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# ENTHALPIES OF ADSORPTION OF METHYLENE BLUE AND CRYSTAL VIOLET TO MONTMORILLONITE

## Enthalpies of adsorption of dyes to montmorillonite

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## Abstract

Calorimetric measurements of the enthalpy of adsorption on montmorillonite indicate different patterns for methylene blue (MB) and crystal violet (CV). The enthalpy of adsorption of MB is endothermic up to 73% of the cation exchange capacity (CEC) (i.e., about 0.6 mmol $g^{-1}$ clay), whereas at higher adsorption ratios the adsorption reaction becomes exothermic. The enthalpy of adsorption of CV is exothermic for all amounts adsorbed. These results were confirmed with adsorption experiments that prove that adsorption of MB increase with temperature, whereas CV adsorption decreases. This behavior indicates changes in the equilibrium coefficient according to Van't Hoff's equation.

**Keywords:** adsorption, clay, crystal violet, enthalpy, methylene blue, montmorillonite

## Introduction

Adsorption of cationic dyes to smectitic clays was widely studied and extensively reviewed [1], since it consists a very good model for adsorption of organic cationic molecules to clays, and it might have industrial, biological, and mineralogical uses [2]. Studies involved several analytical techniques in order to elucidate the exact character of the interaction between the cations and the silicate surface [3]. In this study, changes in the enthalpies of adsorption of the dyes as the process occurs, are reported.

Enthalpies of adsorption are in most cases exothermic [4]. The explanation for this outcome stems from the definition of the Gibbs free energy ($G$):

$$G=H-TS \tag{1}$$

where $H$ denotes the enthalpy, $T$ the absolute temperature and $S$ the entropy of the process. Changes in thermodynamics functions are usually measured during a reaction or a process. For such a case, the difference between the final and the initial state of a parameter ($\Delta$) is important, and Eq. (1) becomes

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$$\Delta G=\Delta H-\Delta(TS)=\Delta H-S\Delta T-T\Delta S \tag{2a}$$

Since chemical processes are usually monitored isothermally, the third term is zero, and that yields:

$$\Delta G=\Delta H-T\Delta S \tag{2b}$$

Adsorption is a spontaneous process, implying that $\Delta G<0$. During the adsorption process molecules that had freedom of mobility in the solution become attached to the surface, leading to an increase in the order of the system. In other words, it might be thought that the entropy of such a process is negative. The absolute temperature is by definition positive thus in order to conform to a negative value of $\Delta G$, the reaction must be exothermic, i.e. $\Delta H<0$.

For adsorption on 2:1 layered charged silicates belonging to the clay minerals family, the statement that $\Delta S<0$ may not be always correct. Since adsorption to these silicates is often accompanied with exchange of ions, and in several cases hydrated water molecules are also released due to adsorption, the change in entropy might be positive, and consequently endothermic heats of adsorption are possible as discussed by Aranda *et al.* [5]. Perez-Rodriguez and Maqueda [6] report that the enthalpy of adsorption of the divalent cationic herbicides diquat and paraquat to vermiculite is endothermic for $Na^+$-clay, exothermic for $Li^+$, $Ca^{2+}$ and $Mg^{2+}$-clays, and near to zero for $NH_4^+$- and $K^+$-clay. Yariv [3] reported that the enthalpy for the adsorption of paraquat (1,1-dimethyl-4,4-bipyridinium) to montmorillonite is about $-11$ kJ mol$^{-1}$, while for a similar molecule without two methyl groups (4,4-bipyridinium), the exothermic enthalpy changes to $-18$ kJ mol$^{-1}$. This difference is ascribed to the hydration of the two $NH^+$ groups at the edges of the bipyridinium ring, inside the montmorillonite interlayer. Such hydration effect does not exist in the case of paraquat adsorption.

There are two widely used methods for evaluating the enthalpy of adsorption. For the mentioned results, direct calorimetric measurements of the adsorption process were performed. Calorimetric measurements showed that the enthalpy of adsorption of surfactants to zeolites [7], is dependent upon the chain length. Short chain surfactants showed a small positive enthalpy of sorption, whereas long chained one showed a negative value of about $-10$ kJ mol$^{-1}$. This negative enthalpy of sorption was interpreted as a further evidence that strong bonds are formed between HDTMA and the zeolite surface.

