

The Effect of Saturating Cations on the Adsorption of Dasanit[®], O,O-diethyl O-[p-(methyl sulfinyl) phenyl] phosphorothioate, by Montmorillonite Suspensions¹

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ABSTRACT

A study was conducted to examine the adsorptive behavior of Dasanit in montmorillonite suspensions as affected by saturating cations and the clay suspension concentration. Adsorption isotherms, similar to Type III or Class "S" isotherms, were constructed for 10 cation-saturated montmorillonites. Infrared spectroscopy was used to examine the relative polarities of the sulfoxide, sulfone, phosphoryl, and carbonyl groups as they occur in Dasanit, in some of its oxidation products, and in several other insecticides. Despite its polar nature, Dasanit did not appear to adsorb on the interlayer surfaces of montmorillonite. X-ray diffraction data for dry Dasanit-montmorillonite systems showed a maximum interlayer expansion of 2.7Å. Kinetic data showed that the adsorption process reached equilibrium in less than 15 min. The sequence of the upper linear segments of the 10 isotherms appeared to be related to valence, atomic weight, and co-ordinating habits of the saturating cations. The Fe-montmorillonite system adsorbed the most Dasanit. At a suspension concentration of 15 mg/ml, this system removed 99% of the Dasanit from solution. The maximum adsorption value obtained for Fe-montmorillonite was 0.354 mg/mg clay at a suspension concentration of 0.25 mg/ml. This value corresponded to approximately 4.8 Dasanit monolayers on the exterior clay surface. Desorption studies indicated that those clays with the greatest adsorption capacity exhibited the least desorption tendency. The decreasing order of desorption was Na- > Ca- > Al- > Cu-montmorillonite.

Additional Index Words: X-ray diffraction, infrared spectroscopy, adsorption isotherm, sulfoxide, desorption, Fensulfothion.

NUMEROUS studies have been done to determine the role of functional groups in the adsorption of organic molecules by clay minerals. Largely as a result of improved infrared spectroscopic techniques, the interactions between clay minerals and most functional groups have been elucidated (3, 4, 19, 35). However, little attention has been focused on interactions of the sulfoxide group in soil. Olejnik et al. (36) found that dimethyl sulfoxide intercalated into kaolin, increasing the basal spacing $d(001)$ from 7.14 to approximately 11.16Å. The dimethyl sulfoxide molecules, enhanced by a small amount of water, apparently broke strong intermolecular hydrogen bonds on the interlayer surfaces of kaolin and created new hydrogen bonds with the hydroxyl surface via the sulfoxide oxygen atoms. Vivaldi et al. (45) have demonstrated that dimethyl sulfoxide vapor (60C) can penetrate the interlayer spaces of several clay minerals including kaolins, smectites, and vermiculite. Dimethyl sulfoxide initially forms a double layer in montmorillonite clay but reverts to a stable mono layer after 12 days, giving a $d(001)$ spacing of 14.2Å. There was no discussion of the nature of the dimethyl sulfoxide-clay surface interaction.

The chemistry of the sulfoxide group has been extensively studied. Much of the research has involved sulfoxide complexes with various cations, especially the transition elements (5, 6, 14, 15, 24, 42, 46). The pyramidal sulfoxide group (6, 13) is one of the more polar organic functional groups (11) and, depending on the particular cation and sulfoxide in question, forms complexes through either the sulfur or the oxygen atom. Gopalakrishnan and Patel (24) reported that Cd(II) and Hg(II) form complexes with dimethyl sulfoxide through the oxygen atom, but with diphenyl sulfoxide through the sulfur atom. Transition elements such as Mn(II), Co(II), Ni(II), Fe(II), Cu(II), and Zn(II) form complexes with the oxygen atom of most sulfoxides (5, 6, 15, 44).

The synthesis of metal-sulfoxide complexes usually requires a relatively large stabilizing anion and a dehydrating agent. Perchlorate is often used as the stabilizing anion and either 2,2-dimethoxypropane (15) or triethyl formate (43) is used to dehydrate the metal perchlorate. It is unknown whether the presence of water on the surface of montmorillonite clay, especially cation hydration water, would preclude the formation of such metal-sulfoxide complexes. Researchers have shown that alcohols can displace hydration water when competing for ligand positions around exchangeable cations (17, 32).

