

ADSORPTION BY ORGANO-CLAY COMPLEXES— PART 2

by

C. T. COWAN

The Fullers' Earth Union Ltd., Patteson Court, Redhill, Surrey

ABSTRACT

A detailed investigation of the adsorption of phenol and *m*-cresol from dilute aqueous solution by dodecyl- and tetradecylammonium bentonites has been carried out. The Freundlich isotherms for the tetradecylammonium bentonite system indicate that during adsorption, the process proceeds in two stages, the partial molar heat of adsorption changing from a positive to a negative value with a relatively small change in concentration of adsorbate. In the light of these findings, the aspects of the adsorption are discussed in terms of thermodynamic quantities, spatial considerations, and interlamellar expansion of the clay mineral.

INTRODUCTION

The ability of the clay mineral montmorillonite to adsorb, absorb, or react with a wide range of both organic and inorganic compounds has been summarized by MacEwan (1951, p. 86), and in this work the complexes of montmorillonite are classified into three main groups:

- (1) with water and inorganic cations;
- (2) with large organic cations; and
- (3) with neutral liquids and inorganic cations.

As the author suggested, many other types are possible but they have not been investigated in detail. In a previous work (Cowan and White, 1962) formation of a new series of complexes was described; namely, those formed by a montmorillonite in which the inorganic cations had been replaced by *n*-aliphatic amine ions and phenolic compounds. It was shown that these complexes are readily formed in the presence of a large excess of water and in fact certain of the alkyl ammonium bentonites were effective as adsorbents for phenolic bodies from dilute aqueous solution. Since the publication of the original work a more detailed examination of the systems tetradecylammonium bentonite-phenol-water and tetradecylammonium bentonite-*m*-cresol-water has been completed and the results compared with those previously obtained for dodecylammonium bentonite-phenol-water. It is apparent from the investigation that a process of adsorption, somewhat more complex than originally postulated, is operative.

EXPERIMENTAL

Since the long chain aliphatic amine derivatives of montmorillonite are essentially hydrophobic (Jordan, 1949) the use of these materials as adsorbents in dilute aqueous solutions introduces the complication that wetting of the solid by the aqueous phase is not always readily accomplished. In view of this, it was considered that all adsorption experiments should be carried out with thoroughly wetted material and the only satisfactory method of achieving this was to preform the amine clay complexes in an aqueous solution and, without further treatment, use the suspension of the organo-clay directly. Furthermore, since the reaction between sodium montmorillonite and tetradecylamine acetate is quantitative (Cowan and White, 1958) the presence of free tetradecylammonium ions in the aqueous phase, which may interfere with the reaction, is eliminated. Although minor quantities of sodium acetate will be present, a detailed investigation showed that the presence of this did not affect the results.

Procedure

To 25 ml of 4.0 percent sodium montmorillonite slurry was added, with vigorous agitation, a predetermined quantity of exactly $M/2$ tetradecylamine acetate. Reaction between the two "solutions" was immediate and the tetradecylammonium bentonite was formed as flocs. To this suspension, 25 ml of accurately standardized phenol solution was added and the boiling tube in which the reaction was carried out was stoppered and placed in a thermostatted water bath for 6 hr. Throughout this period the flocs of amine clay were occasionally redispersed in the solution by shaking. After completion of the adsorption period, a preheated, sintered glass filter thimble was placed in the boiling tube, and when sufficient clear phenol solution had filtered into the crucible the solution was removed with a pipette. The final concentration of phenol was determined using the bromate-bromide method (Ruderman, 1946) and this technique was equally applicable to *m*-cresol.

Since both the starting concentration of the phenol solution and the volume of reactants added were known, the initial concentration could be calculated. The weight of adsorbent present was also obtained by calculation.

Using the technique outlined above, the following parameters were investigated between the specified limits:

- (1) amine concentration, 70–145 meq/100 g clay;
- (2) phenol/*m*-cresol concentration, 1.0–0.05 percent;
- (3) temperature, 20° C, 40° C, 60° C.

