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DETERMINATION OF THE SPECIFIC SURFACE AREA OF LAYERED SILICATES BY METHYLENE BLUE ADSORPTION: THE ROLE OF STRUCTURE, pH AND LAYER CHARGE

Nóra Hegyesi[1,2*], Richárd T. Vad[1,2], Béla Pukánszky[1,2]

[1]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary

[2]Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary

*Corresponding author: Tel: 36-1-463-2967, Fax: 36-1-463-3474, E-mail: hegyesi.nora@mail.bme.hu

ABSTRACT

The specific surface area of three layered silicates was determined by three independent methods; it was estimated from the average dimensions of individual silicate layers, determined by nitrogen adsorption using the BET model and calculated from the adsorption of methylene blue on their surface in aqueous sol. The BET model gave smaller surface areas than expected, because nitrogen molecules cannot penetrate freely into the interlayer space of the silicates. Geometric calculations and the methylene blue approach yielded very similar values for two different types of Laponite when the pH of the dispersion was adjusted to 6.5 or the edges of the silicate were modified with tetrasodium pyrophosphate dispersing agent. The measurement of surface area in water without the control of pH yielded smaller surface area, because methylene blue decreased the pH of the solution resulting in the competitive adsorption of methylene blue cations and protons at the basal surface. The methylene blue approach resulted in larger surface area than expected for the silicate with large ion exchange capacity, because of the tilted orientation of the adsorbed methylene blue molecules. All these factors must be considered during the use of the methylene blue method for the determination of the specific surface area of smectites.

KEYWORDS: methylene blue adsorption, specific surface area, Langmuir isotherm, surface orientation, pH, adsorption mechanism

1. INTRODUCTION

Methylene blue (MB) is routinely used for the determination of the specific surface area of materials in aqueous medium (Cenens and Schoonheydt, 1988; Gürses et al., 2004; Kipling and Wilson, 1960; Ruiz-Hitzky, 2001; Schoonheydt and Heughebaert, 1992). The planar molecule has a rectangular shape with the area of approximately 1.7 nm x 0.76 nm and a thickness of 0.325 nm (Ruiz-Hitzky, 2001), thus one molecule covers 1.30 nm^2 area (Santamarina et al., 2002). Methylene blue can interact with the surface of layered silicates both through ionic and secondary, van der Waals forces, since in water MB dissociates into a cation with one positive charge (MB^+) and an anion (chloride) (see **Fig. 1**). The specific surface area and cation exchange capacity (CEC) of smectites are often determined simultaneously by the adsorption of MB on their surface (Hang and Brindley, 1970; Kahr and Madsen, 1995; Yener et al., 2012). The isotherm obtained can be divided into two sections in which different interactions dominate. Below the optimum flocculation point (OFP) mainly ionic interactions develop between the silicate surface and methylene blue. Above this concentration the permanent

negative charges of the silicate are neutralized by MB cations thus adsorption occurs mainly by physisorption (Kahr and Madsen, 1995). In the case of smectites, the amount of MB necessary to reach the optimum flocculation point is regarded as their cation exchange capacity (Hang and Brindley, 1970) and below this point methylene blue is irreversibly bonded to the surface (Bergmann and O'Konski, 1963). In the second part of the isotherm, the adsorption of MB molecules is in dynamic equilibrium. The various aspects of the adsorption of methylene blue on the surface of smectites have already been investigated in detail (Arab et al., 2015; Chang et al., 2016; Cottet et al., 2014; Gao et al., 2016). The type of the counter ion influences the extent of cation exchange, contrary to sodium ions, calcium ions cannot be completely exchanged to MB^+ ions resulting in smaller apparent specific surface area values (Hang and Brindley, 1970).

In spite of the frequent use of the methylene blue technique for the determination of the specific surface area of layered silicates, a number of factors have not been paid attention to or have not been investigated sufficiently thoroughly yet. Up to now, only a few attempts have been made to determine the influence of cation exchange capacity and layer charge on the measured specific surface areas. Yener and co-workers, for example, studied the effect of cation exchange capacity on the surface area measured, but the CEC values used

were quite small (smaller than 0.34 meq/g clay) (Yener et al., 2012; Gürses et al., 2006). At small ion exchange capacity methylene blue molecules orient parallel to the surface and the surface area determined is proportional to the number of adsorbed molecules.

On the other hand, large layer charge was shown to lead to the tilted orientation of surfactants used for the modification of the clay (Lagaly and Weiss, 1970) with increasing tilting angles at larger surface coverages (Pozsgay et al., 2004). Sponza et al. (Sponza et al., 2015), for example, measured very large, 1295 m^2/g, specific surface area, but they did not characterize their silicate sufficiently (cation exchange capacity and the size of the platelets are missing) and the authors did not give any explanation for the unrealistically large value. Tilting may occur also during the adsorption of methylene blue, but sufficient attention has not been paid to the structure of the adsorbed layer including its effect on the adsorbed amount from which the specific surface area of the silicate is derived. Moreover, large layer charge leads to the aggregation of MB molecules, but its effect on the surface area measured has not been studied either (Bujdák and Komadel, 1997; Gessner et al., 1994; Neumann et al., 2002; Pentrák et al., 2012), and especially not at adsorption levels exceeding the cation exchange capacity of the silicate (Beltrán et al., 2014).

