



# New phenothiazine–laponite hybrid systems: Adsorption and ionization



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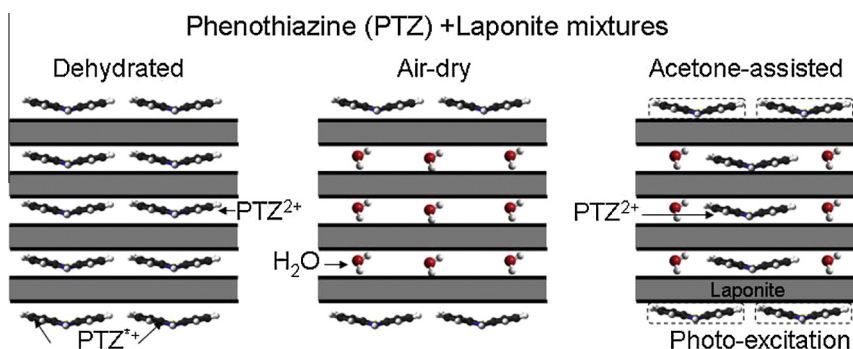
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## HIGHLIGHTS

- Reactivity of phenothiazine (PTZ) and laponite mixtures was studied.
- Creation of long lived charge separated state.
- Effect of confinement on the nature and mobility of adsorbed PTZ.
- Adsorbed PTZ<sup>+</sup> radical cations and intercalated PTZ<sup>2+</sup> di-cations were observed.
- Preparation procedure influenced the ratio of PTZ<sup>2+</sup> and PTZ<sup>+</sup> in the mixture.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The reactivity of phenothiazine (PTZ) in PTZ–laponite mixtures, prepared by three different methods, was investigated using diffuse reflectance UV–visible absorption spectroscopy (DRUVv) at room temperature,  $T = 293$  K. It was shown that the formation of different charge separated states (CSS) could be observed in PTZ–laponite mixtures depending on the procedure of preparing the mixtures. PTZ<sup>+</sup> radical cations, adsorbed on the external surface of laponite, and PTZ<sup>2+</sup> di-cations, intercalated inside the interlayer space, occurred in PTZ–laponite mixtures based on laponite dehydrated under argon. In PTZ–laponite mixtures, based on hydrated laponite (dry-air state), the PTZ-species could be adsorbed only on the external surface of laponite in the form of PTZ<sup>+</sup> radical cations. It is also shown that, using a hydrated powder of laponite with the help of a swelling agent (acetone), PTZ can penetrate into the interlayer space and can be stabilized as a di-cation. The proposed schemes of spontaneous ionization of PTZ are in agreement with the data of wide angle X-ray diffraction analyses. The observed differences in formation of charged separated states in PTZ–laponite mixtures, prepared using different methods, reflect the effects of confinement on the structure and mobility of adsorbed and intercalated PTZ species.

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## 1. Introduction

The aromatic amine phenothiazine (PTZ) and its derivatives find many useful applications as chemical stabilizers, inhibitors, antioxi-

idants, antifungal, antibacterial and shortstopping agents [1,2]. They are relatively inexpensive and nontoxic and are widely used in pharmacology and biomedicine [3–5]. The electron-rich sulfur and nitrogen heteroatoms determine the electron-donating properties of PTZ, which also makes PTZ attractive for applications in devices with unique electronic and optical properties, e.g. in thin film transistors, photovoltaic cells, and light-emitting diodes [6–13].

The ionization potential of PTZ is rather low ( $\approx 6.73$  eV), which can promote activation of spontaneous electron transfer processes

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within a porous medium, e.g. in zeolites [14–16]. The spectroscopic data indicate the presence of spontaneous ionization of PTZ and the formation of the radical cations  $PTZ^{\cdot+}$  and of the di-cations  $PTZ^{2+}$  in the channels of zeolites with various topologies. These observations highlight the combined effects of confinement and local electrostatic fields on sorption and charge-separation kinetics [14]. The lifetimes of these charge-separated states (CSS) are very long (more than 1 year) as compared with those in solution (less than  $10^{-6}$  s), and this effect has been explained by the effects of confinement in the narrow channels of zeolite. Note that the problem of stabilization of CSS is of great practical importance for functionalization of photovoltaic and photosynthesis energy conversion cells.

The present work studies the CSS processes for PTZ molecules adsorbed and intercalated by laponite clay platelets. Laponite is composed of disk-like sheets that are charged heterogeneously: faces have constant negative charge, while the surface charge of the edges is pH dependent and positive in acidic medium [17]. In principle, the attraction between radical cationic complexes  $PTZ^{\cdot+}$  and  $PTZ^{2+}$  and negative faces of clay can promote adsorption of PTZ on the surface of laponite. Similar effects of adsorption of cationic porphyrin complexes and of pyrene on clay surfaces were reported earlier [17–19]. Adsorption inside the internal surface of laponite sheets can be accelerated by expansion of the clay structure in an appropriate solvent, e.g., in water. However, PTZ is practically insoluble in water and the penetration of PTZ inside the laponite structure is expected to be very low in the presence of water. Usually, water-soluble cationic chromophores, like methylene blue (derivative of PTZ), can be strongly bound on the surface of hydrated clays [20]. The rest of this paper discusses different experimental approaches to the preparation of PTZ–laponite hybrids and results of the study of stimulated photo-activity of PTZ on the surface of laponite platelets.