In several cases the enthalpy is evaluated by performing adsorption experiments at different temperatures. Those results are used to calculate the equilibrium coefficients at the various temperatures used. The changes of Gibbs' free energy with temperature are described by the Gibbs–Helmholtz equation:

$$\left(\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right)_{\mathrm{p}}=\frac{-\Delta H}{T^2} \tag{3}$$

where $\Delta G$ and $\Delta H$ are the differences in Gibbs' free energy and enthalpy between the final and the initial state ($\Delta G=G_f-G_i$; $\Delta H=H_f-H_i$). Since at equilibrium $\Delta G=0$, we can relate the equilibrium constant to the standard free energy of the reaction, $\Delta_r G^{\varnothing}$,

$$\Delta_r G^{\varnothing} = -RT\ln K \tag{4}$$

and by combining Eqs (3) and (4), we obtain the Van't Hoff equation,

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_r H^{\varnothing}}{T^2 R} \tag{5}$$

where $\Delta_r H^{\varnothing}$ is the enthalpy of the reaction at standard pressure. For slight changes in temperature, we might assume that the enthalpy of the reaction remains constant. In such a case, Eq. (5) is easily integrated to:

$$\ln\frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta_r H^{\varnothing}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{6}$$

The mean heat of adsorption of nature organic matter (NOM) to montmorillonite was estimated as –17 kJ mol$^{-1}$ evaluated by using Van't Hoff equation and data at 3.5 and 21.5°C, that showed a decrease in the adsorption with increase in temperature [8]. Sorption-desorption data and thermodynamic calculations suggest that there are distinct differences in the soil-sorption enthalpies for the charged and neutral forms of pentachlorophenol [9]. Calculations for the charged form (at pH 7.9) suggest an exothermic adsorption reaction ($\Delta H$=–2.2 kJ mol$^{-1}$). For the neutral form (at pH 4.1), enthalpies were close to zero (–0.5 kJ mol$^{-1}$). Uribe *et al.* [10] used Van't Hoff's equation to evaluate heats of adsorption of neutral molecules to an organo-clay. They found those enthalpies to be low, for the case of adsorption of chlorobenzene, 2-chlorophenol, phenol and aniline to montmorillonite with mixed tallow amine adsorbed, forming an organophilic clay. They deduced very low values of enthalpies, since almost no changes in the adsorbed amounts were observed while temperature was increased from 20 to 44°C.

In this work we measured the enthalpies of adsorption of the organic cationic dyes MB and CV on montmorillonite. Those dyes adsorb on the clay at amounts higher than CEC [11]. Part of the adsorption is by an exchange mechanism releasing exchangeable cations. Recent thermal analysis studies show that at least in the case of CV, water presence is essential for the penetration of the dye molecules and the cations exchange process [12]. However, part of the adsorption is via non-coulombic interactions, of adsorption to the organoclay complex formed by one adsorbed cation and a neutralized clay site [13], which leads to a positively charged complex [14]. In our work we were able to determine the enthalpy of different steps of the adsorption, by adding dye solutions and measuring the heat changes in a microcalorimeter. The trends of the heat of the adsorption were confirmed by adsorption experiments at different temperatures, with amounts of dye lower or higher than the CEC.

## Materials and methods

Wyoming montmorillonite (SWy-1), was purchased from the Source Clays Repository of The Clay Minerals Society (Columbia, MO). Detailed specification of the clay parameters can be found in Rytwo and Tropp (2001) [15]. MB was purchased from

Merck (E. Merck, Darmstadt, Germany). CV was obtained from Fluka Chemica (Fluka Chemie AG, Buchs, Switzerland). All materials were used without further treatment or purification.