The pH dependent charge of the edges of the silicate may also influence adsorption by electrostatic attraction or repulsion. Since the addition of MB into an aqueous dispersion results in the decrease of pH, the edges of the silicate platelets become positively charged below a certain pH value. Positively charged edges repulse MB^+ cations, thus adsorption capacity decreases resulting in smaller apparent specific surface area. According to our knowledge, the effect of pH on the measured surface area of smectites has not been studied in sufficient detail yet. Although Amrhar et al. (Amrhar et al., 2015) observed the dependence of the adsorbed amount of MB on pH for illite, adsorption was very limited and the structure of the mineral differs considerably from that of the clays studied in this work.

The goal of our work was to study questions related to the determination of the specific surface area of smectites, which have not been explored sufficiently yet. The structure of the adsorbed methylene blue layer was studied for a smectite with large CEC value to determine the effect of the orientation of MB molecules on the surface area obtained. We investigated the effect of measurement conditions, and specifically that of pH, on the adsorption isotherm of methylene blue on various layered silicates. The influence of the edge charge of the silicate platelets on their surface area was determined in measurements carried out with and without the control of pH.

Smectites with small diameter were used in the experiments, for which the ratio of the surface of the edges is not negligible compared to the total surface area of the silicate (~7%). A silicate modified at the edges was also used as reference to obtain further information about the role of edge charges in MB adsorption.

2. MATERIALS AND METHODS

2.1. Materials

Sodium montmorillonite (Nanofil 116, NaMt; density (ρ) = 2.86 g/cm^3, CEC = 1.16 meq/g, diameter (d) = 240 nm, height (h) = 0.96 nm) was obtained from Rockwood Clay Additives GmbH, while Laponite XLG (ρ = 2.53 g/cm^3, CEC = 0.55 meq/g, d = 25 - 30 nm, h = 0.92 nm) and Laponite XLS (ρ = 2.53 g/cm^3, CEC: no data, d = 25.0 nm, h = 0.92 nm) were purchased from Byk Additives and Instruments. Laponite XLS is prepared from XLG by modification with pyrophosphate to obtain edges with negative charges in aqueous medium. All three smectites were fine powders and were used as received; they will be abbreviated as NaMt, XLG and XLS, respectively, in the further part of the paper. The chloride salt of methylene blue (MB) trihydrate (>98.5%) and sodium chloride (NaCl, analytical grade) was obtained from Sigma-Aldrich. Phosphoric acid (85 wt%) and sodium hydroxide (NaOH, a.r.) were purchased from Reanal, Hungary. De-ionized water (MilliQ

reagent grade, resistance larger than 18.2 MΩcm, Millipore, USA) was used for sample preparation. All experiments were done at 25 °C unless otherwise indicated.

2.2. Methods

The specific surface area of the silicates was determined by nitrogen adsorption using a Quantachrom Nova 2000 apparatus. Samples were degassed at 200 °C in vacuum for 24 hours before the measurement. The specific surface area was obtained from the Brunauer-Emmett-Teller (BET) model (Brunauer et al., 1938) using 0.162 nm^2 as the area occupied by one nitrogen molecule.

The adsorption isotherm of MB on the silicates was determined in aqueous medium. 1.2 g silicate was dispersed in 100 ml MilliQ water with 10 min ultrasonication. 100 µl of the aqueous silicate sol with the concentration (c) of 12 g/l was diluted with 10 ml 10 mM NaCl or 10 ml phosphate buffer (10 mM, pH = 6.5) to keep the ionic strength constant during the experiments. Various amounts (0-1200 µl) of aqueous MB solution (c = 1.95 mM) was added to the sol and the samples were stirred intensively at 25 °C for 24 h to reach equilibrium. Subsequently the dispersion was centrifuged at 13 500 rpm for 10 min and the absorbance of the supernatant was determined in a glass cuvette (path length = 1 cm) using a Unicam UV 500 UV-Vis spectrophotometer. MB concentration was

calculated after calibration with aqueous solutions (λ = 665 nm, $\varepsilon = 6.24 \cdot 10^5$ $M^{-1}cm^{-1}$). As the silicates were not dried before the adsorption measurements, water content had to be determined to obtain the amount of dry silicate. Water content was deduced from thermogravimetric analysis (TGA6, Perkin Elmer). The weight change of samples of 10-15 mg were measured in nitrogen atmosphere in the temperature range of 30-800 °C with 10 °C/min heating rate. The pH of buffer solutions was checked with a pH/ion analyzer (Radelkis OP-271/1). All adsorption experiments were done in polyethylene centrifuge tubes to avoid the adsorption of MB on the surface of the container. The amount of adsorbed MB was determined by thermogravimetric analysis as well. Solid MB was added to aqueous silicate sols (c = 10 g/l) and left standing for 24 hours. The dispersions were centrifuged, precipitates were dried at 60 °C and then characterized by TGA. Measurements were carried out in oxygen atmosphere in the temperature range of 30-800 °C with 10 °C/min heating rate (TGA6, Perkin Elmer). After MB adsorption and drying the gallery structure of the silicates was characterized by X-ray diffraction using a Philips PW 1830/PW 1050 equipment with CuK_α radiation (0.154 nm) at 40 kV and 35 mA anode excitation with 0.04 step size and 4 s counting time. Zeta potential was determined in the same supernatant solutions used also for the measurement of the concentration of methylene blue in the adsorption

experiments by using a ZetaPALS analyser (Brookhaven Instruments Co.) at 30 °C in polystyrene cuvettes. The Smoluchowski equation (**Eq. 1**) was used for the calculation of zeta potential:

$$\xi = \frac{\mu_E \eta}{\varepsilon} \quad (1)$$

where ξ is zeta potential, μ_E is electrophoretic mobility, while η is the viscosity and ε the permittivity of water (Wall, 2002). Five parallel runs were done on each sample and each run consisted of 10 cycles.

