PROTONATION OF METHYLENE BLUE AND ITS INTERCALATION INTO MONTMORILLONITE

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Abstract:

The protonation of methylene blue (MB) was studied in variously acid aqueous solutions using Vis spectrophotometry. The cations of MB present in acid aqueous solutions, i.e. MB^+, $(MB^+)_n$ and MBH^{2+}, were intercalated into Ca-montmorillonite (SAz-1). Adsorbed amounts of dye were evaluated by Vis spectrophotometry at two wavelengths; at 675 nm (monomeric form MB^+) and at 748 nm (protonated form MBH^{2+}). By this way two independent measurements of equilibrium dye concentration in acid aqueous solutions were obtained and used for the evaluation of the adsorbed amount of methylene blue into SAz-1.

Adsorption curves determined in acid aqueous solutions consist of two separated steps whereas the adsorption curve determined in neutral aqueous solution has only one step. Intercalated MB/SAz-1 samples were studied using X-ray powder diffraction method and SEM. It was found that the first step of adsorption curve relates to ion exchange of MB cations with interlayer Ca^{2+} cations and the second one relates to MB adsorption on outer montmorillonite surface and/or to presence of dye species in precipitated form in aqueous solution.

Keywords: Protonated methylene blue, Intercalation, Montmorillonite.

1. INTRODUCTION

The methylene blue is cationic dye that polymerizes and also forms of protonated forms in acid aqueous solution [1]. In visible spectra the MB species absorbs at different wavelengths; the MB monomer (MB^+) absorb at 650-675 nm, the dimer $(MB^+)_2$ at about 610 nm, higher aggregates $(MB^+)_n$ at 570-590 nm and protonated cations and/or J-aggregates (the head-to-tail cations) (MBH^{2+}) at about 763 nm [2-4]. In methylene blue intercalated montmorillonites the position and shape of individual MB species significantly depend on structure parameters, e.g. number of chromophores, distance between neighboring interacting molecules, etc. [5].

Many authors [6-7] deal with various problems of MB adsorption from aqueous solution but adsorption of protonated MB form has not been studied yet. Therefore the aim of this paper is the study of protonated cations (MBH^{2+}) intercalation into montmorillonite.

2. MATERIALS AND METHODS

2.1 Samples and Chemicals

Ca-montmorillonite (SAz-1) from Source Clays Repository (USA) was used as host. The cation exchange capacity of SAz-1 is 1.50 meq.g^{-1} and specific surface areas is 93.m^2.g^{-1}.

Methylene blue (MB) from Fluka Standard Chemical was used as guest. The diluted MB aqueous solutions were prepared from basic MB solution (1.10^{-2} mol.L^{-1}) by its dilution with distilled water. The exact concentrations of aqueous MB solutions were then determined by Vis spectroscopy.

The hydrochloric acid (HCl) was used as acid reagent to MB protonation. The dilute HCl solutions were prepared by dilution of concentrated (35 %) HCl in distilled water.

2.2 Methods

The Vis absorption spectra of MB in various acid aqueous solutions were recorded on UV-Vis spectrophotometer Lambda 25 at wavelength range 500 – 850 nm in 0.01 to 1 cm cells.

The total concentration of MB solution (C_{MB}) was determined spectroscopically. The determination was performed in very diluted solutions (from about 1.10^{-6} up to 5.10^{-6} mol.L^{-1}) in related acid aqueous solutions in which only monomeric (MB^+) and/or protonated forms (MBH^{2+}) of dye are present. The absorbance of monomeric form (MB^+) was recorded at 675 nm and protonated form (MBH^{2+}) at 748 nm, by this way total MB concentration in acid aqueous solutions was evaluated independently at two wavelengths. The absorbance of solutions was recorded on UV-Vis spectrophotometer Lambda 25 in 5 and/or 2 cm cells.

The intercalation of SAz-1 sample was performed by saturation with neutral or acidified (0.32, 0.8 and 1.6 M HCl) MB solutions using batch method. The suspensions were 2 hrs shaken at ambient temperature. The separation of solid/liquid phases was performed by centrifugation for 20 min at 4500 rpm. The MB equilibrium concentration in fugate was determined as described above.

