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CALORIMETRIC INVESTIGATION OF ADSORPTION OF AN AQUEOUS METACHROMIC DYE (CRYSTAL-VIOLET) ON MONTMORILLONITE *

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ABSTRACT

Crystal-violet is a cationic dye that exhibits metachromasy in aqueous solutions and when adsorbed on various solids; the changes in the absorption spectrum of the dye permit identification of monomeric, dimeric, and polymeric species and can also help in distinguishing between several different kinds of dye-adsorbent interactions. This paper reports the results of calorimetric measurements of enthalpies of adsorption of aqueous crystal-violet on to eight different cationic (Li^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cd^{2+}, and Al^{3+}) montmorillonite clays.

INTRODUCTION

The adsorption of organic material by clay minerals is important in many sub-areas of geochemistry, agriculture, and various industries. Along with our general interest in clay minerals, we are specifically interested in the role that adsorption of organic matter on clay minerals plays in the properties of petroleum and oil (tar) sand deposits and on the recovery of petroleum and bitumen from these important natural resources.

Although there have been many spectroscopic, crystallographic, and thermo-analytical investigations of adsorption of organic substances on clay minerals [1,2], there have been very few calorimetric investigations. In this paper we report the results of our calorimetric investigations of the adsorption of one interesting organic substance (crystal-violet, a cationic, metachromic dye) by a montmorillonite clay. These calorimetric results can be related to the results of our concurrent spectroscopic investigations of these same clay–dye systems [3,4].

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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Crystal-violet (hereafter called CV) is a cationic dye that exhibits "metachromasy" in solution. That is, the color and absorption spectrum of this dye depend on its concentration. Very dilute aqueous solutions of this dye absorb at 589 nm. This absorption band, which is called band α, is due to the monomeric dye species in solution. More concentrated solutions absorb at about 550 nm. This absorption band, called band β, is due to dimers in solution. Still another band (band γ, at about 490 nm) is observed with still more concentrated solutions; this band is attributed to polymeric species in solution.

Band α (due to monomeric species in dilute solutions) has been attributed to a π–π^* transition. The disappearance (or diminished intensity) of this band and the appearance of bands β and γ at shorter wavelengths in the spectra of more concentrated solutions (containing dimers and polymers) is an indication of intermolecular interactions involving the π electrons of the aromatic parts of the dye cations.

CV and other dyes that are metachromic in solution may also be metachromic when adsorbed on various solids. Such metachromasy for dyes adsorbed on montmorillonite is common and has found some practical use in "staining" as a means of identifying this clay mineral [5]. Several previous investigations (X-ray diffraction and IR spectroscopy) of metachromic dyes adsorbed on montmorillonite have shown [6–11] that there are π electron interactions between the aromatic cation and the oxygen plane of the alumino-silicate layer in the clay mineral. Similar π interactions may also occur and be important in natural systems containing aromatic organics (such as humid acids, components of petroleum, etc.) and various minerals containing alumino-silicate layers.

EXPERIMENTAL

Wyoming bentonite (montmorillonite) was obtained from the Source Clay Mineral Repository (Department of Geology, University of Missouri, Columbia, MO, U.S.A.) and gently ground to 80 mesh. Cation exchanged montmorillonites were prepared by equilibrating 10 g of natural clay with 1000 ml of 0.02 molar aqueous solution of the appropriate metal chloride [12]. The exchanged clay was separated from the solution by centrifuging at 7000 rpm, with excess metal chloride removed by repeated washing with distilled water and centrifuging. The resulting suspensions of homoionic clays were stable for periods of time much longer than the duration of a calorimetric measurement. To avoid any effects of drying, the homoionic clays were stored (after washing and centrifuging as described above) in aqueous suspensions of known clay content (2–4 mass%).

The CV was supplied by BDH Chemicals (Toronto, Ontario, Canada) as the chloride salt.