3. RESULTS AND DISCUSSION

The results are presented in three separate sections. The adsorption isotherms of methylene blue on the various silicates is described first together with the fitting of models and the calculation of the specific surface area of the silicates. This section includes the comparison of results obtained by various methods and the interpretation of the differences observed. The effect of pH on the adsorption of methylene blue on the surface of smectites is discussed in the next section followed by considerations about the influence of charge density on the orientation of adsorbed molecules and thus on the specific surface area determined.

3.1. Adsorption isotherms

The three smectites compared have different structure and surface properties. Sodium montmorillonite (NaMt) is a dioctahedral layered silicate with aluminum partially substituted by magnesium in the octahedral sheets, while Laponites are synthetic trioctahedral smectites in which magnesium is partially substituted by lithium. Both types of silicates have negatively charged basal surfaces in aqueous medium, but the surface charge of the edges is different. NaMt and XLG have pH dependent charge at their edges (Pecini and Avena, 2013; Tawari et al., 2001; Willenbacher, 1996), while XLS is modified with tetrasodium pyrophosphate dispersing agent that results in negative charges (Brunier et al., 2016). The specific surface area of the three smectites was determined by three independent approaches. The BET model was applied for the evaluation of the results of nitrogen adsorption measurements and the specific surface area determined in this way is the BET surface (A_{BET}). Surface area was also calculated from the dimensions of the individual platelets, from their average height (h), diameter (d) and density (ρ) to obtain the geometric surface area (A_g). These two values are compared to that obtained by the third method, which was the methylene blue approach (A_{MB}).

The method is based on the determination of an adsorption isotherm, the fitting of models to the isotherms and the

calculation of the specific surface area from them. The adsorption isotherms measured on the three smectites studied is presented in **Fig. 2**. The amount of adsorbed MB converges towards an equilibrium value. The largest adsorption is measured on NaMt and smaller values for the two Laponites. The large difference between the latter two is quite surprising, since the geometry and size of the silicate platelets are the same, only the surface charge of the edges differs. The dissimilarity calls the attention to the importance of the character and behavior of the functional groups located at the edges of the platelets, but also to that of measurement conditions, including the pH of the medium used.

The adsorption of MB onto solid surfaces from aqueous medium is usually described with the Langmuir or the Freundlich isotherm. The Langmuir isotherm assumes an energetically homogenous surface of identical adsorption sites, definite number of these latter, monomolecular coverage and the lack of interaction among the adsorbed molecules. The model has the advantage of providing constants with physical meaning and it usually performs well when the surface is homogeneous and only one type of adsorption site exists. The model can be expressed in the following way to describe liquid-solid equilibrium quantitatively

$$C_s = \frac{K_L S_m C_L}{1 + K_L C_L} \qquad (2)$$

where C_S is the amount of MB adsorbed on the solid surface at equilibrium (M), C_L is the equilibrium concentration of MB (M), S_m is the apparent sorption capacity or adsorption maximum (mol/g) and K_L is the Langmuir coefficient (g/mol). **Eq. 2** can be expressed in a linear form

$$\frac{C_L}{C_S} = \frac{1}{K_L S_m} + \frac{C_L}{S_m} \quad (3)$$

Plotting the results according to **Eq. 3**, i.e. C_L/C_S against the equilibrium concentration of methylene blue (C_L) should result in a straight line from which the maximum amount of adsorbed material and the specific surface area can be determined. The linear plots of the isotherms are presented in **Fig. 3** in this way and straight lines are obtained indeed with very good determination coefficients (R^2) indicating excellent fit. The parameters derived from the fits are compiled in **Table 1**.

The Freundlich model can handle energetically heterogeneous surfaces, multilayer and infinite coverage, but it lacks the proper thermodynamic basis. It can be expressed as

$$q_e = K_F c_e^{\frac{1}{n}} \quad (4)$$

where q_e is the adsorbed amount of the adsorbate (mol/g), c_e the equilibrium concentration of the sorbate (M), K_F (mol/g) relates to adsorption capacity (larger K_F indicates larger maximum capacity), while n gives information about surface

heterogeneity and the interactions between the adsorbent and adsorbate. The Freundlich isotherm can also be linearized and it takes the following form

$$\log q_e = \log K_F + \frac{1}{n}\log c_e \qquad (5)$$

The linear form of Freundlich model was also fitted to the experimental data and the results are shown in **Fig. 4**. The quantities determined are also collected in **Table 1**.

The comparison of determination coefficients (R^2) indicates that the Langmuir model describes the experimental results better than the Freundlich model. The better fit also implies that the surface of the silicates studied is energetically homogenous and a monomolecular coverage develops during adsorption. Accordingly, the maximum sorption capacity and the specific surface area of the silicates were derived from the Langmuir model. The comparison of the specific surface areas obtained by the different approaches allows the drawing of several conclusions. Surface areas resulting from the geometry of the platelets and that determined by the adsorption of methylene blue are larger than values obtained by the BET model. This is not very surprising since the penetration of nitrogen molecules into the gallery space of the dry silicate is quite limited. It is worth to note that some correlation can be seen between the penetration of nitrogen molecules and the regularity of gallery structure.

