# Intermolecular reactivity study to scale adsorption property of para- and meta-substituted nitrobenzene over 2:1 dioctahedral smectite

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# Intermolecular reactivity study to scale adsorption property of para- and meta-substituted nitrobenzene over 2:1 dioctahedral smectite

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Substituted nitrobenzene, a toxic series of molecules with its wide application in pesticides needs to be removed by a suitable sorbent, whose characteristic is to be determined using the reactivity index theory within the helm of the density-functional theory and as well inside the broad subject range of the hard–soft acid-base (HSAB) principle. We studied a series of meta- and para-substituted nitrobenzene molecules (NBMs) starting from $-NH_2$, $-OH$, $-OCH_3$, $-CHO$, $-OCOCH_3$, $-COCH_3$, $-CF_3$, $-CN$, and $-COOCH_3$ to monitor the effect of electrophilicity and nucleophilicity in their adsorption properties. From the values of the local softness and the charge on the hydrogen atom of the bridging/structural (occurring on the surface) hydroxyl attached to the octahedral/ tetrahedral metal site present in smectite, it is concluded that the local acidities of the inorganic material systems are dependent on several characteristics which are of importance within the framework of HSAB principle. We used "group softness" for the interacting molecules, whose values were generated by adding the local softness values of constituent atoms of the respective group and found it can be a better descriptor for intermolecular interactions occurring in these NBMs. A semiquantitave scale is proposed from the group reactivity index present in NBM and the clay cluster. © 2003 American Institute of Physics. [DOI: 10.1063/1.1572131]

## I. INTRODUCTION

Nitroaromatic compounds are widely used as pesticides, explosives, solvents, and intermediates in the synthesis of dyes and other chemicals.[1,2] Most of these compounds have a global toxicological concern. These environmental contaminants are commonly found in the subsurface and pose a potential threat to human health.[3,4] Studies dating from 1960s have documented that clay minerals may function as effective sorbents for pesticides and other organic chemicals.[5–8] It was generally concluded that sorption is facilitated when the clay organic matter ratio is sufficiently high (i.e., >10–30) and was especially important for polar organic compounds. Haderlein *et al.*[9] studied the adsorption of some nitroaromatics by clay minerals and found that clays with high surface areas (e.g., smectites) promoted adsorption. The type and position of substituents on the aromatic ring significantly affect the adsorption. An electron donor–acceptor (EDA) mechanism was proposed to account for the adsorption behavior in aluminosilicate clays. The specific interaction of nitroaromatics to clay was interpreted in terms of coplanar EDA formation with oxygen ligands at the external siloxane surface of clays as electron donors and the $\pi$-system of the molecules as electron acceptors. We wish to monitor the nitroaromatic molecules in the presence of two functional groups with one being electron withdrawing $NO_2$ and the other functional groups located at both meta- and para-position from a wide variety, to see the influence of the electron withdrawing groups on their adsorption property over

smectite clays. We have chosen two different types of smectite clays to rationalize the effect of layer charge on the said adsorption. Montmorillonite and beidellite are members of 2:1 dioctahedral smectite family. They share the common feature that two tetrahedral sites sandwich a sheet of octahedrally coordinated metal ions. The substitution of a bivalent metal ion for octahedral aluminum in montmorillonite and the substitution of a trivalent metal ion for tetrahedral silicon in beidellite result in a net negative layer charge, and the interaction with positive ions (exchangeable cation) to form an interlayer hydrated phase. In any case, the hydroxyl hydrogen either attached with an octahedral metal ion through an oxygen bridge or the structural hydroxyl generated by the tetrahedral substitution at the clay surface, is responsible for the catalytic activity of these clay materials.[10,11]

The hard–soft acid-base (HSAB) principles classify the interaction between acids and bases in terms of global softness. The global hardness was defined as the second derivative of energy with respect to the number of electrons at a constant temperature and external potential, which includes the nuclear field. Pearson proposed the global HSAB principle.[12] The global softness is the inverse of this principle. Pearson also suggested a principle of maximum hardness,[13] which states that for a constant external potential the system with the maximum global hardness is most stable. In recent days, density-functional theory (DFT) has gained widespread use in quantum chemistry. Some DFT-based local properties, e.g., Fukui functions and local softness,[14] have already been used for the reliable predictions in various types of electrophilic and nucleophilic reactions.[15–18] In our earlier study,[19] we proposed a reactivity index scale for het-

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eroatomic interaction with zeolite framework. The scale holds well for unisite interaction or in other way with one active site present in the molecule, the scale does not hold good for systems with two or more active sites. Moreover, Gazquez and Mendez,[20] proposed that when two molecules A and B of equal softness interact, thereby implicitly assuming one of the species as nucleophile and the other as an electrophile, then a new bond would likely form between atoms A and B, whose Fukui function values are close to each other. We have used this methodology, to find a suitable sorbent for dioxins and furans from the 2:1 dioctahedral smectite family.[21] But here again, the interaction is unidirectional or, in other words, it is through a single active atom. Now in the present communication, the different functional groups of NBMs are to interact with the hydroxyl group of clay moiety hence, apart from the local softness calculations, we wish to perform a group softness calculation, the methodology of which is mentioned later in Sec. IV D. The concept of summation of reactivity parameter, like electronegativity, resonance, etc., has been performed mainly by Nalewajski et al.[22] and Geerlings et al.[23,24] Geerlings et al.[23] has used the DFT to calculate group softness, hardness, and electronegativity as "intrinsic" group properties, for 30 organic functional groups without taking into account the contributions of the group molecular environment; whereas Nalewajski et al.[22] has obtained group electronegativities for molecular fragments based on a neglect-of-differential overlap (NDO) calculation scheme. These group electronegativities provided adequate reactivity criteria to reproduce some known substituent effects. Geerlings et al.[24] has also proposed group softness, where it is calculated for the group of atoms individually and not at the equilibrium or when the atoms are a part of the molecule. Recently, Pal et al.[25] calculated the group softness as a sum of local softness values for the relevant atoms. They mentioned that the group for each series of molecules can vary in itself and chemical intuition is required to identify the group. Once the group is correctly defined for a series of molecules, group softness is an effective parameter to choose the most reactive molecule among the given series. They have used this methodology for the measurement of correct acidity trends for carbonyl compounds and acetic acids. This calculation is restricted to intramolecular reactivity trends; but we wish to extrapolate this methodology based on group softness to propose intermolecular interaction trends. The group softness calculated in this article has used the same concept of additivity as proposed by other authors,[22–25] but there exists a marked difference between these two concepts as elaborated next. We considered the groups in molecules and calculated the group softness by adding up the local softness of the atoms connected directly to the active site of the reacting molecule. This is different from summing up the local softness of the substituent atoms. We have tested this difference in intermolecular level interactions.