German and Harding (21), in their studies of alcohol adsorption by montmorillonite clay, found that the chain length of the alcohol and the saturating cation determined the shape and extent of the adsorption isotherm. Langmuir-type adsorption occurred for the miscible alcohols (chain length C_4) in Ca-montmorillonite suspensions, and the amounts adsorbed were considerably less than for the higher chain length alcohols (C_5 to C_{10}). For n-pentanol and n-hexanol, initially the amount adsorbed was small, but as the equilibrium concentration increased, adsorption increased very rapidly due to interlamellar penetration and to the formation of hydrophobic flocs. For the lower, completely miscible alcohols, changing the saturating cation from Ca to Na did not greatly influence the adsorption process. The greater adsorption of the more insoluble alcohols was ascribed to adsorption in intercrystalline porous regions in mineral aggregates.

Bissada et al. (7) showed that the number of molecules of ethanol or acetone associated with exchange cations in montmorillonite varied greatly with the cation present. Their results showed increasing association in the order $K < Na < Ba < Ca$. Potassium and Na associated with two and three molecules, respectively, or acetone or ethanol whereas Ba associated with four molecules of acetone or ethanol and Ca associated with four molecules of acetone and five molecules of ethanol.

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Parfitt and Mortland (37) and Bowman et al. (8) have demonstrated that carbonyl groups form H bonded water bridges to the exchangeable cations on interlayer surfaces of montmorillonite. Cairns et al. (11) stated that dimethyl sulfoxide is a more effective proton acceptor in H bond formation than the corresponding ketone, acetone. Thus two possibilities exist for sulfoxide-exchangeable cation interactions: (i) direct complex formation between the exchangeable cation and the sulfoxide group; and (ii) formation of a H bonded water bridge between the sulfoxide oxygen atom and the highly polarized hydration water shell surrounding the exchangeable cation.

The need for studying the behavior of sulfoxide-soil interactions has become increasingly important since the introduction of some insecticides which are sulfoxides, i.e. Dasanit. However, there are several registered insecticides which contain the sulfide linkage, thereby having the potential to oxidize to the sulfoxide in soil, i.e. phorate (O,O-diethyl S-(ethylthio) methyl phosphorodithioate), disulfoton (O,O-diethyl S-2-(ethylthio) ethyl phosphorodithioate), demeton (mixture of O,O-diethyl S-(and O)-2-(ethylthio) ethyl phosphorothioates), and carbophenothion (S-[(p-chlorophenylthio) methyl] 0,0-diethyl phosphorodithioate). Of these, phorate (1, 22) and disulfoton (34, 41) have been shown to oxidize to their respective sulfoxides in soil. Harris and Hitchon (26) have shown by bioassay techniques that disulfoton sulfoxide is highly persistent in soil.

The primary object of this investigation was to investigate the adsorption of Dasanit, a typical sulfoxide insecticide, on montmorillonite clay.

MATERIALS AND METHODS

Preparation of Clay—Montmorillonite No. 25, a Wyoming bentonite, obtained from Ward's Natural Science Establishment, Rochester, New York, was used in this study. The < 2- μ fraction, obtained by repeated sedimentation, was divided into 10 portions for saturation with the chloride salts of the following cations: H⁺, Li⁺, Na⁺, Mg²⁺, Ca²⁺, Cu²⁺, Pb²⁺, Al³⁺, Fe³⁺. One portion was left untreated. The H-montmorillonite was prepared by eluting a dilute suspension through a H-saturated cation-exchange resin column just prior to use. The other eight portions of clay were saturated three times with 1N salt solutions using the batch method, then washed five times with distilled water so that no chloride was detected with AgNO₃. Because of its limited solubility, a saturated PbCl₂ solution was used to prepare the Pb-montmorillonite suspension.

The clay-suspension concentrations were adjusted to approximately 30 mg/ml. Suspension concentrations were confirmed by pipetting duplicate 2-ml aliquots into aluminum moisture dishes and drying in an oven at 105C for at least 6 hours. The high viscosity of the H-montmorillonite suspension limited its suspension concentration to only 23.8 mg/ml.

Purification of Dasanit—Ninety-one percent technical Dasanit was purified to at least 99.8% purity (verified by GLC analysis) by successive petroleum ether extractions from a saturated aqueous solution. It was then extracted from the aqueous phase with chloroform, the chloroform evaporated with a rotary evaporator, and the product dried in a vacuum oven at 23C, 20 x 10⁻³ Torr, for several hours prior to storage.

Generation of Adsorption-Desorption Data—Fifteen milliliters of the appropriate clay suspension (approximately 30 mg/ml) and 15 ml of aqueous Dasanit solution were mixed for the adsorption isotherms. The theoretical Dasanit concentration following addition to the clay suspension, but before adsorption commenced, is referred to as the presorption concentration. Each datum point in Fig. 2 represents the average of triplicate samples.