346 The X-ray diffractogram of NaMt indicates a relatively large
347 degree of order, while regularity is much smaller for the two
348 Laponites (**Fig 5**). Regular stacks with large diameter result
349 in a BET surface area for NaMt one order of magnitude smaller
350 than the geometric surface area, while the Laponite powders
351 consist of more randomly arranged disks with small diameter.
352 Differences can be observed also between surface areas
353 obtained by MB adsorption and geometric calculations for NaMt
354 and XLG. The deviations are unexpected because the MB method
355 is widely accepted and used for the determination of the
356 specific surface area of smectites and they obviously need
357 further study and considerations.
358
359 **3.2. Competitive adsorption, the effect of pH**
360 The surface area determined by the adsorption of
361 methylene blue on XLG is considerably smaller (654 m^2/g
362 calculated from the sorption capacity of 0.838 mmol/g clay)
363 than its geometric surface area, A_g (922 m^2/g). On the other
364 hand, the MB surface area of XLS is significantly larger
365 (1.175 mmol/g silicate, 917 m^2/g) and equals the geometric
366 one. Since XLS is produced from XLG by the modification of its
367 edges, this dissimilarity in binding capacity must be caused
368 by the influence of the tetrasodium pyrophosphate dispersing
369 agent. XLG has Si-OH and Mg-OH groups on their edges. Si-OH
370 groups are deprotonated above pH = 4.5-5, while for oxides and

hydroxides of magnesium zero charge is reached above pH = 10 (Kosmulski, 2016), i.e. the charge of the edges depends on pH. The dependence of MB adsorption on pH has been observed before (Amrhar et al., 2015). The pH of silicate sols decreases upon the addition of methylene blue as shown by **Fig. 6** resulting in the protonation of the edges thus repulsive interactions may develop between them and MB^+ cations.

However, the difference between the measured specific surface area and the area of the basal surface (268 m^2/g) is larger than the surface area of the edges (63 m^2/g). As a consequence, another effect must hinder the adsorption of MB^+ onto the surface of XLG at small pH values. The increase in proton concentration results in the competitive adsorption of MB^+ cations and protons onto the basal surface of this smectite, i.e. in smaller equilibrium MB^+ adsorption. In the case of XLS, the lack of competitive adsorption can be explained with the larger pH of XLS dispersions (see **Fig. 6**) and the permanent negative charge of its edges due to the modification with tetrasodium pyrophosphate.

The repulsive forces between XLG and MB^+ were confirmed by zeta potential measurements. In **Fig. 7** zeta potential is plotted against the amount of MB added to the sol for the XLG sample suspended in distilled water or in a buffer solution at pH 6.5, and also for XLS as reference. At small amount of MB the zeta potential of the sol containing the silicate

particles is negative both in water and in the buffer solution. Without pH control XLG has a negative to positive transition in zeta potential as a function of the amount of MB, because of its positively charged edges. On the other hand, the zeta potential of the sol buffered to pH 6.5 containing XLG and that of the sol prepared from XLS does not take positive values independently of the added amount of MB showing that repulsive electrostatic forces do not develop among the components.

In order to prove the effect of pH, adsorption measurements were carried out with XLG in a buffered solution at pH = 6.5 and an adsorption isotherm was recorded. The Langmuir model was fitted to the experimental data, and the maximum amount of adsorbed MB determined at controlled pH was 1.162 mmol/g silicate corresponding to a specific surface area of 906 m^2/g. This value almost equals the geometric (922 m^2/g) and the MB surface area of XLS (917 m^2/g) that strongly corroborates our hypothesis about the competitive adsorption of MB^+ and H^+.

When pH is controlled, the adsorption of MB^+ cations is favored on the silicate surface and they neutralize the negative charges of the surface. Instead of protonation, functional groups at the edges and the negatively charged basal surface of the silicate are covered by MB^+ cations resulting in zero zeta potential (Pecini and Avena, 2013). In this case, the amount of adsorbed MB is determined only by the

surface area of the silicate.

3.3. Cation exchange capacity, orientation

The other surprising result which needs explanation is the large specific surface area obtained for sodium montmorillonite by the methylene blue approach. Literature references give a value of 750 m^2/g (Santamarina et al., 2002) specific surface area for this silicate and the value obtained from geometric calculations is 734 m^2/g (see **Table 1**). However, the maximum amount of MB adsorbed by NaMt was 1.377 mmol/g that translates to a specific surface area of 1074 m^2/g, which exceeds considerably both values mentioned above. The difference can be explained with the large cation exchange capacity of the NaMt used which is 1.16 meq/g. If all the charges were neutralized by MB cations, the covered surface would be 904 m^2/g assuming that the absorbed molecules are oriented parallel to the silicate platelets. The only reasonable explanation is that MB molecules are tilted to the basal surface of NaMt, or coverage is not monomolecular. The tilted orientation of adsorbed molecules (surfactants) was observed earlier on layered silicates, when CEC was sufficiently large (Lagaly and Weiss, 1970).

The gallery structure of the silicate samples was checked by XRD measurements and layer distance was calculated from the position of the silicate reflection observed in the recorded

XRD patterns. The orientation of MB molecules among the silicate layers was determined as a function of the adsorbed amount of MB. This latter was measured by TGA on centrifuged and dried silicate samples. The layer distance of all investigated silicates increased as a result of MB adsorption indicated by the shift of the silicate reflection towards smaller 2θ degrees in the diffractograms (not shown). The dependence of layer distance on the amount of adsorbed MB is presented in **Fig. 8**.