In this article, our aim is to compare the local/group softness of the active atoms present in the NBMs for a series of functional groups: $-NH_2$, $-OH$, $-OCH_3$, $-CHO$, $-OCOCH_3$, $-COCH_3$, $-CF_3$, $-CN$, and $-COOCH_3$ along with the $NO_2$ at both meta- and para-positions to that of the

clay moiety, to probe the effect of the electron withdrawing group in the adsorption behavior of these molecules. A scale is proposed in terms of the activity. The results show that relative group neucleophilicity/electrophilicity can be a better descriptor. The coplanar structure of nitroaromatics with interacting species, a primary condition of EDA, is tested in terms of interaction energy calculation. This methodology can be extrapolated to other molecules with complicated electronic structures.

## II. THEORY

In the DFT, hardness $(\eta)$ is defined as[26]

$$\eta = -(\delta^2 E/\delta N^2)v(r) = -(\delta\mu/dN)_v,$$

where $E$ is the total energy, $N$ is the number of electrons of the chemical species, and $\mu$ is the chemical potential.

The global softness, $S$, is defined as the inverse of the global hardness, $\eta$,

$$S = 1/2\eta = (\delta N/\delta\mu)_v.$$

Using the finite difference approximation, $S$ can be approximated as

$$S = 1/(IE - EA), \tag{1}$$

where $IE$ and $EA$ are the first ionization energy and electron affinity of the molecule, respectively.

The Fukui function $f(r)$ is defined by[14]

$$f(r) = [\delta\mu/dv(r)]_N = [\delta\rho(r)/\delta N]_v. \tag{2}$$

The function "$f$" is thus a local quantity, which has different values at different points in the species, $N$ is the total number of electrons, $\mu$ is the chemical potential, and $v$ is the potential acting on an electron due to all nuclei present. Since $\rho(r)$ as a function of $N$ has slope discontinuities, Eq. (1) provides the following three reaction indices:[14]

(1) $f^-(r) = [\delta\rho(r)/\delta N]_v^-$ (governing electrophilic attack);
(2) $f^+(r) = [\delta\rho(r)/\delta N]_v^+$ (governing nucleophilic attack); and
(3) $f^0(r) = -[f^+(r) + f^-(r)]$ (for radial attack).

In a finite difference approximation, the condensed Fukui function[27] of an atom, say $x$, in a molecule with $N$ electrons is defined as:

$$f_x^+ = [q_x(N+1) - q_x(N)] \quad \text{(for nucleophilic attack)},$$

$$f_x^- = [q_x(N) - q_x(N-1)] \quad \text{(for electrophilic attack)}, \tag{3}$$

$$f_x^0 = [q_x(N+1) - q_x(N-1)]/2 \quad \text{(for radical attack)},$$

where $q_x$ is the electronic population of atom $x$ in a molecule.

The local softness $s(r)$ can be defined as

$$s(r) = (\delta\rho(r)/\delta\mu)_v. \tag{4}$$

Equation (3) can also be written as

$$s(r) = [\delta\rho(r)/\delta N]v[\delta N/\delta\mu]_v = f(r)S. \tag{5}$$

Thus, local softness contains the same information as the Fukui function $f(r)$ plus additional information about the

total molecular softness, which is related to the global reactivity with respect to a reaction partner, as stated in the HSAB principle.

Atomic softness values can easily be calculated by using Eq. (4), namely,

$$s_x^+ = [q_x(N+1) - q_x(N)]S,$$
$$s_x^- = [q_x(N) - q_x(N-1)]S, \qquad (6)$$
$$s_x^0 = S[q_x(N+1) - q_x(N-1)]/2.$$

## III. COMPUTATIONAL METHODOLOGY AND MODEL

In the present study, all calculations have been carried out with the DFT[28] using the DMOL code of MSI Inc. A gradient corrected functional BLYP[29,30] and DNP basis set[31] was used through out the calculation. Basis set superposition error was also calculated for the current basis set in nonlocal density approximation using Boys–Bernardi method.[32] Geometries of the interacting nitrobenzene molecules (NBMs) with functional groups: $-NH_2$, $-OH$, $-OCH_3$, $-CHO$, $-OCOCH_3$, $-COCH_3$, $-CF_3$, $-CN$, and $-COOCH_3$ along with the representative individual clay cluster models (chosen in terms of the origin of layer charge through substitution either in octahedral aluminum or tetrahedral silicon), were fully optimized for calculating the reactivity index. Single point calculations of the cation and anion of each molecule, at the optimized geometry of the neutral molecule were also carried out to evaluate Fukui functions and global and local softness. The condensed Fukui function and atomic softness were evaluated using Eqs. (3) and (6), respectively. The gross atomic charges were evaluated by using the technique of electrostatic potential (ESP) driven charges. The definition of group softness is discussed in Sec. IV D.