For some air dried MB/SAz-1 samples from adsorption measurements X-ray diffraction patterns were recorded by INEL X-ray powder diffractometer with the PSD 120 position-sensitive detector. The measurements were carried out under following conditions: the reflection mode, rotating sample holder (capillary) and $CuK_{K\alpha1}$ radiation. The mixture of silicon and Ag-behenate was used as a calibration standard for PSD.

3. RESULTS AND DISCUSSION

3.1 Protonation of methylene blue in aqueous solutions

Methylene blue reacts with H^+ ions in strong acid aqueous solution forming monoprotonated dye cation (MBH^{2+}) [1] as follows:

A) in concentrated MB solution ($\sim 10^{-3}$ mol.L^{-1}) dye contains except MBH^{2+} mainly higher aggregates (see Fig. 1A)

$$(MB^+)_n + H^+ \quad \rightleftharpoons \quad MBH^{2+} + (MB^+)_{n-1} \tag{1}$$
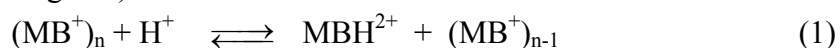
B) in diluted MB solution ($\sim 10^{-5}$ mol.L^{-1}) dye contains except MBH^{2+} mainly monomers (see Fig. 1B)

$$MB^+ + H^+ \quad \rightleftharpoons \quad MBH^{2+} \tag{2}$$
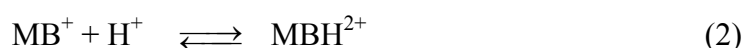
where *n* = 2 for dimer, 3 for trimer, etc.

The protonated cations (MBH^{2+}) can be very good distinguished in Vis absorption spectrum because maximum absorbance of MBH^{2+} is present at higher wavelength in comparison with maximum absorbance of other MB species.

Visible spectra recorded for different MB concentrations and different acid aqueous solutions are presented in Fig. 1. In Vis spectra the dye is occurred as monomer (675 nm), higher agglomerate (590 nm) and protonated cation (748 nm). The total concentration of MB in acid aqueous solution is given by following equation:

$$C_{MB} = \left[MB^+ \right] + \left[MBH^{2+} \right] + \left[(MB^+)_n \right] \tag{3}$$

In concentrated aqueous solutions of MB (see Fig. 1A) higher agglomerates predominate whereas in diluted ones (see Fig. 1B) monomers prevail [9]. The absorbance at 748 nm increases with increasing concentration of HCl and it is supposed that in 3.2 M HCl its reaches of maximum. The isobestic point is formed at about 680 nm only at low dye concentrations (at range 10^{-6} to 10^{-5} mol.L^{-1}). The concentrated dye solutions (10^{-3} M mol.L^{-1}) at acid environment do not form the isobestic point because there are more than two MB variable species.
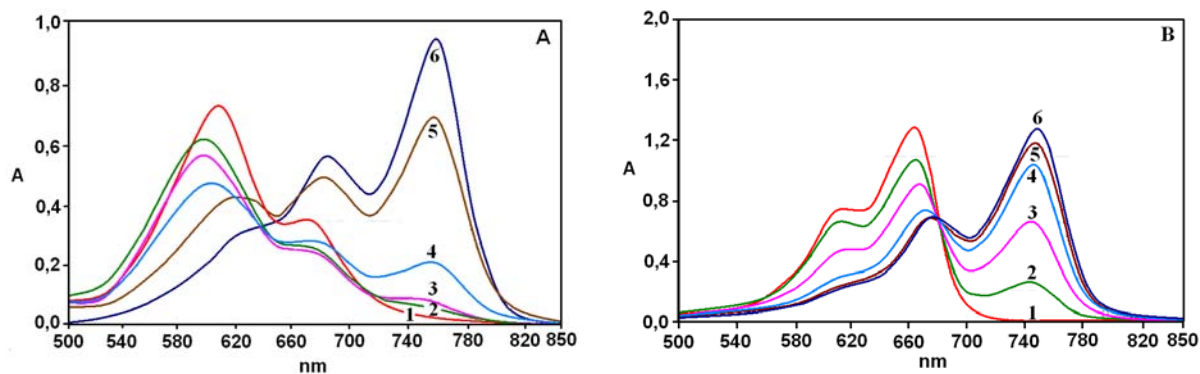