Tilted orientation can be confirmed by comparing the dependence of layer distance on MB content for NaMt and XLG, respectively. Layer distance increases stepwise for XLG having an ion exchange capacity of 0.55 meq/g (see **Fig. 8**). Below 0.6 mmol MB/g Laponite, the layer distance indicates monolayer coverage. The thickness of one MB molecule is 0.325 nm, while that of an XLG platelet is 0.92 nm. Layer distance is 1.37 nm when the amount of adsorbed MB is less than 0.62 mmol/g, which is close to the combined thickness of the platelet and the dye molecule (1.25 nm). At larger amount of adsorbed MB, above 0.62 mmol/g, the dye molecules can only be arranged in a double layer among the collapsed silicate disks. In this case, the layer distance is 1.5 nm, which is close to the sum of the thicknesses of one silicate layer and two MB molecules (1.57 nm). In the case of NaMt having large CEC, a continuous increase of layer distance is observed with increasing MB

content that indicates the tilted, non-parallel orientation of the adsorbed molecules among the silicate layers. In this case, dye molecules do not lie parallel to the surface of the clay and the specific surface area determined from MB adsorption is apparently larger than at monomolecular coverage and parallel orientation. Specific surface area can be calculated through geometric consideration by taking into account the tilting of the molecules. Values between 724 and 803 m2/g were obtained in this way, which agree well with published data and the value determined from the geometry of silicate platelets.

4. CONCLUSIONS

The specific surface area of three layered silicates was determined by three different approaches and good agreement was observed for some of the results, while considerable discrepancies in other cases. If adsorption occurs through attractive ionic forces and the adsorbed molecules are arranged parallel to the silicate layers in a monomolecular coverage, the agreement between surface areas calculated from the geometry of the plates and those determined by the adsorption of methylene blue agree well with each other. The specific surface area of a silicate with relatively small size (Laponite XLG) was smaller than expected because of the dependence of the adsorbed amount of MB molecules on pH. The

addition of methylene blue solution decreases pH considerably leading to particles with positive charge, as shown by zeta potential measurements, to smaller methylene blue adsorption and small specific surface area. Modification of the clay or the control of pH by a buffer solve the problem, and real values for surface areas are obtained which agree well with geometric calculations. At large ion exchange capacity (NaMt, CEC = 1.16 meq/g), the molecules adsorb in a tilted orientation and not parallel to the surface. Tilted orientation results in larger than monomolecular coverage and the specific surface area calculated from MB adsorption is considerably larger than the real surface of the silicate.

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CAPTIONS

Fig. 1 The chemical structure of methylene blue.

Fig. 2 Adsorption isotherm of methylene blue on the surface of the investigated silicates. Symbols: (△) NaMt, (○) Laponite XLS, (□) Laponite XLG.

Fig. 3 Fitting of the Langmuir model onto the adsorption isotherms of **Fig. 1**. Symbols: (△) NaMt, (○) Laponite XLS, (□) Laponite XLG.

Fig. 4 Correlations obtained by the fitting of the Freundlich model to the isotherms presented in **Fig. 1**. Symbols: (△) NaMt, (○) Laponite XLS, (□) Laponite XLG.

Fig. 5 X-ray diffractograms of Laponite XLG (black), XLS

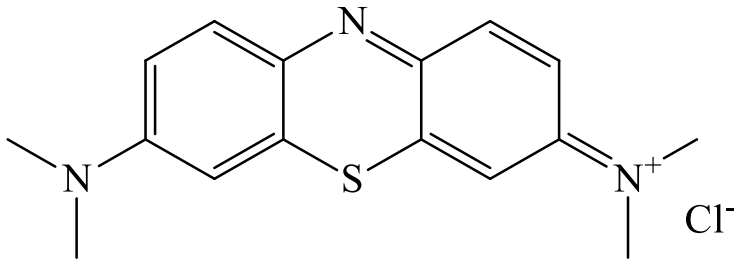
(red) and NaMt (blue).

Fig. 6 The pH of the silicate sols plotted against the added amount of methylene blue in water. Symbols: (△) NaMt, (○) Laponite XLS, (□) Laponite XLG.

Fig. 7 Zeta potential of the silicate particles plotted as a function of the added amount of MB. Symbols: Laponite XLG with (▽) and without (□) pH control, Laponite XLS (○) shown as reference.

Fig. 8 Layer distance of silicates plotted against the amount of adsorbed methylene blue. Symbols: (△) NaMt, (□) Laponite XLG.