The ideal formula of the clay montmorillonite, a member of the 2:1 dioctahedral smectite family, is $(Na_x^+, nH_2O)$ $\times (Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$.[33] The $Al_2Si_6O_{24}H_{18}$ cluster was generated from the clay structure as shown in Fig. 1. It displays the top view of one tetrahedral and one octahedral sheet, showing the hexagonal cavities at the oxygen surface of the silicon layers. Two localized clusters were generated to represent two types of 2:1 dioctahedral smectite (a) montmorillonite and (b) beidellite. The formula of the clusters are $MgSi_4O_{16}H_{10}$ and $AlSi_3AlO_{16}H_{11}$, respectively, where the adjacent silicon and aluminum atoms present in the clay lattice were replaced by hydrogens to preserve the electroneutrality of the model. The clusters are shown in Figs. 2(a) and 2(b), respectively.

## IV. RESULTS AND DISCUSSION

The aim of this article is to monitor the adsorption of nitroaromatic molecules over 2:1 dioctahedral smectite. The two most commonly available varieties of smectite are chosen with different locations of layer charge, which is responsible for its activity. Varieties of NBMs were chosen to monitor the role of the electron withdrawing nitrogroup on their adsorptive behavior, resulting from the presence of other functional groups at meta or para with respect to the nitrogroup. The activities of clay clusters were calculated and
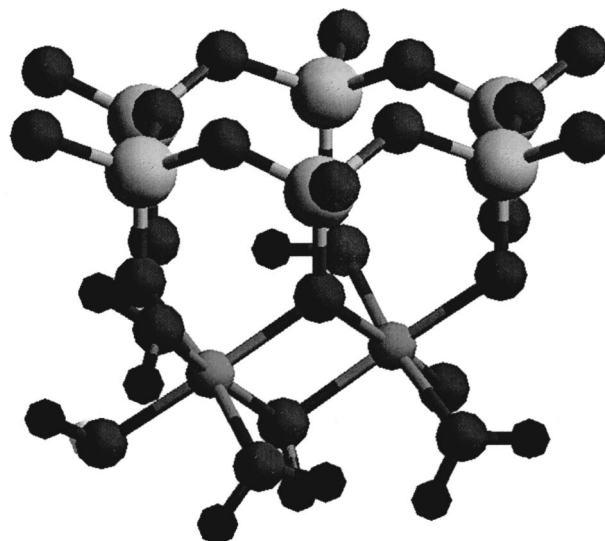


FIG. 1. The cluster model of montmorillonite with six tetrahedral silicons and two octahedral aluminums. It is the top view of the cluster. The color code is as follows: biggest gray ball (silicon); smallest gray ball (octahedral aluminum); blackish ball (oxygen); and smallest black ball (hydrogen).

compared with that of NBMs to propose the feasibility of the adsorption process. The electronic and structural properties of the interacting nitroaromatic molecules and the clay cluster models are first rationalized. First, a qualitative trend is proposed in terms of the local reactivity descriptors in the helm of HSAB, to trace a selectivity of clays for the respective organic pollutants in terms of their active centers. The relative nucleophilicity and electrophilicity of the interacting centers of the interacting molecules to trace the pseudobond formation process[34] were also calculated as described in our earlier paper.[21] We further introduced group softness to elucidate the activity of the functional groups. In the clay cluster, two different types of hydroxyl hydrogen have been observed: (1) the structural hydroxyl present during a tetrahedral substitution in a beidellite type of clay and (2) hydroxyl hydrogen attached with the substituted octahedral metal cation present in the montmorillonite variety. The orientation of the optimized interacting molecular conformation is monitored to understand its intermolecular interaction with a octahedral/tetrahedral metal ion present in the clay framework.

### A. Activity of clay cluster in terms of reactivity index

The initial configurations of the representative clusters are shown in Figs. 2(a) and 2(b), respectively. In each case, the cluster was totally optimized. The global softness values in Table I showed that the cluster containing octahedral $Mg^{2+}$ has a lower value than that of the $Al^{3+}$-substituted tetrahedral one. We compared the localized properties for both clusters. The aim is to compare the activity of structural and bridging hydroxyl hydrogen present in the clay structure. The results are shown in Table II. This shows that for a situation with tetrahedral $Al^{3+}$ substitution, the surface hydroxyl is more active than the bridging hydroxyl attached to octahedral aluminum. Now, it is observed that in terms of hydroxyl hydrogen, montmorillonite is more active than the
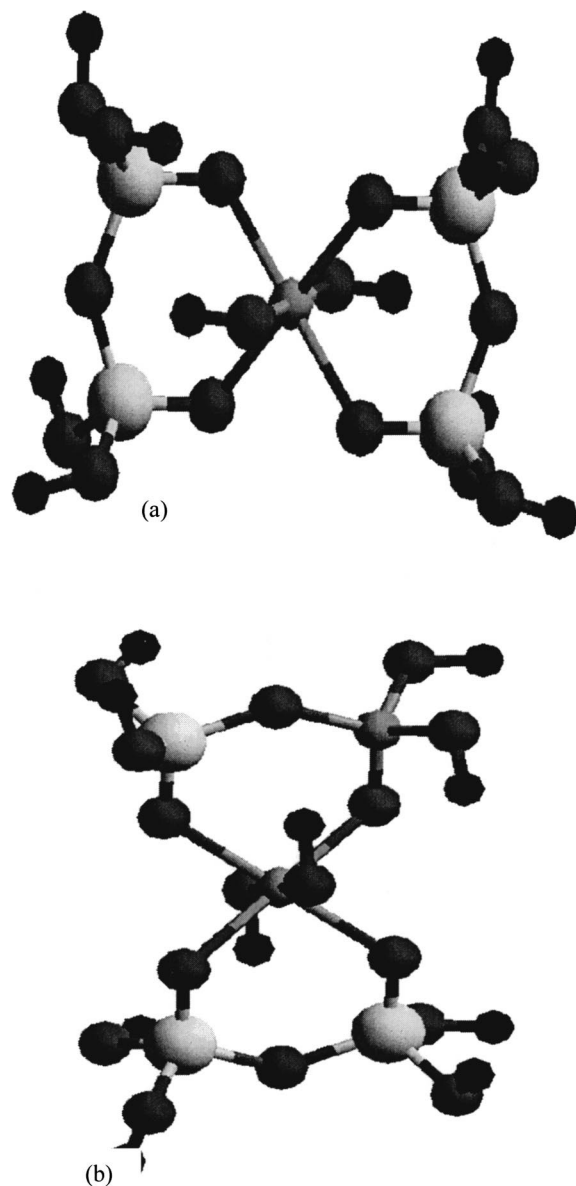
TABLE I. Global softness values (in a.u.) for clay clusters and nitroaromatic molecules. NB indicates nitrobenzene.