The equilibrium shaking period was established by shaking identical samples (presorption Dasanit concentration of 200 μ g/ml) for times varying from 15 min to 16 hours, with reported shaking times including centrifugation time. When establishing adsorption times less than 0.5 hour, adsorption mixtures were placed in large test tubes and mixed on vortex mixers. It was found that centrifuging for 10 min at 43,500 x g, followed by a 2.5-min deceleration period, was sufficient to throw down the clay. For the 15-min adsorption period, this allowed approximately 0.5 min for mixing the clay and Dasanit before centrifugation and 1.0 min following centrifugation for transferring the samples. Although the equilibrium adsorption period was less than 15 min, for convenience all samples and blanks were shaken overnight for 16 hours.

The desorption data were obtained by putting the samples through the adsorption procedure including the 16-hour shaking period. The samples were then diluted with an equal volume of distilled water (30 ml) and shaken for a further 24-hour period before centrifugation and extraction. Appropriate aliquots of the supernatant solutions from both adsorption and desorption samples were extracted from Dasanit analysis with three 30-ml aliquots of distilled chloroform. The chloroform was evaporated with a rotary evaporator and samples were made to volume with a solution of 10% v/v acetone in hexane. This solvent mixture gave Dasanit recoveries of 99 \pm 1%. Therefore no corrections for Dasanit recovery were made in this study.

Dasanit was analyzed by a Varian Aerograph Hy Fi Model 600C GLC. The operating parameters were: column: Pyrex glass 91.44 cm by 2 mm ID, column packing: 5% GE XE-60 on Aeropack-30 (100/120 mesh), nitrogen pressure: 64 psig, oven temperature: 208C, detector: tritium foil electron capture.

X-ray Diffraction Analyses—X-ray diffraction slides were prepared by two different procedures:

(i) 4 ml of the appropriate clay suspension (same as used for isotherm studies) were added to 4 ml of 600- μ g/ml Dasanit solution in a 10-ml glass vial. The mixture was shaken for 16 hours and centrifuged at 1,085 x g for 40 min. The supernatant solution was discarded and 1.5 ml of distilled water were added to each vial. The clay-Dasanit mixture was resuspended, transferred to a microscope slide, and allowed to dry over anhydrous P₂O₅.

(ii) This procedure varied from the first procedure after centrifugation of the adsorption mixtures. Only 6 ml of the supernatant solution was discarded, leaving 2 ml of the equilibrium solution with which to resuspend the clay-Dasanit mixture for deposition on the microscope slide. The slides were allowed to dry over anhydrous P₂O₅.

X-ray diffraction analyses were performed with a General Electric XRD-5 diffractometer using the following operating parameters: accelerating voltage: 40 kv, current: 15 ma, radiation: Cu Ka, scanning speed: 2 $^{\circ}$ 2 θ /min. Because of rapid hydration of the montmorillonite samples during analysis, a Plexiglas cylindrical chamber was fitted over the sample holder assembly. Two slits were cut in the cylinder and covered with Mylar film to allow unobstructed beam passage. Dry nitrogen gas purged the sample chamber until constant d(001) spacings were obtained (usually 0.75 to 2 hours, depending on the saturating cation).

RESULTS AND DISCUSSION

Infrared Spectroscopy Studies

The sulfoxide group is one of the more polar functional groups. Engberts and Zuidema (18) have shown the rather large stretching frequency perturbations of the phenolic-OH group to be associated with intermolecular H bond formation with the sulfoxide oxygen atom. Using the procedure of Engberts and Zuidema (18), Table I shows the relative proton donor tendencies obtained for several sulfoxides, sulfones, and a carbonyl-containing compound (malathion). These results show the sulfoxide group to be the most polar functional group, followed in decreasing order by the phosphoryl, the sulfone and carbonyl groups, the latter two groups exhibiting similar basicities in 2 X 10⁻²M phenol.

Table 1—Intermolecular hydrogen bonding of phenol (in carbon tetrachloride) with several compounds containing carbonyl, phosphoryl, sulfone, or sulfoxide functional groups

Compound*	Proton acceptor group	$\Delta\nu_{\text{OH}}$ (cm ⁻¹) [†]
Dasanit	>S=O	-310
Dasanit sulfone	>SO ₂	-150
Dasanit O-analog sulfone	>SO ₂ , >P=O	-150, -270 [‡]
Phorate sulfoxide	>S=O	-330
Di-Syston sulfoxide	>S=O	-360
Malathion	>C=O	-150

* Solution was 2 x 10⁻²M with respect to each compound and with respect to phenol.
[†] $\Delta\nu_{\text{OH}} = \nu_{(\text{H-bonded OH})} - \nu_{\text{OH}}$ where $\nu_{\text{OH}} = 3,610 \text{ cm}^{-1}$
[‡] $\Delta\nu_{\text{OH}} = 270 \text{ cm}^{-1}$ is the value attributed to the H-bonded P=O group