Hegyesi, Fig. 1



694 Hegyesi, Fig. 2

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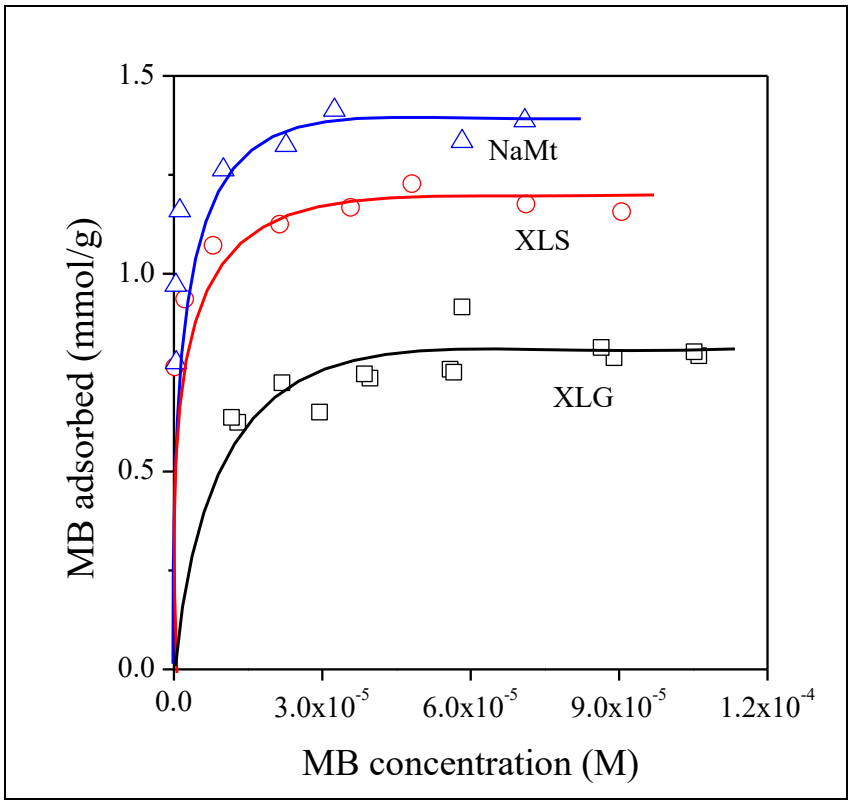

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705 Hegyesi, Fig. 3

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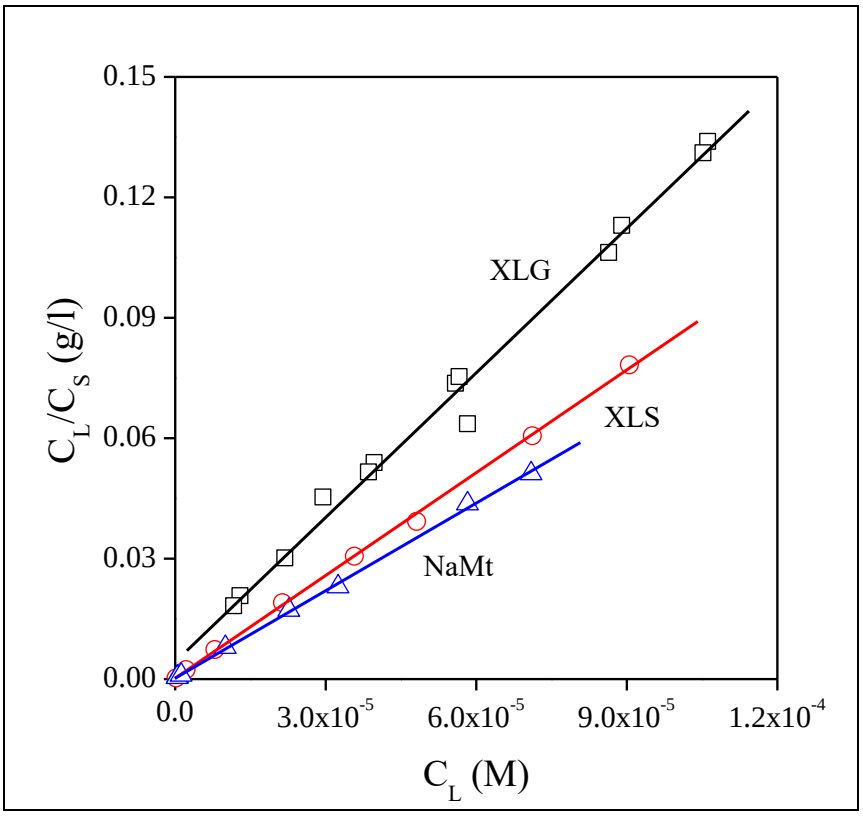

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716 Hegyesi, Fig. 4

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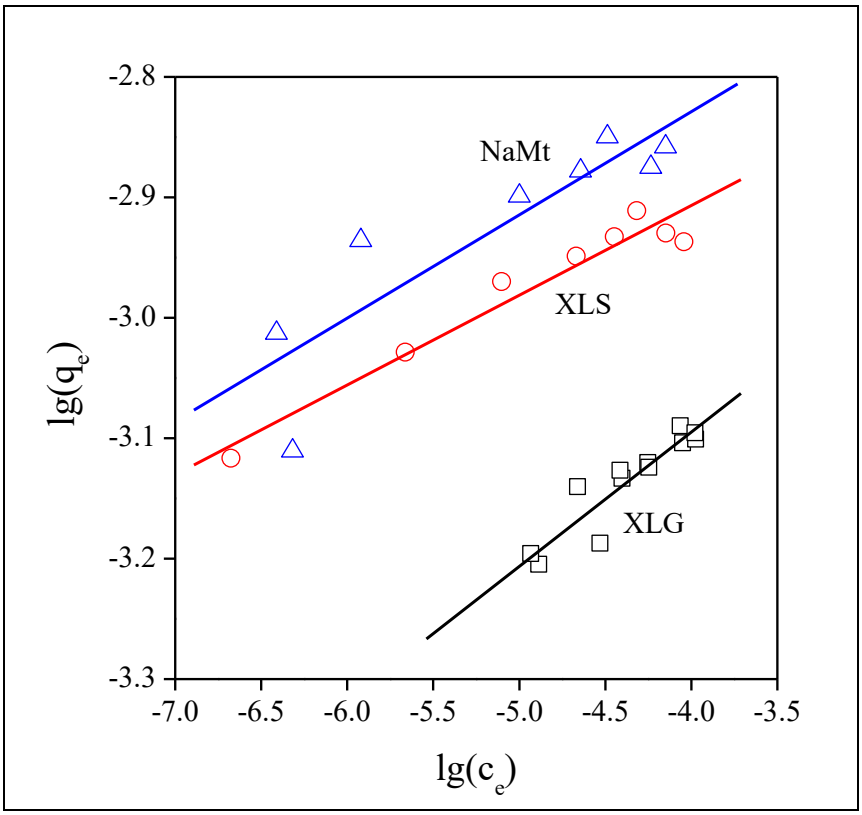