| Molecules | Global softness (a.u.) |
|---|---|
| $[MgSi_4O_{16}H_{10}]^-$ | 1.521 73 |
| $AlSi_3AlO_{16}H_{11}$ | 2.226 |
| $p$-NH$_2$NB | 3.405 |
| $m$-NH$_2$NB | 3.698 |
| $p$-OHNB | 2.023 |
| $m$-OHNB | 2.082 |
| $p$-OCH$_3$NB | 1.177 |
| $m$-OCH$_3$NB | 1.647 |
| $p$-CHONB | 2.022 |
| $m$-CHONB | 1.989 |
| $p$-OCOCH$_3$NB | 1.397 |
| $m$-OCOCH$_3$NB | 1.456 |
| $p$-COCH$_3$NB | 1.670 |
| $m$-COCH$_3$NB | 1.726 |
| $p$-CF$_3$NB | 1.323 |
| $m$-CF$_3$NB | 1.047 |
| $p$-CNNB | 1.873 |
| $m$-CNNB | 1.830 |
| $p$-COOCH$_3$NB | 1.474 |
| $m$-COOCH$_3$NB | 1.520 |

the presence of an electron-withdrawing group $-NO_2$ have any influence. The qualitative order of the interacting NBMs are as follows: $m$-NH$_2$NB $> p$-NH$_2$NB $> m$-OHNB $> p$-OHNB $> p$-CHONB $> m$-CHONB $> p$-CNNB $> m$-CNNB $> m$-COCH$_3$NB $> p$-COCH$_3$NB $> m$-OCH$_3$NB $> m$-COOCH$_3$NB $> p$-COOCH$_3$NB $> m$-OCOCH$_3$NB $> p$-OCOCH$_3$NB $> p$-CF$_3$NB $> p$-OCH$_3$NB $> m$-CF$_3$NB.

These results show that, for a strong electron-releasing group, like $-NH_2$ and $-OH$, the global softness is higher. This order gradually decreases until $-CF_3$ substituted NBM. The functional group $-CN$ as well being a strong electron-withdrawing group; surprisingly, places at the intermediate position in that order. So, we calculated the electrophilic local atomic softness ($s_x^-$) values for the constituent atoms of all the NBM using the ESP method with the DFT and the results of the active atoms are shown in Tables III and IV. It seems that the localized parameters can be a better performer in comparison to the results generated from global property



FIG. 2. The initial configuration of clay cluster having the formula (top) TSi$_4$O$_{14}$H$_{10}$ (representing montmorillonite) and (bottom) AlSi$_3$AlO$_{16}$H$_{11}$ (representing beidellite) is shown. The color code is as follows: biggest gray ball (silicon); smallest gray ball (octahedral aluminum); blackish ball (oxygen); and smallest black ball (hydrogen).

beidellite type of clays, whereas, the reverse is true for structural hydroxyl group. At this point, the results suggest that the hydroxyl hydrogens of 2:1 smectite clays can behave as a nucleophilic center.

## B. Activity of interacting nitrobenzene molecules in terms of reactivity index

We have studied both para- and meta-substituted NBMs with the substituents ranging from $-NH_2$, $-OH$, $-OCH_3$, $-CHO$, $-OCOCH_3$, $-COCH_3$, $-CF_3$, $-CN$, to $-COOCH_3$. It is observed from the global softness values that $p$-CF$_3$NB has the lowest value and $m$-NH$_2$NB has the highest value. The values are not quantitative. But still, the numbers raise a concern as to whether the locations of different types of functional groups present in NBM varieties in

TABLE II. Condensed local softness (a.u.) from clay clusters representing montmorillonite (with Mg$^{2+}$ at octahedral position) and beidellite (with Al$^{3+}$ at tetrahedral position).

| | Substituent cation for tetrahedral Si$^{4+}$ and octahedral Al$^{3+}$ | |
|---|---|---|
| | Mg$^{2+}$ (for octahedral Al$^{3+}$) | Al$^{3+}$ (for tetrahedral Si$^{4+}$) |
| Atoms | $s_x^+$ | $s_x^+$ |
| T1[a] | 0.268 | 0.574 |
| Si | 0.135 | 0.289 |
| O-structural | 0.123 | 0.594 |
| O-hydroxyl | 0.719 | 0.423 |
| O-hydroxyl | 0.743 | 0.498 |
| H-structural | 0.028 | 0.823 |
| H-hydroxyl | 0.598 | 0.436 |
| H-hydroxyl | 0.743 | 0.449 |

[a]T1=Substituent cation Mg$^{2+}$ (for octahedral Al$^{3+}$) and Al$^{3+}$ (for tetrahedral Si$^{4+}$) for montmorillonite and beidellite respectively.