To measure adsorption enthalpy of MB and CV at 25°C±0.01, an LKB 2107 Sorption Microcalorimeter (LKB, Stockholm, Sweden) was used. 0.72 mL of 5% clay suspension were placed in the batch cell of the microcalorimeter. Aliquots of 60 μL of an aqueous $5\cdot10^{-2}$ M solution of dye were added using a peristaltic pump, at a flow rate of 8 mL $h^{-1}$. Dye aliquots – each one equivalent to 10.5% of the CEC of the clay in the cell – were added after the reaction of the previous 'dose' has reached completion, as reported by the instrument display. The pump worked continuously, pumping air bubbles to the cell between the doses, causing continuous agitation. Dye bottles were kept in the same thermostatic bath as the microcalorimeter, at 25°C±0.02, to minimize the difference in temperature between the cell and the dye solution. Temperature changes in the calorimeter were measured using thermocouples and recorded as mV with an arbitrary offset. Calibration of the instrument was made before each experiment by connecting measured constant DC currents ($I$, in amperes) for various periods of time ($t$, in seconds) to the instrument. The total energy ($H$, in joules) of the process can be then described by:

$$H=I^2Rt=K_{ec}\int_0^{\infty}V\mathrm{d}t=K_{ec}A \tag{7}$$

where $R$ is the resistance in Ω of the microcalorimeter block. $A$ is the area obtained by the integral of the voltage ($V$, in volts) *vs.* time and $K_{ec}$ is the proportion constant [16]. $K_{ec}$ can be obtained by calculating regression parameters of various known currents and time periods. At the end of each experiment, another calibration was performed to verify the calculated parameters.

To measure adsorption of the dyes, aliquots of the needed amounts of an aqueous $5\cdot10^{-3}$ M solution of each dye were added to 1 mL of a 0.5% *w*/*w* clay mineral suspension in 20 mL polyethylene bottles. The final volume of all bottles was brought to 10 mL with deionized water, before adding the dye. The bottles were sealed and kept at three different temperatures: 9±1, 25±1 and 48±0.2°C. After 7 days, the suspension was filtered through S&S FP030/2 disposable filters (Schleicher & Schuell, Dassel, Germany), with 0.2 μm pore diameter cellulose acetate membranes. The remaining concentration of the dyes in each of the filtrates was determined by measuring the absorption at 662 nm (MB, $\varepsilon$=61000 $M^{-1}$ $cm^{-1}$), and 588 nm (CV, $\varepsilon$=83000 $M^{-1}$ $cm^{-1}$), using a Genesys 20 UV-Visible spectrophotometer (Thermo-Spectronic, Rochester, NY). Limits of detection of the dyes were $1.6\cdot10^{-7}$ and $1.2\cdot10^{-7}$ M for MB and CV, respectively, corresponding to an optical density of 0.01. Experiments were carried out in triplicate.

## Results and discussion

Figure 1 shows the results of the microcalorimeter experiments with CV and MB for added amounts between 21 and 140% of the CEC. At added dye amounts lower than 20%, dye addition causes a change in the baseline in both dyes, thus the heat of the reaction cannot be calculated. Table 1 presents results of the experiments normalized and transformed to enthalpy of the reaction, in J mole$^{-1}$. The results indicate that the adsorption reaction of CV is exothermic, whereas that of MB is endothermic up to 73% of the CEC (around 0.6 mmol g$^{-1}$ clay, whereas at higher adsorption ratios the adsorption reaction becomes exothermic. The mean enthalpy of adsorption of CV, –13.5 kJ mole$^{-1}$, is in the same order of magnitude to those reported in the past for paraquat [4]. The mean enthalpy of adsorption of MB is slightly endothermic (+3.9 kJ mole$^{-1}$).

**Table 1** Enthalpies of adsorption of CV and MB to montmorillonite. The enthalpies are calculated separately for each step of added dye

| Dose | Amount added/% of CEC | $\Delta H_{ad}$ CV | $\Delta H_{ad}$ MB |
|---|---|---|---|
| | | kJ mole$^{-1}$ | |
| 1 | 0–11 | # | # |
| 2 | 11–21 | –4329 | # |
| 3 | 21–31 | –13725 | 10184 |
| 4 | 31–42 | –13013 | 9030 |
| 5 | 42–52 | –17020 | 15444 |
| 6 | 52–62 | –23837 | 10836 |
| 7 | 62–73 | –17547 | –1288 |
| 8 | 73–83 | –16254 | –1467 |
| 9 | 83–93 | –17396 | –1944 |
| 10 | 93–104 | –17107 | –2456 |
| 11 | 104–114 | –9966 | –3078 |
| 12 | 114–125 | –7251 | * |
| 13 | 125–135 | –3916 | * |
| mean | 0–135 | –13447 | 3918 |

