraction. At these extremes the curve tapers off severely and it is difficult to extrapolate to the limit. These drawbacks can be overcome by using data from the Langmuir isotherm plot because it can be represented by a straight line.

Using only values taken from the Langmuir plot of the data (Fig. 2) to calculate the points for k_c, a plot of log k_c versus N_{TM} was drawn and is shown in Figure 3. Graphical integration of this curve yields a value for log K of -0.25, thereby making K, the equilibrium constant, equal to 5.6×10^{-1}.

Comparison of the two equilibrium constants obtained from Figure 3 show that they agree within five per cent. Therefore, it can be concluded that the Langmuir type equation is a valid representation of the data. Furthermore, correlation shows that there is a relation between the Langmuir adsorption isotherm and the mass action relation.

The magnitude of the equilibrium constant, about 0.6 indicates that under the equilibrium conditions of these experiments effectively large amounts of organic cation exchange takes place on the montmorillonite. Assuming that such exchange occurs in greases, the alteration of the gel
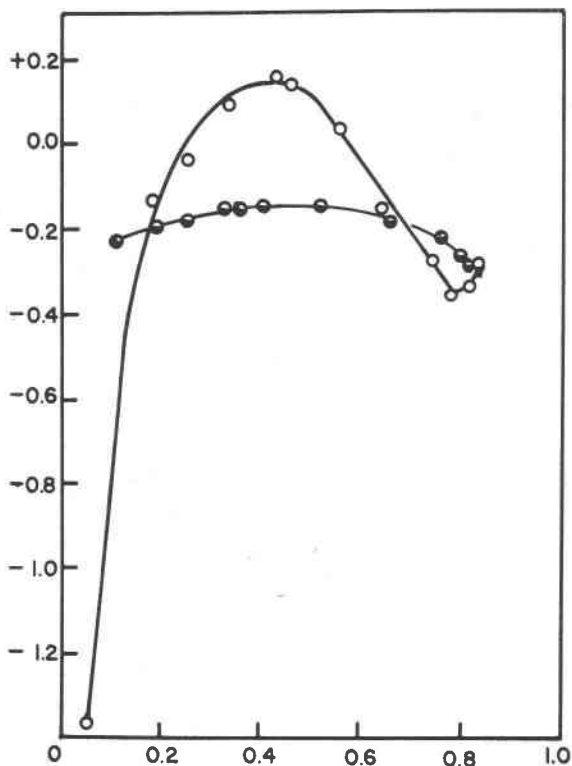
Fig. 3. Variation of selectivity coefficient, K_c, with mole fraction of triethylamine-montmorillonite using data from Figs. 1 and 2.

Data from Fig. 1.   ○
Data from Fig. 2.   ◒
ordinate: log k_c
abscissa: mole fraction, TREAC-montmorillonite

properties to either thicker or thinner gels can be accounted for since it is well recognized that the rheological properties of an organo-clay is highly dependent on the organic material associated with the clay.

It should be mentioned that attempts were made to approach the equilibrium from the clay-TREAC side of the reaction. It was found impossible to disperse this organo-clay in isooctane-isopropanol solvent. Because of this, no reproducible results could be obtained. However, the order of magnitude of the amounts of exchange were as they should be for the proposed reaction to represent a true equilibrium.

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