Fig. 1 *The influence of different MB and HCl concentrations on formation MBH^{2+} cation.*
1 – 0 mol.L^{-1} HCl; 2 – 0.32 mol.L^{-1} HCl; 3 – 0.80 mol.L^{-1} HCl; 4 – 1.60 mol.L^{-1} HCl; 5 – 2.40 mol.L^{-1} HCl;
6 – 3.20 mol.L^{-1} HCl
A - CMB = $2.5.10^{-3}$ mol.L^{-1} in 0.01 cm cuvette
B - CMB = $2.5.10^{-5}$ mol.L^{-1} in 1 cm cuvette

3.2   Intercalation of methylene blue from aqueous solution into montmorillonite

Adsorbed amounts of MB from aqueous neutral and/or acid solutions on SAz-1 were evaluated using batch method and calculated according formula:

$$q_{ads} = \frac{V(c_o - c_{eq})}{m} \tag{4}$$

where c_o is saturating concentration of MB (mmol.L^{-1}), c_{eq} is equilibrium concentration of MB (mmol.L^{-1}) and V/m is water –to- montmorillonite ratio (L.g^{-1}).

The equilibrium concentration of MB in aqueous solution was determined by spectrophotometric method. The dye absorbance was measured at 675 nm for neutral aqueous solutions while for acid aqueous solutions the evaluation was performed using both wavelengths, i.e. 675 and 748 nm. The adsorption curve determined for neutral aqueous environment is plotted in Fig. 2A, the absorption curves in acid aqueous solution are plotted

in Fig. 2B, 2C and 2D. Only a little difference in adsorption data was found in data evaluated from calibration curves prepared at 675 and or 748 nm.