#Shifts in the baseline of the thermogram were too large for accurate determination of the area
*The peaks in the thermogram were too unclear to accurately determine the area

Other differences in the patterns of the interactions between MB and CV with montmorillonite were reported [11]. Those studies were based on X-ray diffraction, UV, IR, linear dichroism IR (LDIR) studies and model calculations. The LDIR technique led to the conclusion that the planes of MB molecules are oriented parallel or close to parallel to the clay mineral platelets. XRD measurements of the basal spacing confirmed that at low MB adsorbed concentrations (below 0.4 mmol g$^{-1}$ ) the dye molecules were arranged in monolayers, whereas the basal spacing observed in this case was smaller than in the absence of the dye. This decrease was interpreted as dehydration, and was confirmed by IR measurements, that showed decrease in the amount of water sorbed to the montmorillonite platelets. Figure 1 and Table 1 show an endothermic reaction at this stage. As the adsorbed amount approaches the CEC, Fig. 1 and Table 1 show that MB adsorption be-

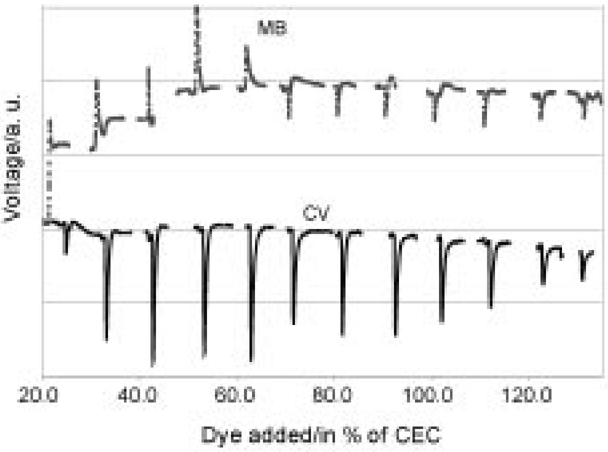

**Fig. 1** Calorimetric voltages measured for the adsorption of CV and MB to montmorillonite. Each dose of added dye is as a continuation of the previous step

comes exothermic. Model calculations [11] evaluated that at low loads (i.e, 6/8 of the CEC) the charged complex formed by one site and two MB molecules, $(PMB_2)^+$, covers less than 5% of the clay sites, e.g. 10% of the MB molecules are part of charged complexes. This state can be described as two dye layers between the clay platelets: each MB layer attached to each clay platelet. At higher MB loads, XRD measurements [11] showed a basal spacing that corresponds to four layers of dye molecules in a perfect planar orientation between the clay plates. At that stage, each clay platelet is attached to two MB molecules, and interaction between two adsorbed MB molecules is exhibited. Our current results show exothermic enthalpies for that stage. Model calculations [11] deduce that at 130% of the CEC adsorbed, at least 50% of the dye molecules are associated in charged complexes.

The interactions of CV molecules with montmorillonite differ in certain aspects from those of MB. The model calculations for the adsorption of CV [11] showed that the binding coefficient for the formation of the charged complex between two CV molecules and one site, $(PCV_2)^+$, is several orders of magnitude larger than for a formation of a neutral complex. Consequently, model calculations indicate formation of a charged complex even at very low adsorbed amounts: for loads of 3/8 of the CEC, 99% of the CV molecules were at charged complexes. Those results were supported by several other analytical measurements: UV-Visible spectra of CV-montmorillonite complexes [11], showed a band at 485 nm (band c), attributed to polymeric species (molecular aggregates), rather than metachromatic shift [17] – that appears even at very low CV coverages (0.2 mmol $g^{-1}$). Consequently the electronic spectrum is affected at low adsorbed loads of CV, similarly to the effect observed by formation of aggregates at high dye concentrations in solution. IR spectra showed presence of water attached to the clay platelets and no decrease in the basal spacing (XRD) was observed at low adsorbed concentrations of CV [11]. Figure 1 and Table 1 show that enthalpies of adsorption of CV are exothermic for all the added amounts.

