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Adsorption study of dimethylaminostyryl benzazoles onto Na-montmorillonite

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ABSTRACT

The adsorption of 2-(4′-dimethylaminostyryl)benzoxazole (DMASBO) and its benzothiazole analogue (DMASBT) onto Na-montmorillonite (Na^+-MMT) was studied. The adsorption data have been fitted with Freundlich and Dubinin–Radushkevich (*D–R*) equation to find the characteristic parameters of each model. From *D–R* isotherm, it was concluded that the adsorption is of chemical nature. The equilibrium adsorption constant, K_c, was determined and has been used to calculate the enthalpy and entropy of the adsorption process. The mechanism of the adsorption has been investigated by fluorescence, IR, X-ray and ESR spectroscopic measurements. These measurements indicate oxidation of the styryl dyes by the Lewis acidic sites of the clay and formation of radical cations at Na^+-MMT surface without intercalation into the interior.

1. Introduction

The photophysical and photochemical behaviour of photoactive molecules in heterogenous media may differ significantly from that in homogeneous solutions. Therefore, the photochemistry and photophysics of organic molecules in heterogeneous media are current areas of much interest. Clays and silica are important substrates for controlled photochemical reactions of organic and inorganic photoactive species [1], which found wide applications in molecular devices necessary for optics [2]. The wide range of applications of clays is owing to their large surface area, high cation-exchange capacity and shape specificity as well as high chemical and mechanical stability. The chemical nature and pore structure usually determine the sorption ability of clays [3]. Montmorillonite is among swelling clays that has often been used in chemical, technological and environmental applications [4,5]. Montmorillonite has a layered structure which is negatively charged aluminosilicate layers. This negative charge is due to the isomorphic replacement of some cations in the montmorillonite structure by others of lower charge and similar size. Generally, various cations such as alkali metal ions are adsorbed within the interlayer for balancing the electrostatic changes [6–8]. It is believed that such cations can be readily exchanged by not only other metal cations, but also atomic or molecular species having larger size, which are well known as intercalation reagents [9,10].

Clay surfaces have Bronsted and Lewis acidic properties. Lewis acidity arises from incompletely coordinated Al-sites. Bronsted acidity arises as a result of replacing the cations with hydrogen ions by treatment of the clay with sulfuric acid [11] or when the exchangeable cations become hydrated.

Recently, several spectroscopic studies have been devoted to examine the behaviour of intercalated clay complexes with photoactive organic guests [12–15].

The goal of the present study is to examine the adsorption of highly sensitive fluorescent probes namely: 2-(4′-dimethylaminostyryl)benzoxazole (DMASBO) and its benzothiazole analogue (DMASBT) onto Na-montmorillonite (Na^+-MMT). The adsorption capacity of the clay towards both styrylbenzazoles is examined using the adsorption isotherm. The effect of the contact time and temperature on the adsorption process was also studied. In addition, the mechanism of the adsorption of both DMASBO and DMASBT onto the swelling Na^+-MMT has been explained and characterized using spectroscopic techniques.

Styrylbenzoxazoles have widespread applications based on their efficiency as cytotoxic [16,17], gasteric acid secretion inhibitors [18] and anti-HIV activity [19]. They are also suitable sensitizers for photographic halide emulsions [20]. The photophysics and photochemistry of 2-(4′-dimethylaminostyryl)benzazoles (Scheme 1) have been studied in organic solvents [21,22], micellar and protein solutions [23,24], different polymer matrices and adsorbed on silica surface [25] with the aim of probing the properties of their microenvironment.

2. Experimental section

2.1. Materials

The host clay mineral, montmorillonite (Southern clay products, Inc., Gonzales, TX) containing 6.39% Fe^{3+}, 0.88% Mg^{2+},

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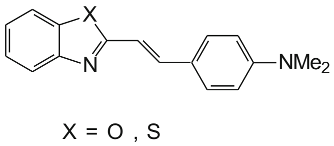

Scheme 1

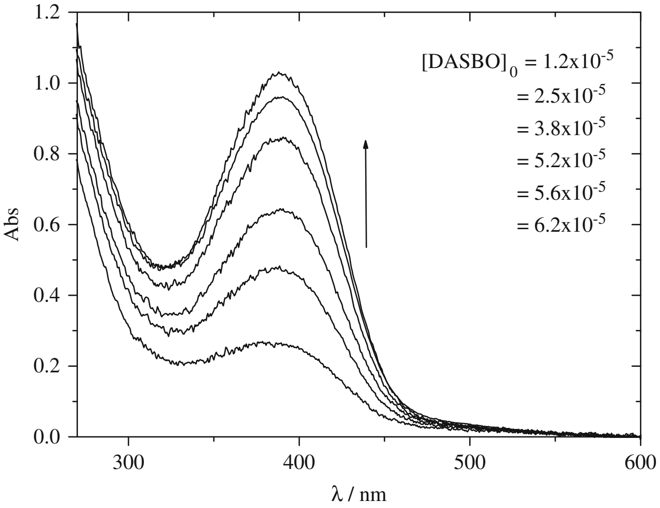

Fig. 1. Adsorption isotherm of DMASBO of various concentrations onto/Na$^+$-MMT (1 g/l) at 25 °C.