Moreover, for two samples (1 and 2) in each isotherm (Figs. 2A, 2B, 2C and 2D) X-ray diffraction patterns were recorded. Their d_{001} values characterizing the related interlayer spacing are given in each isotherm in Figs. 2A, 2B, 2C and 2D. It can be seen that there are not difference in d_{001} values of each isotherm. From this we can summarize that amount of intercalated MB species is the same for each isotherm and not depended on equilibrium concentration of MB (c_{eq}) in equilibrium aqueous solution. In the contrary d_{001} spacing decreases with acidity of adsorption environment (see Figs 2A, 2B, 2C and 2D). The concentration of MBH^{2+} increases with increasing acidity (Fig. 1) and therefore for compensation of negative charge in the montmorillonite interlayer less amount of MB is necessary. It is because 1+ cations $(MB^+)_n$ are replaced by divalent cation MBH^{2+}, i.e. half amount of dye is necessary for charge compensation.
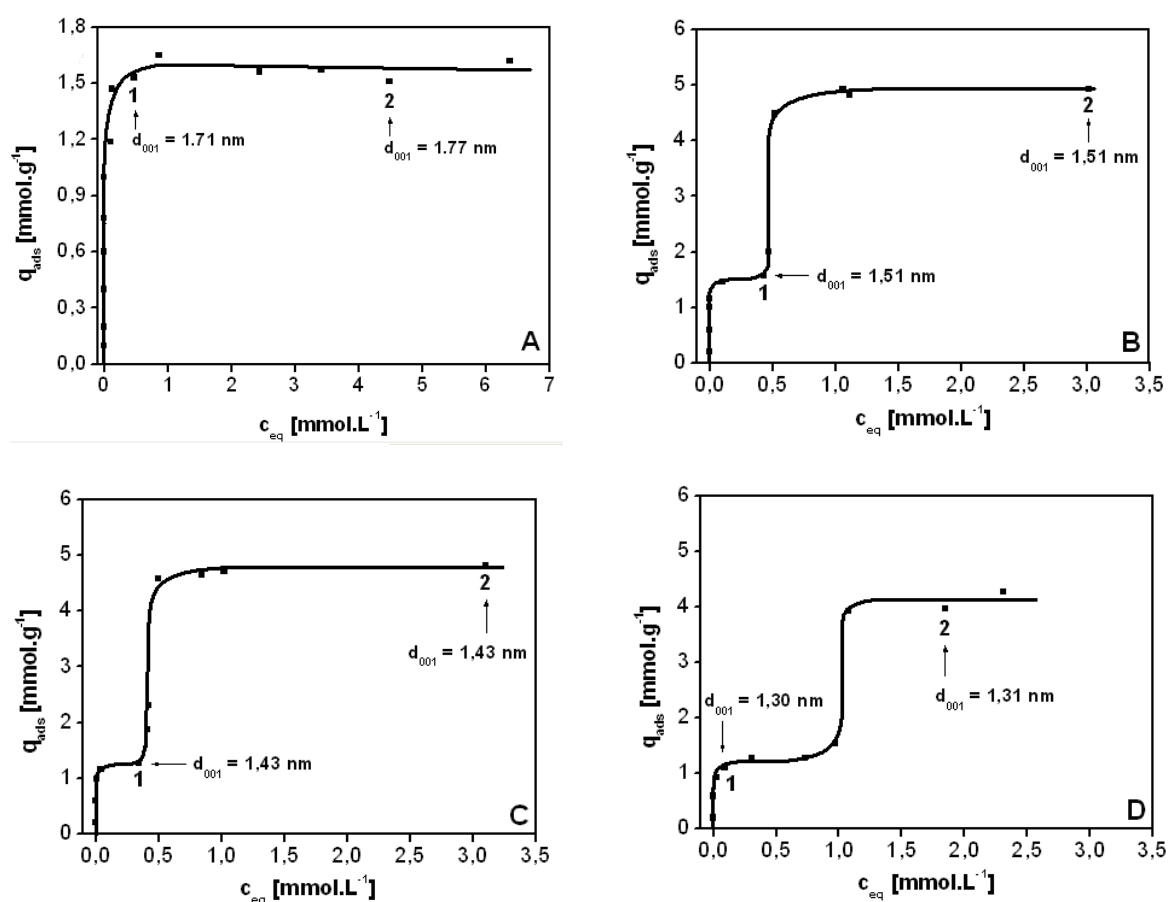

Fig. 2 *Adsorption curves of MB on SAz-1 determined in aqueous environment.*
A - neutral, B - 0.32 mol.L^{-1} HCl, C - 0.80 mol.L^{-1} HCl and D- 1.60 mol.L^{-1} HCl

In neutral aqueous environment the typical absorption curve was measured with maximal adsorbed amount (q_{ads}) about 1.65 mmol.g^{-1} whereas in acid aqueous environment the absorption curves are formed by two separated steps with much higher maximal q_{ads} (Fig. 2). It can be supposed that after ion exchange (Ca^{2+} ions for MB cations) the next adsorption step on the outer surface and/or presence of dye species in precipitated form in aqueous solution take place. This agrees with d_{001} spacing, that doesn't exchange with amount of adsorbed methylene blue.

4. CONCLUSION

The protonation of methylene blue in aqueous solutions was studied by spectrophotometric method. The absorbance at 748 nm, i.e. absorbance of protonated MB increases with increasing concentration of HCl.

Adsorption of methylene blue from neutral aqueous solutions into SAz-1 fits very well with Langmuir type isotherm and maximum adsorbed amount of dye is about 1.6 mmol.g^{-1}. Adsorption of methylene blue from acid aqueous solutions proceeds at two separated steps. In the first step the adsorption follows the ion-exchange mechanism in the interlayer and the second step is realized by the adsorption of dye on the outer surface of SAz-1 and/or by dye precipitation in aqueous solution.

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