The differences in the dehydration of the clay can be part of the explanation for the differences in the enthalpy at low dye loads: MB causes release of adsorbed water with the corresponding increase of entropy. Such a process conforms with an endothermic reaction (Eq. (2b)). Since for the adsorption of CV there is not such an entropy increase, the reaction must be exothermic.

Previous studies [18] proposed that CV molecules lie on the silicate layers at a slightly oblique configuration, while MB lies directly parallel to the clay platelet. The relatively weaker interaction between the montmorillonite platelets and CV (in comparison with MB) is compatible with the oblique orientation, which corresponds to smaller area of close contact. This orientation also strengthens the interaction between the adsorbed CV molecules themselves. We deduce that the enthalpy of the interaction dye-clay is endothermic, whereas the interaction dye-dye at the clay surface is exothermic.

**Table 2** Adsorption of CV and MB to montmorillonite at different temperatures. Standard deviation for all adsorbed amounts was less than 1.0%

| Dye | Temperature/°C | Added amount/ | Adsorbed amount/ | Optical density |
|---|---|---|---|---|
| | | mmol dye $g^{-1}$ clay | | |
| CV | 9 | 0.4 | 0.396 | 0.117±0.027 |
| CV | 25 | 0.4 | 0.393 | 0.219±0.047 |
| CV | 48 | 0.4 | 0.386 | 0.446±0.068 |
| CV | 9 | 1.6 | 1.575 | 1.042±0.118 |
| CV | 25 | 1.6 | 1.569 | 1.261±0.066 |
| CV | 48 | 1.6 | 1.563 | 1.530±0.079 |
| MB | 9 | 0.4 | 0.400 | complete adsorption |
| MB | 25 | 0.4 | 0.400 | complete adsorption |
| MB | 48 | 0.4 | 0.400 | complete adsorption |
| MB | 9 | 1.2 | 1.032 | 5.130±0.235* |
| MB | 25 | 1.2 | 1.024 | 5.377±0.274* |
| MB | 48 | 1.2 | 1.077 | 3.763±0.273* |

*Samples were diluted 1:3 before measurement

To confirm the differences in the pattern of adsorption, adsorption experiments were performed between the two dyes and montmorillonite at two loads: one lower than the CEC (0.4 mmol dye $g^{-1}$ clay) and the other above the CEC (1.2 and 1.6 mmole dye $g^{-1}$ clay for MB and CV, respectively) at three different temperatures. The results of the experiments are concentrated in Table 2. We can see a total adsorption of MB below the CEC. The adsorption above the CEC increases while the temperature rises from 25 to 48°C. The increase might be considered minimal when transformed to adsorbed amounts, but the values of optical density and the standard deviation of it show that the change is significant.

Table 2 shows that for CV there is a decrease in the adsorption with temperature, as can be deduced from Van't Hoff's equation for an exothermic reaction. The influence of temperature shows the same tendency below and above the CEC.

## Conclusions

Calorimetric measurements and adsorption experiments at different temperatures point to consistent differences in the patterns of adsorption of CV or MB on montmorillonite. While enthalpy of CV is exothermic for all added amounts, the enthalpy of adsorption of MB is endothermic at low loads, but becomes exothermic at loads close to the CEC and higher. We ascribe these results to the differences in the pattern of adsorption as reported in previous studies: the MB molecules interact strongly with the clay platelets, and only after filling a great deal of the clay charged sites, the interactions between MB molecules become predominant. On the other hand, intermolecular interactions between CV molecules are predominant even at very low adsorbed amounts.

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## Abbreviations

| | |
|---|---|
| CEC | cation exchange capacity |
| CV | N-[4-[bis[4-(dimethylamino)-phenyl]methylene]-2,5-cyclohexadien-1-ylidine]-N-methyl-methanaminium chloride (crystal violet) |
| HDTMA | hexa-decyl tri-methyl ammonium |
| MB | 3,7-bis(dimethylamino)phenazathionium chloride (methylene blue) |
| SWy-1 | Wyoming montmorillonite |

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