## 2. Materials and methods

### 2.1. Materials

Laponite RD (Lap) (Rockwood Additives Ltd., UK) is synthetic swelling clay mineral with the following formula:  $Na_{0.7}[(Si_8Mg_{5.5}Li_{0.4})O_{20}(OH)_4]$  [17]. Note that the charge deficit induced by the partial substitution of  $Mg^{2+}$  by  $Li^+$  is compensated by the presence of  $Na^+$  cations located in the inter-sheet space. Laponite was purchased in the form of a white microcrystalline powder.

The specific surface area  $S_f$ , determined by adsorption of methylene blue is equal to  $360 \text{ m}^2/\text{g}$  [21]. The laponite was composed of charged disk-like sheets with a thickness about  $h_f = 1 \text{ nm}$  and an average diameter about  $d_f = 25\text{--}30 \text{ nm}$ .

The structure of phenothiazine (PTZ,  $C_{12}H_9NS$ , Fluka) is presented in Fig. 1. The conformation of PTZ is non-planar (butterfly) in the ground state [22]. The solubility of PTZ in water (0.00051 wt.%) is considerably less than in ethanol (1 wt.%) and acetone (20 wt.%). At room temperature PTZ is composed of yellow crystals.

All compounds were purchased as reagent grade and used without further purification.

### 2.2. Preparation of PTZ–laponite hybrids

PTZ–laponite hybrids were prepared by thorough mechanical mixing of components (PTZ/laponite ratio was 1/100 by weight) at  $T = 313 \text{ K}$  for 5 min. Three different mixtures were prepared:

- Mixture 1 ( $M_1$ ) was prepared using the powder of laponite preliminarily dried under an argon flow ( $T = 473 \text{ K}$ ,  $t = 24 \text{ h}$ ).

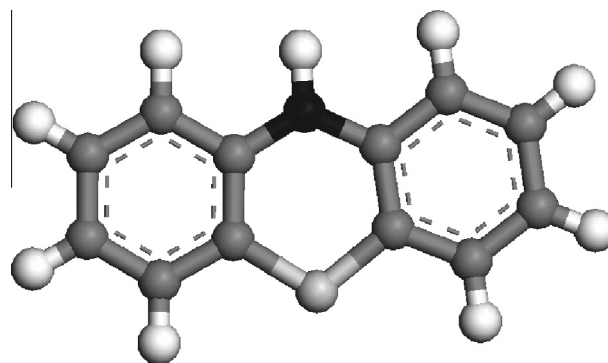


Fig. 1. Schematic structure of phenothiazine ( $C_{12}H_9NS$ ). The white and shaded balls and sticks represent the H and C atoms of the phenothiazine (PTZ) molecule, respectively. Black and light gray atoms represent N and S atoms of the molecule.

- Mixture 2 ( $M_2$ ) was prepared using the powder (dry-air state) of pristine laponite.
- Mixture 3 ( $M_3$ ) was prepared using the powder (dry-air state) of pristine laponite with acetone as a swelling agent. Acetone was added to the PTZ–laponite mixture (10/1 by weight). The mixture was then hermetically incubated for 2 h, after which the acetone was evaporated for 24 h.

All preparation procedures were performed at  $T = 313 \text{ K}$ . In order to exclude possible effects of light illumination, the mixtures were prepared and stored in the dark.

### 2.3. Instrumentation

The processes of PTZ sorption and ionization in laponite samples were monitored as a function of time using diffuse reflectance UV–visible absorption spectroscopy (DRUVv). The studies were done using Suprasil quartz cells in a Cary 6000i (Varian) double-beam spectrometer. The instrument, with an operating range 200–1800 nm, was equipped with an integration sphere for diffuse reflectance detection. Polytetrafluoroethylene (PTFE) was used to establish the baseline and placed in the reference optical path during experiments. The sample thickness was 5 mm, which was sufficient for considering the laponite-containing samples to be infinitely thick. Accordingly, the DRUVv spectra were plotted as the Kubelka–Munk function [23]:

$$F(\lambda, t) = (1 - R)^2 / 2R = K/S_c \quad (1)$$

where  $R$  represents the ratio of the diffuse reflectance of the loaded laponite to that of the Teflon reference,  $K$  is an absorption coefficient (proportional to the chromophore concentration  $C$ ), and  $S_c$  is the scattering coefficient of the powder. The spectrum intensity  $F$  was presented in Kubelka–Munk units and was registered as a function of  $\lambda$  (wavelength) at several values of  $t$  (time).

The structure of PTZ–laponite mixtures was investigated using a wide-angle X-ray diffraction (XRD) instrument DRON-2 (Bouevestnik, Inc., St. Petersburg, Russia.) with a  $CuK\alpha$  emission source of at the wavelength  $\lambda = 0.154 \text{ nm}$ . The classical Debye–Scherrer transmission geometry was used. The air scattering effects were corrected by subtraction of the scattering of the empty chamber. The interlayer distance inside the clay stacks,  $d$ , was calculated using the Bragg formula  $d = 0.5\lambda/\sin\theta$ , where  $\theta$  is half of the diffraction angle.

The PTZ–laponite hybrids were exposed to photo-excitation during 1 min using an irradiation lamp (Hamamatsu, Lightning-cure LC8,  $3 \text{ W}/\text{cm}^2$ ) in order to excite the sample in the UV spectral

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