TABLE III. Condensed local softness for all the constituent atoms except the benzene ring present in NBMs.

| Atom | $s_x$ | | | | | | | | | |
|------|-------|-------|------|------|--------|--------|-------|-------|-------|-------|
|      | $p$-NH$_2$ | $m$-NH$_2$ | $p$-OH | $m$-OH | $p$-OCH$_3$ | $m$-OCH$_3$ | $p$-CHO | $m$-CHO | $p$-CF$_3$ | $m$-CF$_3$ |
| O | 0.354 | 0.232 | 0.220 | 0.174 | 0.243 | 0.108 | 0.228 | 0.272 | 0.194 | 0.121 |
| N | 0.061 | 0.092 | 0.232 | 0.272 | 0.062 | 0.041 | 0.329 | 0.294 | 0.198 | 0.168 |
| O | 0.354 | 0.281 | 0.214 | 0.191 | 0.166 | 0.133 | 0.196 | 0.302 | 0.195 | 0.146 |
| C |   |   |   |   |   |   | 0.604 | 0.549 | 0.076 | 0.196 |
| O |   |   | **0.372** | **0.385** |   |   | **0.784** | **0.602** |   |   |
| O |   |   |   |   | **0.246** | **0.265** |   |   |   |   |
| C |   |   |   |   | 0.085 | 0.052 |   |   |   |   |
| H | 0.166 | 0.203 | 0.064 | 0.074 | 0.063 | 0.107 | 0.192 | 0.171 |   |   |
| H | 0.166 | 0.192 |   |   | 0.018 | 0.044 |   |   |   |   |
| H |   |   |   |   | 0.055 | 0.100 |   |   |   |   |
| F |   |   |   |   |   |   |   |   | 0.072 | 0.106 |
| F |   |   |   |   |   |   |   |   | 0.074 | 0.063 |
| F |   |   |   |   |   |   |   |   | **0.219** | **0.236** |
| N | **0.623** | **0.750** |   |   |   |   |   |   |   |   |

calculations. The most probable active centers present in the functional groups and in NBMs, including the nitrogroup, are tabulated in terms of the local softness values of the constituent atoms. There are four different active centers present in these sets of NBMs with para- and meta-substitution. The activity of the atom centers does not change with the location of the functional group (meta/para). The active center lies in terminal fluorine atom for $-$CF$_3$NB, where as, for $-$CNNB, the center is carbon and for $-$NH$_2$NB, the center is nitrogen. The active center for the rest of the molecules is the oxygen, as present in the functional group other than that the nitrogroup. Now, if the NBMs are arranged in terms of their electrophilic affinity, the order is as follows: $p$-CNNB$>$m-CNNB$>$p-CHONB $>m$-NH$_2$NB$>p$-COCH$_3$NB $>p$-NH$_2$NB$>m$-CHONB $>m$-COCH$_3$NB$>m$-COOCH$_3$NB $>p$-COOCH3NB $>m$-OHNB $>p$-OHNB$>m$-OCH$_3$NB$>p$-OCH$_3$NB $>m$-OCOCH$_3$NB $>p$-OCOCH$_3$NB$>m$-CF$_3$NB$>p$-CF$_3$NB. The $-$CF$_3$NB group has the lowest local softness with fluorine in NBMs. The $-$CNNB with its carbon center has the highest local softness value among NBMs. This suggests two things, first, the location of functional groups with respect to the electron-withdrawing group has a marked influence in the local properties. Second, the strong electron-withdrawing group pre-

dominates over the $-$NO$_2$, like $-$CN; whereas, in cases where both the strong electron-withdrawing and electron releasing groups are present, as in $-$NH$_2$NB, the localized parameters explain the phenomenon better. But still, the order is not quantitative, there are some anomalies. The contradictions are not only for the strong electron-releasing groups, like $-$NH$_2$, $-$OH, $-$OCH$_3$, $-$OCOCH$_3$, and $-$CF$_3$, but also for other substituents. We need to find a better match for these potential electrophilic centers in search of a suitable sorbent for these toxic NBMs.

## C. Reactivity index scale with local softness

The aim of the current study is to find a material from the smectite family suitable for NBM adsorption. It is observed that, in terms of global softness values as shown in Table I, most of the NBM varieties have higher values in comparison to the clay clusters. The order of global softness for representative clay clusters is as follows: Al$^{3+}$ (substituted at tetrahedral Si$^{4+}$) $>$Mg$^{2+}$ (substituted at octahedral Al$^{3+}$). We present the results of Fukui functions and condensed local softness for the most nucleophilic atom present in the cluster using ESP techniques, as shown in Table II. The results show that both in terms of Fukui functions and

TABLE IV. Condensed local softness for all the constituent atoms except the benzene ring present in NBMs. M$=$CH$_3$.