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727 Hegyesi, Fig. 5

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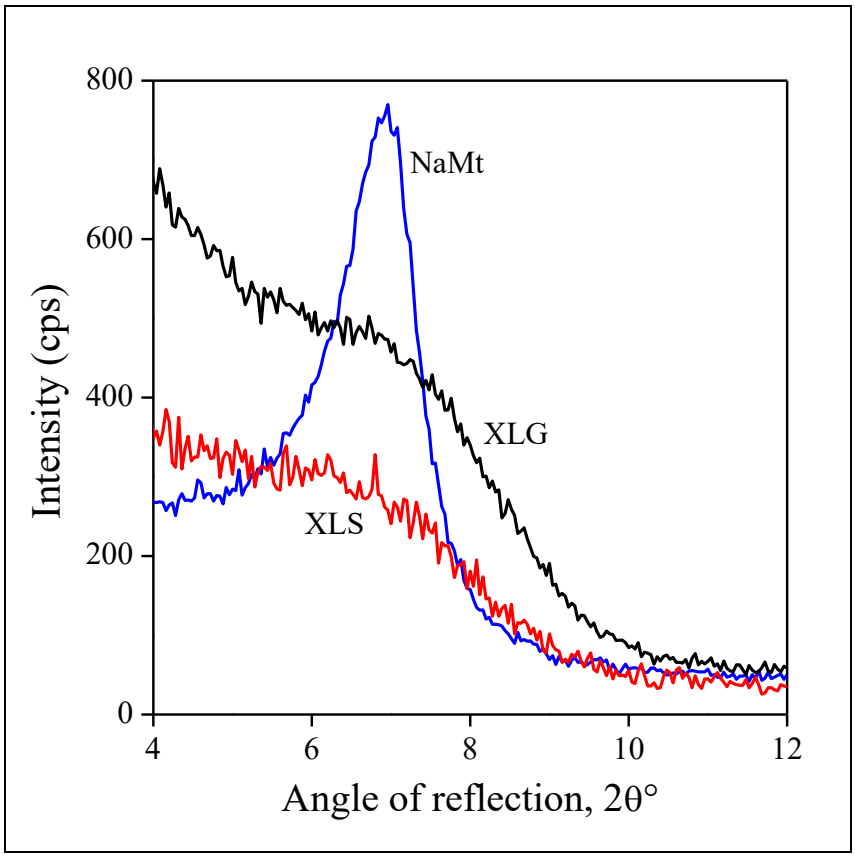

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737 Hegyesi, Fig. 6

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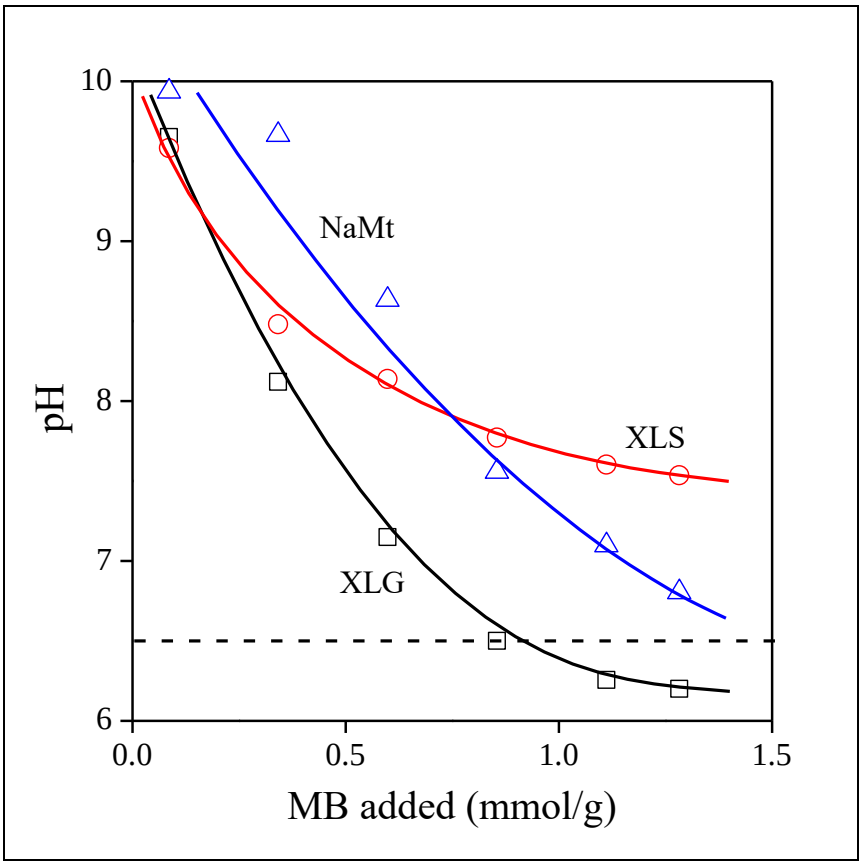