RESULTS

Full results are not presented in detail but the Freundlich isotherms for some typical examples are given in Fig. 1. The variation of the extent of adsorption of phenol with temperature is shown in Fig. 2 for both dodecylammonium bentonite and tetradecylammonium bentonite. The fundamental

difference between the two adsorbents is apparent and whilst dodecylammonium bentonite shows typical behavior, i.e. the adsorption decreases with increasing temperature, characteristic of an exothermic process, tetradecylammonium bentonite shows wide variation from this. As the temperature

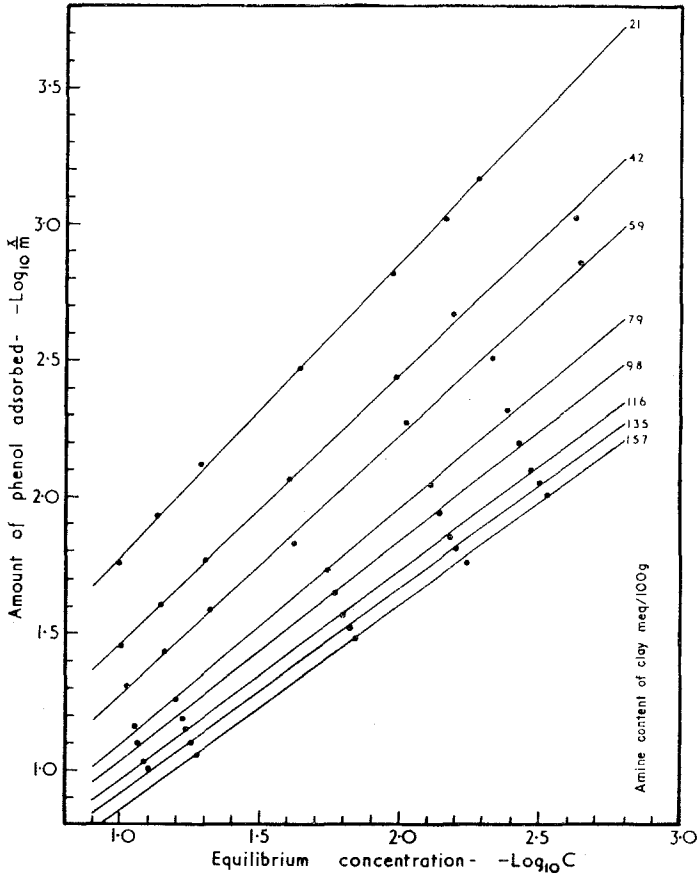


FIGURE 1.—Typical Freundlich isotherms for the system dodecylammonium bentonite-phenol-water.

increases from 20°C to 40°C, at high equilibrium concentrations of solute ($-\log_{10}C = 1.0$ to 1.5) behavior is quite normal, whereas in more dilute solutions greater adsorption is exhibited at the higher temperature, indicating an endothermic process.

In the range 40–60°C, at all the investigated equilibrium concentrations, the isotherms show the typical exothermic process.

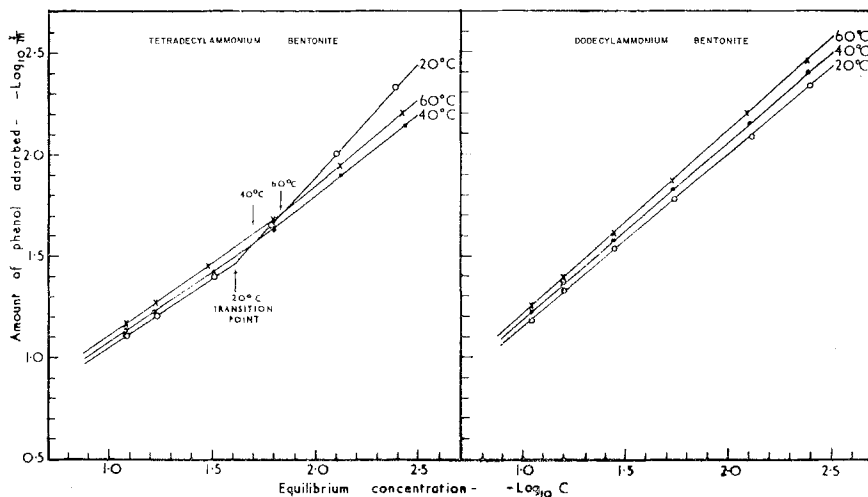


FIGURE 2.—The adsorption of phenol from dilute aqueous solution by dodecyl- and tetradecylammonium bentonites at various temperatures.