| Atom | $s_x$ | | | | | | | |
|------|-------|--------|-------|-------|-------|-------|--------|--------|
|      | $p$-OCOM | $m$-OCOM | $p$-COM | $m$-COM | $p$-CN | $m$-CN | $p$-COOM | $m$-COOM |
| O | 0.131 | 0.106 | 0.147 | 0.172 | 0.245 | 0.201 | 0.253 | 0.171 |
| N | 0.177 | 0.174 | 0.255 | 0.259 | 0.339 | 0.316 | 0.224 | 0.209 |
| O | 0.155 | 0.125 | 0.125 | 0.188 | 0.275 | 0.188 | **0.266** | **0.231** |
| C | 0.113 | 0.020 | 0.038 | 0.110 | **1.206** | **1.200** | 0.042 | 0.042 |
| O | 0.173 | 0.168 | **0.640** | **0.526** |   |   | 0.418 | 0.446 |
| O | **0.191** | **0.244** |   |   |   |   | 0.110 | 0.085 |
| C | 0.020 | 0.193 | 0.347 | 0.284 |   |   | 0.113 | 0.062 |
| H | 0.001 | 0.061 | 0.115 | 0.053 |   |   | 0.060 | 0.018 |
| H | 0.064 | 0.043 | 0.041 | 0.070 |   |   | 0.035 | 0.033 |
| H | 0.034 | 0.037 | 0.030 | 0.070 |   |   | 0.042 | 0.018 |
| N |   |   |   |   | 0.886 | 0.891 |   |   |
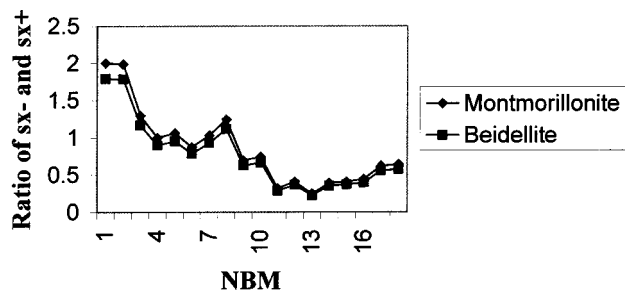
FIG. 3. Ratio of local softness values for nucleophilic H of clay clusters both hydroxyl hydrogen in montmorillonite (♦) and structural hydrogen in beidellite (■) to that of electrophilic centers of different NBM varieties is plotted against each of the interacting organic toxic molecules. The molecules are represented as follows: $p$-CNNB, $m$-CNNB, $p$-CHONB, $m$-CHONB, $p$-COCH$_3$NB, $m$-COCH$_3$NB, $p$-NH$_2$NB, $m$-NH$_2$NB, $p$-COOCH$_3$NB, $m$-COOCH$_3$NB, $p$-OCOCH$_3$NB, $m$-OCOCH$_3$NB, $p$-CF$_3$NB, $m$-CF$_3$NB, $p$-OCH$_3$NB, $m$-OCH$_3$NB, $m$-OHNB, and $p$-OHNB.

condensed local softness, the hydroxyl hydrogen attached to octahedral $Mg^{2+}$ in a clay cluster representing a montmorillonite type clay is more active in comparison to hydroxyl hydrogen attached to octahedral $Al^{3+}$ in a beidellite type of clay cluster, whereas the trend is reversed for structural hydrogen resulted from tetrahedral substitution. This can be correlated with the location of layer charge. At the same time, it is observed from the local softness values that for beidellite, the hydrogen activities are comparable with each other (structural and hydroxyl) where as for montmorillonite, the activity of structural hydroxyl is very low compared to the hydroxyl hydrogen. Now to find the match between the electrophilic centers of the organic toxic molecules to that of nucleophilic center of the clay clusters, we calculated the ratio of $s_x^+$ and $s_x^-$. The idea of relative nucleophilicity/electrophilicity has been proposed by Roy et al.[34] to predict intramolecular and intermolecular reactivity sequences of carbonyl compounds. We have used a similar ratio to find the best dioctahderal smectite for nitrogen heterocyclics adsorption.[35] This is a ratio of electrophilicity and nucleophilicity of two interacting species to choose the active center of a molecule from a range of molecules, whose local softness values are in close match. The results are shown in Fig. 3. Between the two sets of curves shown, one corresponds to the hydroxyl hydrogen present in the montmorillonite type of clay and the other one is for the structural hydroxyl present in beidellite. Now, the results show that the qualitative trend for the NBMs are same irrespective of the nature of hydroxyl hydrogen, this means that any variety of 2:1 dioctahderal smectite can be used for sorption of NBMs, but the montmorillonite type behaves better. The order of activity is as follows: $p$-CNNB>$m$-CNNB >$p$-CHONB >$m$-NH$_2$NB > $p$-COCH$_3$NB >$p$-NH$_2$NB >$m$-CHONB >$m$-COCH$_3$NB >$m$-COOCH$_3$NB>$p$-COOCH$_3$NB >$m$-OHNB >$p$-OHNB >$m$-OCH$_3$NB>$p$-OCH$_3$NB >$m$-OCOCH$_3$NB>$m$-CF$_3$NB >$p$-OCOCH$_3$NB>$p$-CF$_3$NB. The order is almost same as the order predicted from local softness values of the active centers present in NBMs with the exception in the last three molecules. Generally, the trend holds well in terms of its activities. But, here again, the monotones of the curve are not

observed and the locations seem to play a role in the activity. It is observed that apart from the top four NBMs, the rest are behaving in an ambiguous order. Similarly though qualitative, the results show that hydroxyl hydrogen present in montmorillonite may act as better sorbent for NBMs in comparison to the structural hydrogens of beidellite. This is in contradiction with our earlier studies performed for dioxin and nitrogen heterocyclics.[21,35] Beidellite should act a better sorption material over montmorillonite, as it allows the interaction to occur on the surface of beidellite. Our concern is for the situations where a strong electron-withdrawing group is present along with an electron-donating one. Hence, we feel that a methodology, which deals with the localized reactivity phenomenon of the total functional group, can resolve the issue.

### D. Reactivity descriptors in terms of group softness

Local softness is a measure of nucleophilicity or electrophilicity of a particular atom of a molecule. Here, in the case of NBMs, it seems that the activity of the group is more relevant than the activity of a single atom of the specified group. In the case of NBMs, there exists an electron-withdrawing group $-NO_2$, which influences the electronic property of the other functional groups present in the molecule at meta- or para-position locally. The reactivity of a single atom of a functional group could as well be influenced by the variations of electron density surrounding the atom. This can be handled efficiently by adding up the localized properties for the atoms of a group in molecules. Here, we define group softness according to the definition proposed by Pal et al.[25] We define the group softness $s_g$ as