Our "home made" solution calorimeter consisted of a glass vessel (90–95 cm^3 capacity) suspended in a brass can that was immersed in a constant temperature bath maintained at 25.00 ± 0.01° C and held constant during each calorimetric measurement to ±0.001° C. Titrant solution was delivered to the calorimeter by a motor driven buret-titrator (Metrohm 645 Multi-Dosimat, from Brinkman Instruments, Toronto, Ontario, Canada). Small temperature changes in the calorimeter were measured with high sensitivity (better than 1×10^{-4} degrees) with a thermistor (No. 44045, Yellow Springs Instrument Co. Inc., Yellowsprings, OH, U.S.A.) combined with a Current Comparator Bridge (Model 9975, Guildline Instruments, Smith Falls, Ontario, Canada). The calorimeter was calibrated electrically after each calorimetric titration measurement.

We have checked the accuracy of this calorimetric system by way of measurements of the enthalpy of solution of KCl(c) in distilled water, the enthalpy of solution of 4-aminopyridine in excess aqueous perchloric acid [13], and the enthalpy of neutralization of aqueous tris(hydroxymethyl)aminoethane ("THAM" or "tris") by excess aqueous acid. Results of these measurements, as fully reported elsewhere [14] along with a detailed description of the calorimeter, agreed to within 0.5%, 0.04% and 0.02%, respectively, with values from the literature.

Calorimetric titration measurements were carried out as follows. A known amount of homoionic clay suspension of known clay content was added to 84 g of distilled water. Total amounts of clay in each measurement ranged from 100 to 300 mg, with 150 mg being used in many of the measurements. After the clay suspension in the calorimeter reached equilibrium with the constant temperature bath, a known amount of an aqueous solution of CV was titrated (passing through the constant temperature bath) into the calorimeter. Reaction (adsorption, ion exchange) of the CV with the clay was complete within 200–300 s, as judged by the observed temperature–time curve following addition of the dye to the suspension of clay in the calorimeter.

RESULTS AND DISCUSSION

The results of the calorimetric measurements on eight different cation-montmorillonites have been expressed in terms of enthalpies of adsorption (kJ mol^{-1} of adsorbed dye) and are summarized in Figs. 1–5 as graphs of molar enthalpies of adsorption against amounts of dye adsorbed. Uncertainties in these enthalpies are about ±0.7 kJ mol^{-1}.

The most obvious generalization to be made about our results is that the molar enthalpies of adsorption of CV on all clays (except Cs^+-montmorillonite) become less exothermic as more dye is adsorbed. For adsorption of CV on Cs^+-montmorillonite we observe the usual general trend, complicated

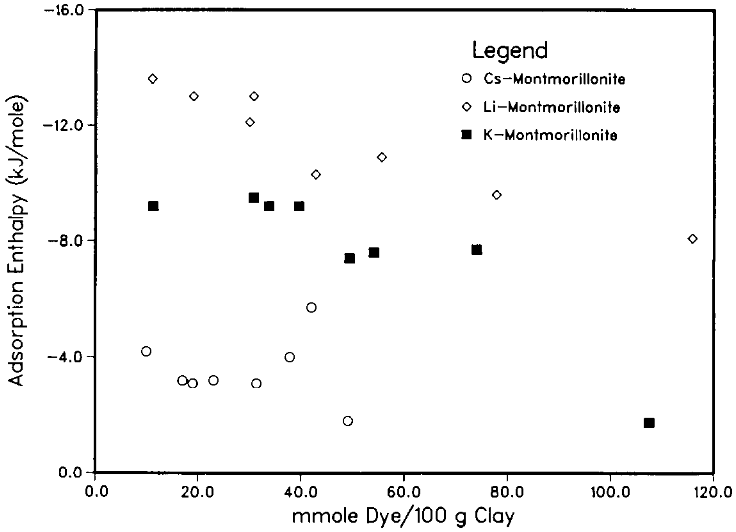

Fig. 1. Enthalpies of adsorption of aqueous CV on M^+-montmorillonites.

by a "spike" in the enthalpy of adsorption at about 40 mmol of adsorbed dye/100 g of clay. We also see that the rate of change of the ΔH of adsorption with increasing amount of dye adsorbed is in the order M^{3+}-clay > M^{2+}-clay > M^+-clay.

Further consideration of our enthalpies requires background information from spectroscopic investigations [3,4].