15.50% Al^{3+} and 77.28% Si^{4+} under the trade name of mineral colloid Bp was used. The cation-exchange capacity (CEC) of the clay (Na$^+$ form) equals 108 meq/100 g [26]. The BET surface area of the clay particles is about 21 m^2/g, and has an average hydrodynamic radius of 0.0728 μm. The photoactive organic guests, 2-(4′-dimethylaminostyryl)benzoxazole (DMASBO) and its benzothiazole analogue (DMASBT) were from previous works [21,22]. Spectroscopic grade ethanol (BDH) and double distilled water were used for preparation of solutions. The stock solution of Na$^+$-MMT (1 g/l) was prepared in ethanol–water mixed solvents (10% v/v), for solubility requirements of the styryl derivatives, and stirred overnight to be completely suspended and achieve high swelling.

2.2. Adsorption measurements

Adsorption experiments were carried out at 25 °C as follows: to a definite volume of suspended Na$^+$-MMT (1 g/l, aqueous solution), certain amount of the organic guest (10^{-4} M ethanolic solution) is added to obtain a fixed final volume (6 ml). The mixtures were shaken at 120 rpm in a temperature controlled shaking water bath for 4 h to reach the equilibrium. The suspensions were centrifuged at 6000 rpm for 5 min. The adsorption process was followed spectrophotometrically by measuring the absorbance of the supernatant solutions at λ_{max}=400 and 392 nm for DMASBT and DMASBO, respectively, using Shimadzu UV/vis 2001-S spectrophotometer (Fig. 1). The adsorbed amount of the probe, C_{ads} mol/g was calculated from the difference of its initial and equilibrium concentrations, C_w mol/l, in the supernatant solutions.

The adsorption experiments were also carried out using different concentrations of DMASBT and/or DMASBO in the range 5×10^{-6}–5×10^{-5} M and 1.2×0^{-5}–6×10^{-5} M, respectively, to obtain the adsorption isotherm. The effect of temperature on the equilibrium concentration of the adsorbed organic guest has been studied to determine the equilibrium constant (K_c) and the corresponding thermodynamic parameters.

2.3. Solid state measurements

Solid samples of DMASBT and DMASBO adsorbed at the surface of Na$^+$-MMT were separated by centrifuge of the dispersed suspension at 6000 rpm to get the solid residue, brought to constant weight in a drying oven at 80 °C for 24 h and kept in a desiccator. The emission spectra of solid samples of adsorbed styryl dyes on Na$^+$-MMT were measured using a front surface arrangement in a solid state sample holder at room temperature (λ_{exc}=490 nm). IR spectra were recorded on Perkin Elmer Model 1600 IR spectrophotometer as KBr disks within the range 4000–400 cm^{-1}, while the electron spin paramagnetic resonance spectra were recorded on JEOL JES-FE2XG ESR spectrometer. X-ray powder diffraction pattern was recorded on a shimadzu Model XD-3X-ray powder diffractometer with Cu-K$_\alpha$ radiation.

3. Results and discussion

3.1. Adsorption efficiency and the effect of contact time

Both DMASBT and DMASBO are highly adsorbed onto Na$^+$-MMT surface with different loadings depending on the initial concentration of the probe. Upon mixing of an ethanolic solution of the styryl derivative with the clay suspension, its faint yellow colour disappears gradually with formation of a pink or orange coloured suspension, respectively. Fig. 2 shows the change of the absorption spectrum of DMASBT/clay suspension with time. As illustrated in this figure, the absorption peak of DMASBT/Na$^+$-MMT solution (λ_{max} at 400 nm) decreases on standing and a new peak is developed at 490 nm with an enhancement of its intensity as the contact time increases.

Loading of DMASBT at the surface is higher than that of DMASBO, L=0.4×10^{-2}–0.2×10^{-3} and L=3×10^{-2}–0.5×10^{-2} mmol/g Na$^+$-MMT, respectively. This means that DMASBT is highly adsorbed onto Na$^+$-MMT (~80%) than DMASBO (~20%). This is attributed to the electronegativity difference between the benzothiazole and benzoxazole moieties which affects the charge density on the basic site (–NMe$_2$ group) that is responsible for the interaction with the Lewis acidic sites on the clay [27], vide infera. Charge density

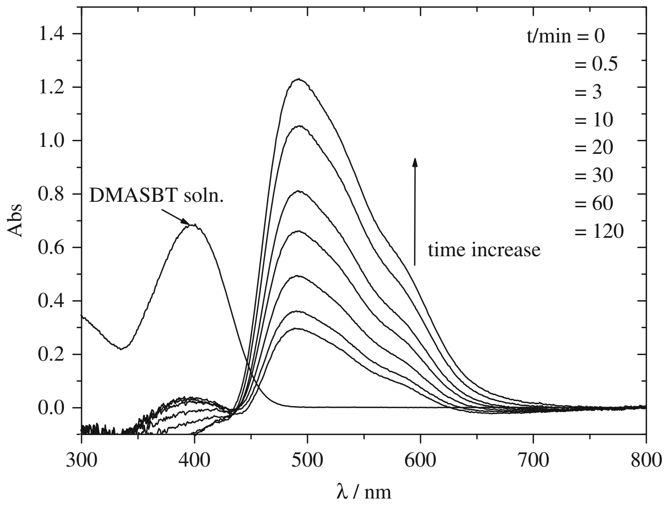

Fig. 2. Absorption spectra of DMASBT in ethanol and DMASBT/Na$^+$-MMT system at different time intervals at 25 °C.