$$s_g = \sum_{K=1}^{n} , \qquad (7)$$

where $n$ is the number of atoms bounded to the active atom, $s_k$ is the local softness of the atom $k$, and $s_g$ is the group softness calculated after adding over the local softness of all the neighboring atoms, For the NBMs, we calculated $s_g$ for all the constituent atoms present in the functional groups except nitro. We calculated $s_g$ for the hydroxyl group only, in case of the clay cluster. We did not consider the rest of the atoms present in the cluster not directly connected with the OH. We did not consider the nearest neighbor of the concerned functional groups both for NBMs and the clay clusters. This is due to the fact that, for NBMs, the benzene is common for all the cases and for clay except the OH, the rest of the cluster is same. This seems to be the rational choice. In local softness, individual atom centers are considered and are used for property evaluation, which can be erroneous as the atom concerned is as well, linked with atoms at its nearest neighbor. Like in case of the nitrogroup, the nitrogen with the highest local softness is the active center but the influence of neighboring oxygens is not considered in localized properties, which may result in the erroneous conclusion in terms of the reactivity of molecules. In group softness, we incorporate the neighbors by $n$, which is the number of all the atoms connected to the reactive atom and also the atoms connected to the atoms bonded to the reactive atom. The
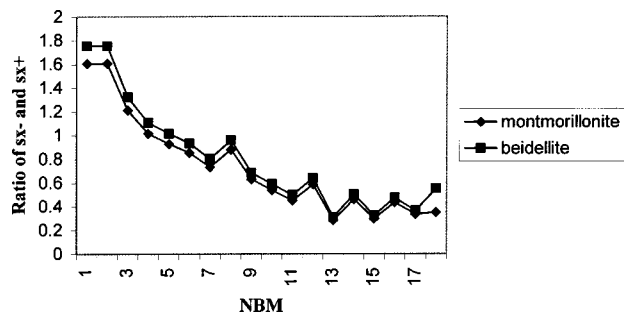
FIG. 4. Ratio of group softness values for nucleophilic OH group of clay clusters; both hydroxyl hydrogen in montmorillonite (♦) and structural hydrogen in beidellite (■) to that of electrophilic centers of different NBM varieties is plotted against each of the interacting organic toxic molecules. The molecules are represented as follows: *p*-CNNB, *m*-CNNB, *p*-CHONB, *m*-CHONB, *p*-COCH$_3$NB, *m*-COCH$_3$NB, *p*-NH$_2$NB, *m*-NH$_2$NB, *p*-COOCH$_3$NB, *m*-COOCH$_3$NB, *p*-OCOCH$_3$NB, *m*-OCOCH$_3$NB, *p*-CF$_3$NB, *m*-CF$_3$NB, *p*-OCH$_3$NB, *m*-OCH$_3$NB, *m*-OHNB, and *p*-OHNB.

formulas for interaction energy according to the local HSAB can be generalized using group softness. Thus, soft–soft interactions between two molecules can occur when the interacting groups of both molecules have a higher group softness, and hard–hard interactions are likely to occur when the interacting groups of both molecules have a lower group softness. We have tested this through interaction energy calculations as mentioned later in Sec. IV E. Then, we extrapolated the group softness to locate the intermolecular interaction through groups with similar group softness values. We have also made a relative group softness using the same principle of relative electrophilicity/nucleophilicity, earlier applied for localized parameters. The ratio of electrophilic group softness for the functional group present in the meta- or para-position of NBMs to the group softness of nucleophilic –OH (both hydroxyl and structural) present in clay cluster was calculated and the results were plotted in Fig. 4. The results show that beidellite is a better performer than montmorillonite, which matches with our earlier predictions. The curve is more consistent with few humps or glitches as observed with local reactivity descriptors for *m*-NH$_2$NB, *m*-OCOCH$_3$NB, *m*-CF$_3$NB, *m*-OCH$_3$NB, and *m*-OHNB. This can be explained in terms of the competition between nitro and these five groups. These five functional groups have a strong electron-releasing tendency, in the presence of nitro, there is a considerable change in the trend, but this influence is less pronounced in the parapositions as observed in Fig. 4. But the remaining NBMs follow a nice order in terms of their activity toward sorption over clay. The order is as follows: *p*-CNNB>*m*-CNNB>*p*-CHONB>*m*-CHONB >*p*-COCH$_3$NB>*m*-NH$_2$NB>*m*-COCH$_3$NB>*p*-NH$_2$NB >*p*-COOCH$_3$NB>*m*-OCOCH$_3$NB>*m*-COOCH$_3$NB>*m*-OHNB>*m*-CF$_3$NB>-OCOCH$_3$NB>*m*-OCH$_3$NB>*p*-OH NB>*p*-OCH$_3$NB>*p*-CF$_3$NB. This shows that the scale based on group softness is a better descriptor of the situation. Simultaneously, it can also be concluded that that the meta series can be split into two categories: one with and one without a carbonyl group directly attached to the aromatic ring and the rest.
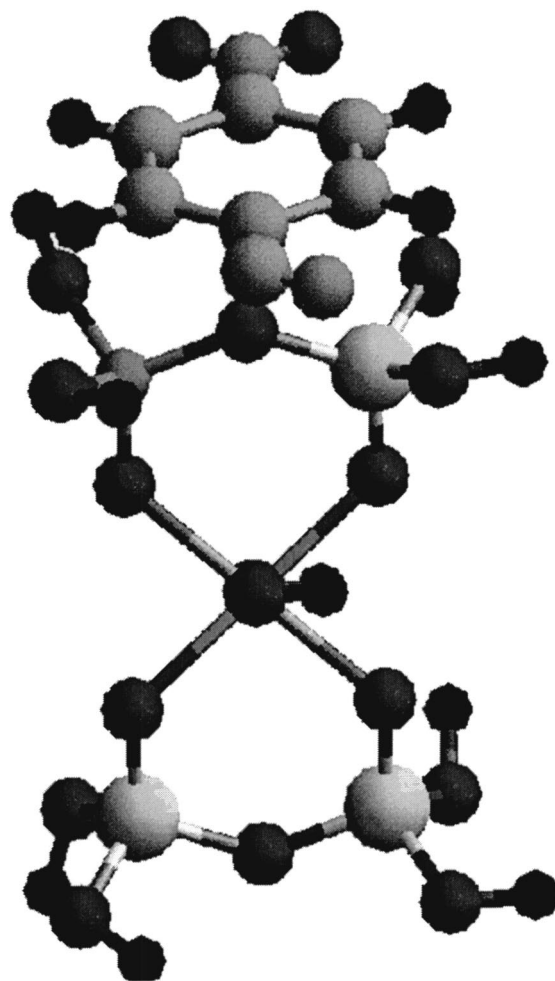


FIG. 5. Initial structure of *p*-CNNB molecule during interaction with aluminum substituted beidellite type of clay cluster. The color code is as follows: biggest gray ball (silicon); smallest gray ball (octahedral aluminum); blackish ball (oxygen); smallest black ball (hydrogen); medium size gray ball (carbon); and smaller size deep gray ball (nitrogen).