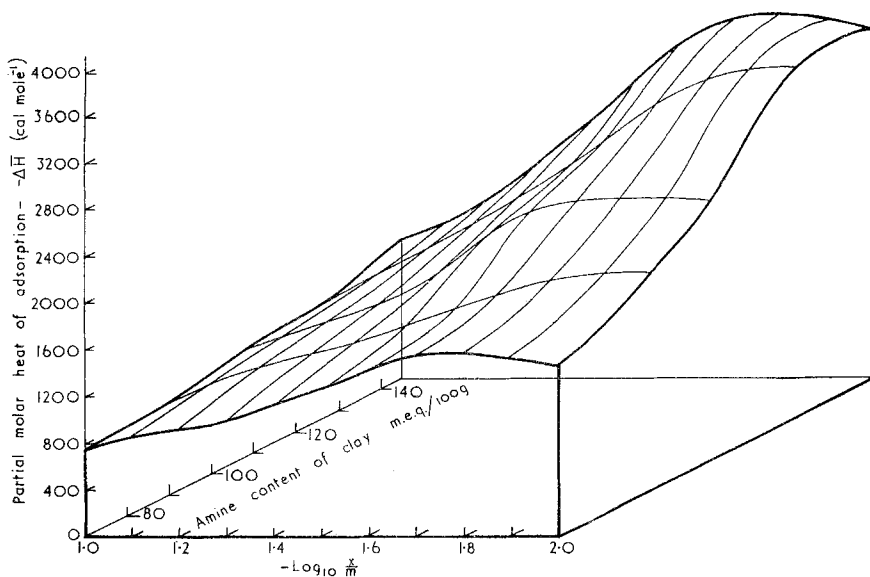


FIGURE 3.—The partial molar heat of adsorption for the system dodecylammonium bentonite-phenol-water.

By applying the Clausius-Clapeyron equation in the integrated form to data abstracted from the Freundlich isotherms, the partial molar heats of adsorption were calculated, at various specific levels of surface coverage;

i.e.
$$\frac{d \ln C_e}{d(1/T)} = \frac{\Delta \bar{H}}{R}$$

where C_e = equilibrium concentration of the solute in the aqueous phase,
 $\Delta \bar{H}$ = the partial molar heat of adsorption,
 x/m = grams phenol sorbed per gram of organo-clay complex.

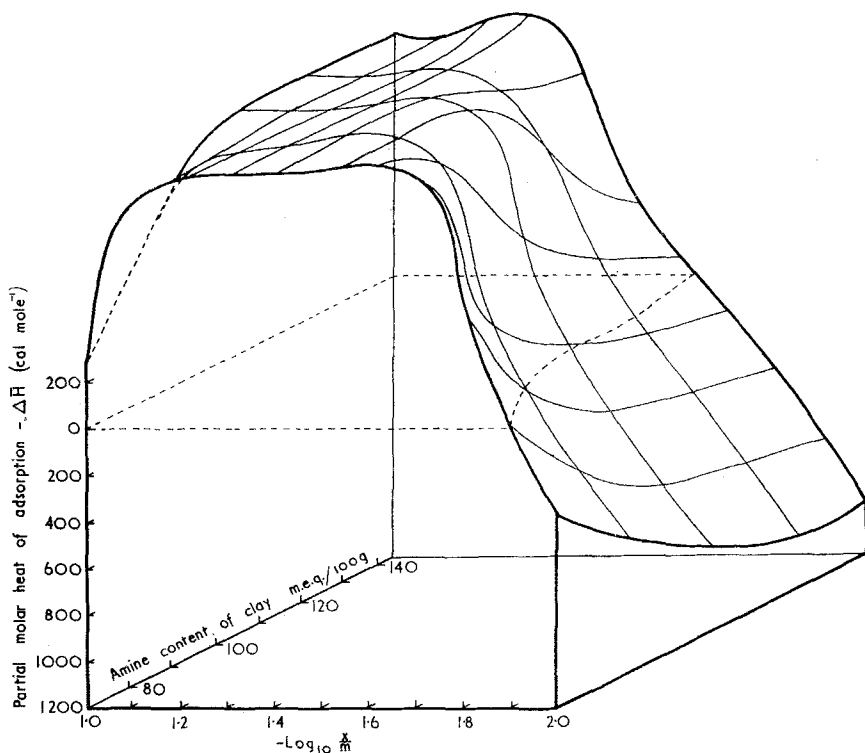


FIGURE 4.—The partial molar heat of adsorption for the system tetradecylammonium bentonite-phenol-water.

Using these data, the three-dimensional graphs that were obtained are shown in Figs. 3-5. The plots of $-\Delta \bar{H}$ vs. $\log_{10} x/m$ vs. amine content of the clay clearly show how the parameters affect the overall heat of adsorption. By interpolation the actual values for $\log_{10} x/m$ at which $\Delta \bar{H} = 0$ were obtained and are shown in Table 1.