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747 Hegyesi, Fig. 7

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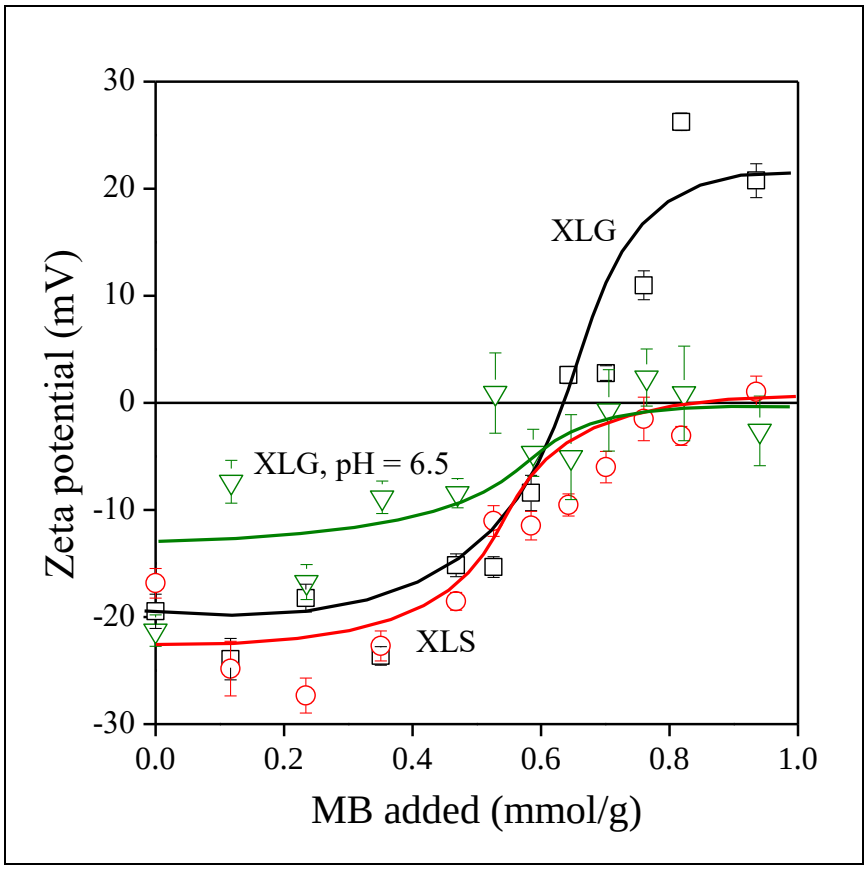

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757 Hegyesi, Fig. 8

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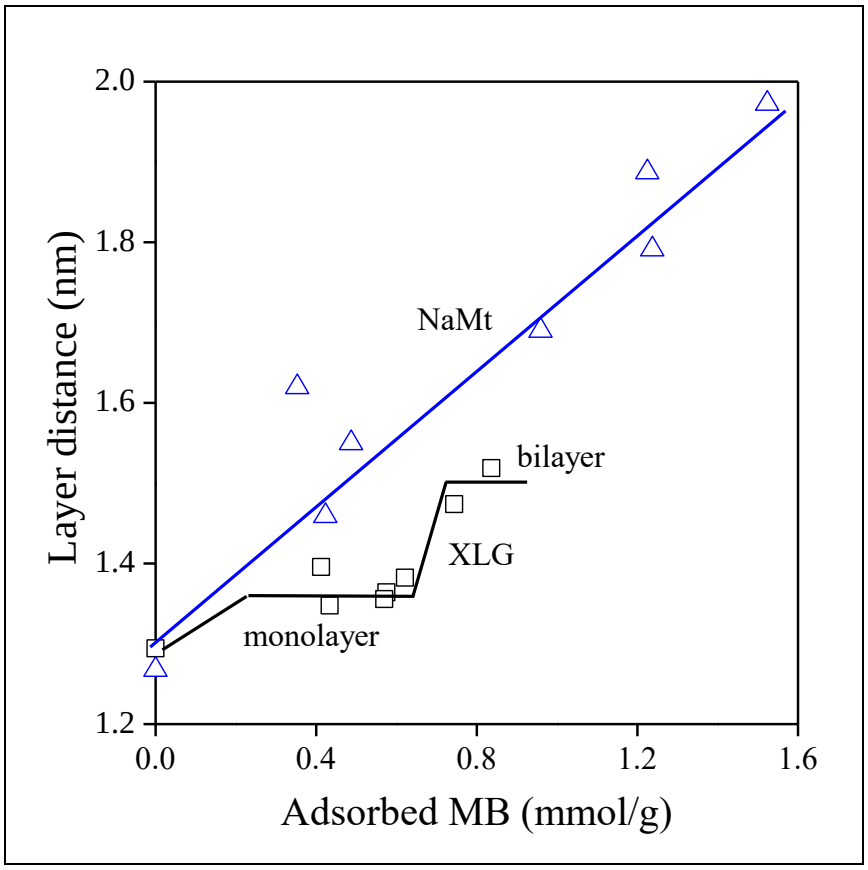

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