## E. Interaction energy calculation

Now, the EDA mechanism proposed[9] assumes a coplanar structure of the interacting molecule with the siloxane surface. A recent *ab initio* study by Pelmenschikov *et al.*,[36] has shown that interaction of 1,3,5-trinitrobenzene with siloxane of clay is mainly governed by a dispersion interaction. This type of interaction, being short ranged in nature, explains the stronger binding of planar nitroaromatics compared to those with branched alkyl substituents.[9] The nonplanarity hinders the maximum closeness of the molecules to the surface. They further recommended reconsideration of the EDA mechanism. We therefore wish to test the situation with a noncoplanar structure of the interacting species to (1) justify the observation of Pelmenchikov *et al.*[36] and (2) validate the proposition of group softness in terms of activity of clay surface. As the group softness calculation predicts, the beidellite will be a better material for NBM adsorption in comparison to the other variety of 2:1 dioctahedral smectite. The results are tested with the interaction energy calculation to trace the validity of the trend. We have chosen two NBMs: (1) with –CN, and (2) –COOCH$_3$ as functional groups for
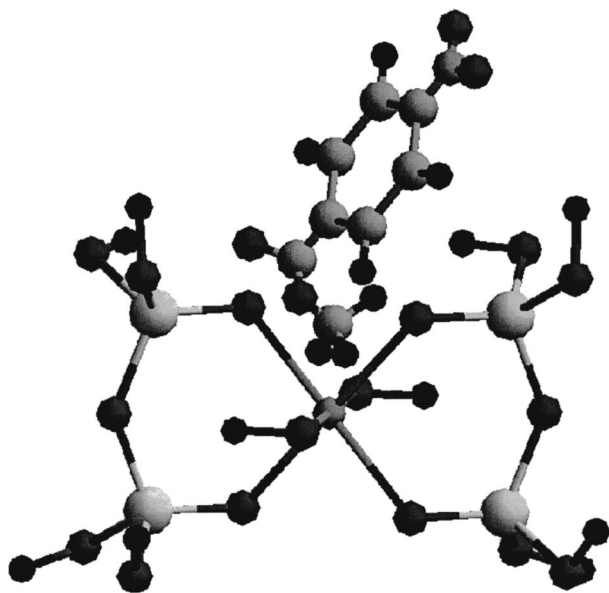
FIG. 6. Initial structure of $p$-COOCH$_3$NB molecule during interaction with montmorillonite type of clay cluster. The color code is as follows: biggest gray ball (silicon); smallest gray ball (octahedral aluminum); blackish ball (oxygen); smallest black ball (hydrogen); medium size gray ball (carbon); and smaller size deep gray ball (nitrogen).

the interaction energy calculation. The para-substituted NBMs are considered and the NBMs are placed at a distance of 2.5 Å for both the conformation on top of the structural hydroxyl of beidellite and on top of hydroxyl hydrogen of montmorillonite. The initial structure for each of the clay clusters with one of the NBMs is shown in Figs. 5 and 6. The NBMs were fully relaxed with fixed clay clusters. The inter-action energy was calculated by the difference between the energy sum for the individual free conformations before the adsorption reaction and the energy of the adsorption complex resulted from the adsorption of the molecule over the repre-sentative clay cluster. The interaction energy values for the interaction –CN with beidellite and that for montmorillonite are $-78.23$ kcal/mol and $-52.16$ kcal/mol, respectively. The energy order is same for $-$COOCH$_3$. The interaction energy for its interaction with beidellite is $-64.25$ kcal/mol and that for montmorillonite is $-40.76$ kcal/mol. The results justifi-ably show the better sorption ability of beidellite over mont-morillonite. The results also validate that coplanarity cannot be a deciding factor in NBM interaction with smectite clay surfaces.

## V. CONCLUSION

This study finds beidellite (a member of the smectite family) to be the suitable sorbent for adsorption of various meta- and para-substituted NBMs. A semiquantitative scale, in terms of group softness, for the interacting NBMs is pro-posed. The local reactivity descriptors, which have so far been established as tools to scale intermolecular interaction for the cases where softness values for electrophilic and nu-cleophilic site matches, proves to be a misnomer for the in-teraction of NBMs. Group softness seems to be a better de-scriptor for the set of molecules where interactions are more

through a functional group rather than an active center. The results show that the location of functional group in NBMs plays an important role in their reactivity. It locates the active group in smectites and validates our earlier proposition with dioxins and nitrogen heterocyclics about the superiority of beidellite over montmorillonite in terms of molecular level interaction. The scale has still a little limitation. It does not predict the situations for molecules where both electron-withdrawing and electron-releasing groups are strong and their exists a competition between them. Our work to resolve this issue is in progress. The interaction energy calculations show that the coplanarity cannot be a criterion for NBM interaction with clay. The current methodology can certainly be implemented as a better tool to account for intermolecular interactions. The relative group nucleophilicity and electro-philicity show it promises. This methodology will serve as a good indicator to choose a material for adsorption of com-plicated toxic moiety, which is becoming a concern due to the global pollution.

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