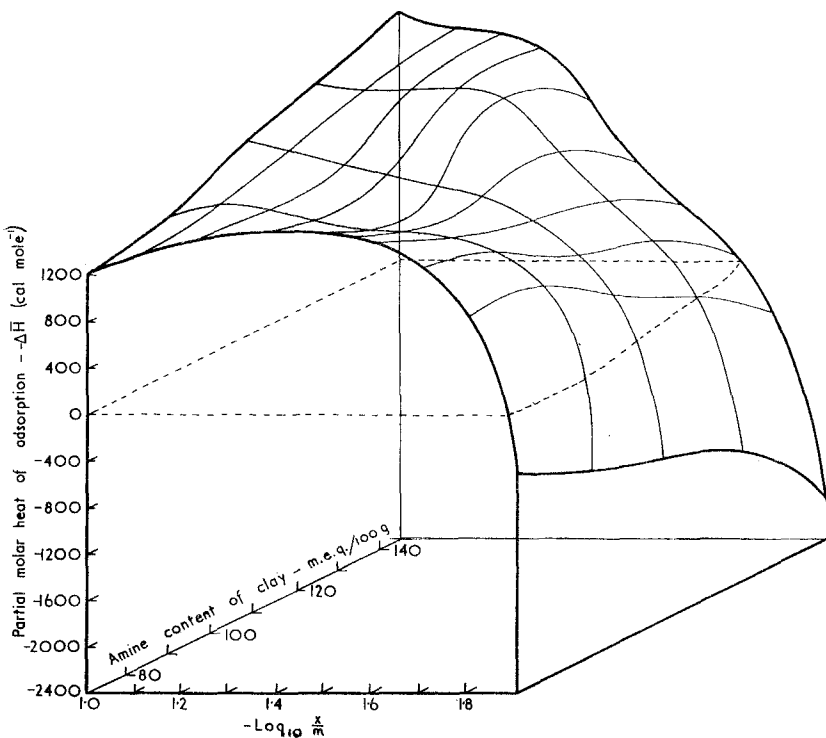


FIGURE 5.—The partial molar heat of adsorption for the system tetradecylammonium bentonite-*m*-cresol-water.

TABLE I.—VALUES FOR $\log_{10} x/m$ AT WHICH $\Delta\bar{H} = 0$

Amine content of organo-clay meq/100 g	$\Delta\bar{H} = 0$	
	$-\log_{10} x/m$ phenol	$-\log_{10} x/m$ <i>m</i> -cresol
71	1.90	1.89
89	1.79	1.87
108	1.74	1.84
125	1.69	1.80
145	1.64	1.70

DISCUSSION

On the basis of semiquantitative X-ray data (White, private communication, 1960), it has been found that adsorption of phenols from dilute aqueous solutions by organically modified montmorillonite may involve the expansion of the clay lamellae. Therefore, where "condensation" of phenol onto the clay surface occurs, several processes may be involved. Depending on the available interlamellar space and on the size and amounts of adsorbate molecules undergoing condensation, work may have to be performed on the clay complex in order to expand the lamellae to an extent sufficient to allow the intercalation of adsorbate molecules.

With the system dodecylammonium bentonite-phenol-water it was postulated (Cowan and White, 1962) that the *c*-axis spacing of the organo-clay complex was 8 Å but the interlamellar surface coverage was only just in excess of 50 percent. On this basis, there is a considerable amount of available interlamellar space and hence adsorption can occur without the clay lattice undergoing further expansion. The adsorption results for this system, shown in Fig. 3, are quite compatible with this reasoning, and it is seen that the partial molar heat of adsorption is always a negative value indicating a normal adsorption process. As the extent of coverage of the clay surface with adsorbate molecules becomes greater, the value of $-\Delta\bar{H}$ decreases, which is again consistent with normal adsorption phenomena.

Reference to Fig. 4 shows that with the system tetradecylammonium bentonite, a completely different situation exists and, up to a point, the value of $\Delta\bar{H}$ changes from positive to negative with increasing extent of surface coverage by adsorbate molecules; i.e. the process of adsorption changes from an endothermic to an exothermic one over a relatively small change in surface coverage. This is in complete contradiction to normal processes of adsorption which are generally recognized as being exothermic. It is proposed that with tetradecylammonium bentonite, before intercalation can occur the clay lattice must undergo expansion to accommodate the adsorbate molecules, and the work involved in carrying out such a process is in excess of that liberated by the adsorption. At low values of x/m (which is in effect surface coverage) the extent of intercalation is correspondingly small. However, since interlamellar positions are occupied by the substituting amine ions, the lattice must undergo expansion to a minimum critical distance before intercalation can occur. Once the energy barrier of lattice expansion has been overcome, further quantities of phenol can be adsorbed with the utilization of much smaller quantities of work. In other words, once the clay lattice has been initially opened to the minimum critical distance, the amount of readily available interlamellar surface greatly increases and adsorption of phenol can then proceed without the intervention of other physical processes. The values obtained for $\Delta\bar{H}$ indicate that the amount of work involved in initially opening the clay lattice is greater than that liberated by the accompanying process of adsorption, and hence $\Delta\bar{H}$ has a positive value. After the lattice has been opened to an extent sufficient to permit unhindered intercalation, the value

of $\Delta\bar{H}$ changes from positive to negative and the results become comparable with a system where adsorption is not prefaced by lattice expansion; e.g. dodecylammonium bentonite–phenol–water.