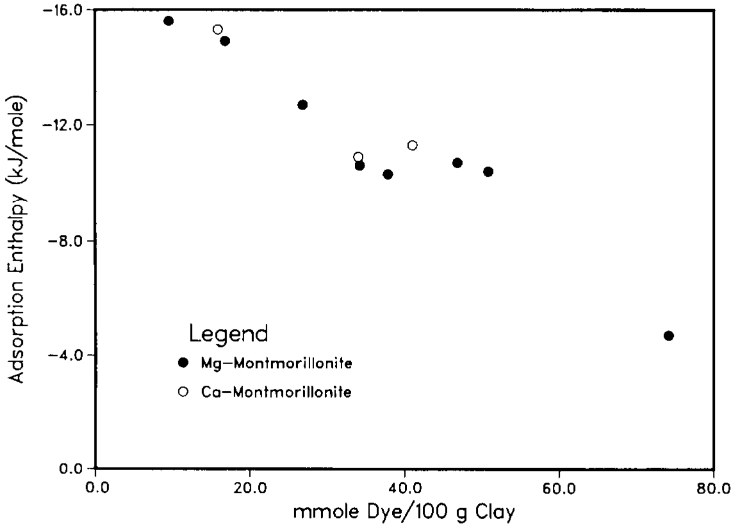

Fig. 2. Enthalpies of adsorption of aqueous CV on Mg^{2+}-montmorillonite and on Ca^{2+}-montmorillonite.

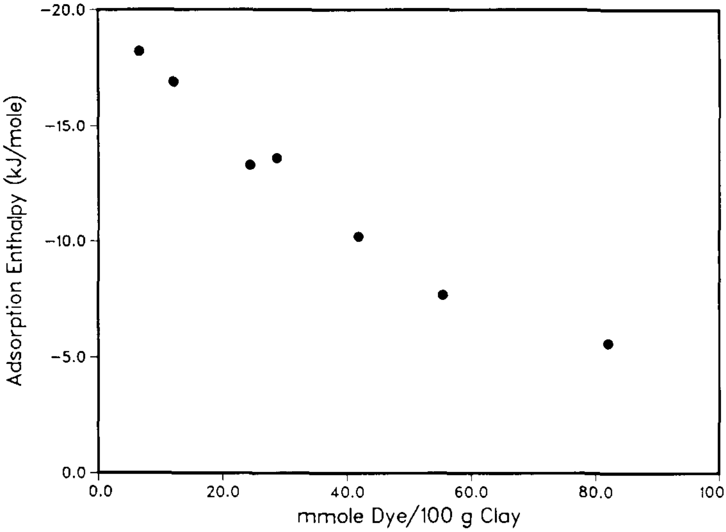

Fig. 3. Enthalpies of adsorption of aqueous CV on Ba^{2+}-montmorillonite.

These spectroscopic investigations [4] led to identification of four kinds of interactions (here labelled types A, B, C, and D) between adsorbed cations and clays. Type A interactions, which are identified by way of band α, involve monomeric CV cations on the clay particle surface, probably at the "broken bonds". Type B interactions, also identified by way of band α, involve monomeric CV cations in the "interlayer space". Type C interac-

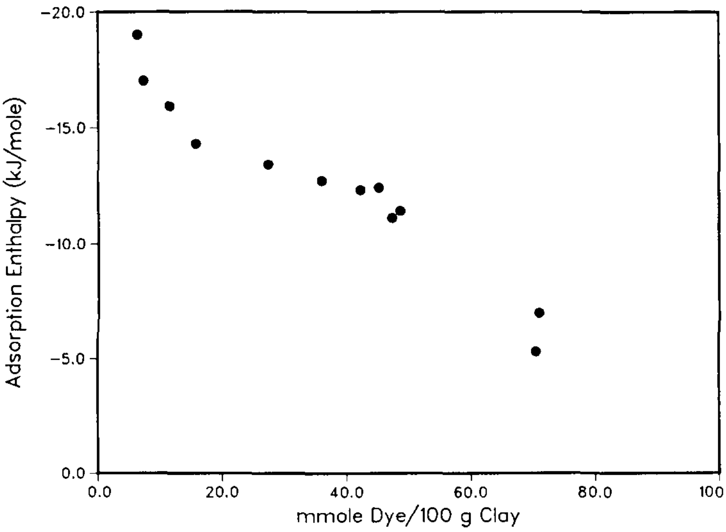

Fig. 4. Enthalpies of adsorption of aqueous CV on Cd^{2+}-montmorillonite.