At still higher values of x/m the interlayer surface becomes more crowded and, as would be expected, the value of $\Delta\bar{H}$ becomes slightly less negative. It could be argued that this decrease in $-\Delta\bar{H}$ is associated with the further expansion of the clay lattice to accommodate a second (?) layer of adsorbate molecules but, if this were the case, complexes containing the larger quantities of amine would be the first to exhibit the effect, whereas it is in the clays containing the least amount of replacement with amine that the effect is most pronounced. Since with these clays there is a rapid fall in the value of $-\Delta\bar{H}$, and since with this adsorbent the interlamellar space will be less crowded than with the more fully amine-saturated clays, it is suggested that there will be greater interlamellar space for condensation of adsorbate molecules. However, this is not reflected in the enthalpy changes of the process and, therefore, it can be concluded that whilst the availability of space is one of the criteria, a further and important one is the site at which condensation of the adsorbate molecule occurs. Since the value of $\Delta\bar{H}$ at high values of x/m is proportional to the amine content, it is strongly suggested that the amine ions on the clay surface are in fact the sites at which condensation occurs. It should be added, however, that this statement in no way invalidates the postulate that for adsorption both hydrophilic, i.e. natural clay surface, and hydrophobic, i.e. amine ions, are essential (Cowan and White, 1962).

The general theory which has been advanced for the system tetradecylammonium bentonite–phenol–water is also applicable to the system tetradecylammonium bentonite–*m*-cresol–water (Fig. 5), but in this case it is noted that the transition of $\Delta\bar{H}$ from a negative to a positive value occurs at a lower surface coverage (Table 1). Although consideration of steric factors and the extra energy involved in expanding the lattice to accommodate the somewhat larger *m*-cresol molecules would indicate that $\Delta\bar{H} = 0$ at higher surface coverage than observed with phenol, the extra energy required is overridden by the somewhat larger partial molar heat of adsorption associated with *m*-cresol.

Whilst it must be admitted that a full X-ray investigation would be necessary if indisputable evidence were to be provided for the theories which have been forwarded, it is interesting to note that a theory having many points of similarity has been advanced by Barshad (1955, p. 70). In this case the adsorption of water by barium-saturated montmorillonite was examined, and it was shown that the partial net heat of adsorption changed from a positive to a negative value as water molecules were reoriented from the external surfaces to interlamellar positions.

Summing up, it is seen that evidence has been presented which shows that with the higher aliphatic amine bentonites, intercalation of adsorbate molecules is prefaced by lattice expansion. The heat required for this process is partly or wholly, depending on the amount of surface coverage which

condensation of adsorbate produces, supplied by the adsorption process, and in consequence the partial molar heat of the reaction may be either positive or negative. The actual point at which the transition occurs is, in consequence, dependent not only on the size of the intercalated molecules but also on the amount of replacement by organic cations which the clay has undergone and hence the available interlamellar space.

REFERENCES

- Barshad, Isaac (1955) Adsorptive and swelling properties of clay water system: in *Clays and Clay Technology*, California Div. Mines, Bull. 169, pp. 70-77.
- Cowan, C. T. and White, D. (1958) The mechanism of exchange reactions occurring between sodium montmorillonite and various *n*-primary aliphatic amine salts: *Trans. Faraday Soc.*, v. 54, pp. 691-697.
- Cowan, C. T. and White, D. (1962) Adsorption by organo-clay complexes: in *Clays and Clay Minerals*, v. 9, Pergamon Press, New York, pp. 459-467.
- Jordan, J. W. (1949) Organophilic bentonites. I, Swelling in organic liquids: *J. Phys. Colloid. Chem.*, v. 53, pp. 294-306.
- MacEwan, D. M. C. (1951) The montmorillonite minerals (montmorillonoids): in *X-ray Identification and Crystal Structures of Clay Minerals*, Mineralogical Society, London, pp. 86-137.
- Ruderman, I. W. (1946) Bromination of phenols and phenol alcohols: *Ind. Eng. Chem. (Anal. Ed.)*, v. 18, pp. 753-759.