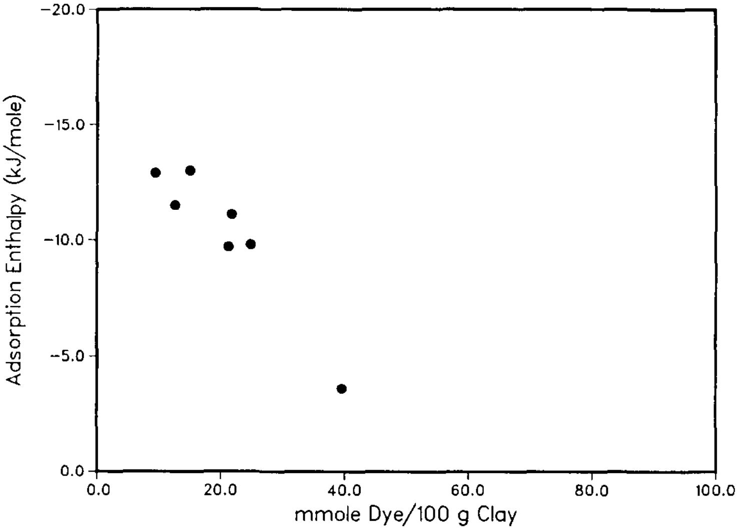

Fig. 5. Enthalpies of adsorption of aqueous CV on Al^{3+}-montmorillonite.

tions, which are identified by way of band β, probably involve π interactions between CV cations in the interlayer space and the oxygen plane of the aluminum silicate layer. Type D interactions, which are identified by way of band γ, probably involve electrostatic attractions between a tactoid and polymeric CV cations that are located in the interparticle space of a floc. Relative amounts of interactions of these various types can be estimated from the intensities of bands α, β, and γ.

The spectroscopic results [4] showed that Type D interactions are negligible under the conditions of our calorimetric measurements, so only interactions of Types A, B, and C need be considered in relation to our calorimetric results.

In general, we expect that interactions of Type C will lead to the most exothermic ΔH of adsorption, with interactions of type B leading to less exothermic ΔH of adsorption. Interactions of Type A are expected to lead to the least exothermic (possibly even slightly endothermic) ΔH of adsorption because these interactions appear only at high degrees of saturation, where the clays are only slightly negatively charged or may even carry small positive charges.

The electronic spectra of adsorbed CV cations show that interactions of Types B and C occur when only a little dye has been adsorbed, whereas interactions of Type A occur when larger amounts of dye have been adsorbed. We have defined the "transition region" as the smallest concentration or degree of saturation at which interactions of Type B cannot be detected spectroscopically, which also corresponds to the degree of saturation at which interactions of Type A are first detected.

Spectra [4] of CV on Li-montmorillonite and K-montmorillonite showed that band β was predominant at all low concentrations, which in turn showed the predominance of interactions of Type C. Similar spectra of CV on Cs-montmorillonite showed that interactions of Type B were predominant at low concentrations of adsorbed CV, with interactions of Type A becoming more important at higher concentrations of adsorbed CV. At still higher concentrations (above the transition region) of adsorbed CV, interactions of Types B and C have been largely replaced by interactions of Type A. These conclusions based on the results of spectroscopic measurements [4] are consistent with the observation (Fig. 1) that ΔH values for adsorption of CV on Li-montmorillonite and on K-montmorillonite are more exothermic than ΔH values for adsorption of Cs-montmorillonite, and also account for the "spike" in the ΔH of adsorption of CV on Cs-montmorillonite.

For all of the other clays investigated (Figs. 2–5) the calorimetric ΔH values for adsorption of CV become less exothermic with increasing concentration of adsorbed clay. This decline in exothermicity is generally in parallel with the relative proportions of interactions of Types B and C at low concentrations and Type A at higher concentrations.

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