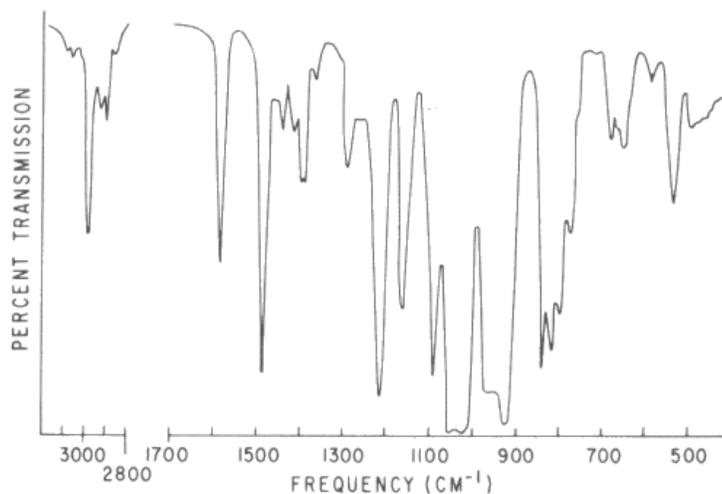


Fig. 1 -Infrared spectrum of Dasanit (capillary film between KBr plates).

In an aqueous system, the absolute proton acceptor tendencies of these groups would be different but their overall order should remain the same.

Various cation-saturated montmorillonite films were prepared as described previously (8), coated with Dasanit, and scanned from 4000 to 400 cm⁻¹ on a Beckman IR-20A infrared spectrophotometer. There was little change in the spectrum of adsorbed Dasanit. The absorption band at 1213 cm⁻¹ in pure Dasanit (Fig. 1) increased by 7 to 9 cm⁻¹ in the moist Fe- and Al- montmorillonite systems, suggesting that some interaction had occurred. No positive assignment of this band has been made, although it is believed to be associated with the oxygen-phenyl ring vibrations. The sulfoxide stretching band which occurs near 1050 cm⁻¹ was masked by the Si-O stretching vibrations of the clay. If the sulfoxide stretching band had been observable, perturbations due to hydrogen bonding could not have been properly interpreted because of coupling between the sulfoxide stretching vibrations and those of the adjacent CH₃ group (15). Thus, from infrared spectra, no conclusions can be made regarding hydrogen bond formation between the sulfoxide oxygen and the hydrated cations.

The second possibility for sulfoxide interaction is direct complex formation between the metallic cation and the sulfoxide oxygen atom. Berney and Weber (6), in their infrared studies of sulfoxide complexes with transitional metallic cations, observed a strong absorption band in the 400 to 550-cm⁻¹ region of the spectrum. They assigned this band to the stretching vibration of the metal-oxygen bond of the sulfoxide complex. The Dasanit-coated montmorillonite films were scanned through this region to determine if such a band existed. Unfortunately, two intense clay adsorption bands masked much of this region. There was no sign of shoulder band formation or changes in the intensity of existing bands after Dasanit application. As noted in the introduction, it might be necessary to completely dehydrate the montmorillonite-Dasanit system before any direct cation-sulfoxide complex could be expected to form. The temperature required to achieve complete surface dehydration of the clay would probably degrade the Dasanit, producing questionable results.

Although the properties of the sulfoxide group would suggest penetration and interaction with the interlayer surfaces of montmorillonite, only slight perturbation of Dasanit's 1213-cm⁻¹ band observed in the Fe- and Al-systems. Infrared spectroscopic evidence was insufficient to reach any conclusions regarding bonding mechanisms of Dasanit on montmorillonite.

Rate of Adsorption Studies—The time required for the adsorption process to reach equilibrium was less than 15 min, including centrifugation time, for all montmorillonite-Dasanit systems studied. If adsorption of Dasanit occurs primarily on interlayer surfaces of montmorillonite, this equilibrium time seems somewhat short in comparison with other results in the literature. Huang and Liao (29) showed DDT and heptachlor adsorption onto montmorillonite to be a two-stage process, with almost instantaneous adsorption onto the exterior surfaces accompanied by a gradual adsorption onto the interior surfaces requiring approximately 1 hour to reach equilibrium. However, dieldrin reached maximum adsorption in 5 to 10 min, followed by slight desorption during the next hour. They found that DDT and heptachlor were adsorbed in greater amounts than dieldrin and concluded that orientation of initially adsorbed dieldrin molecules created physical hindrances preventing further molecular diffusion into the interlayer spaces. However, Bailey (2) disagrees, contending that with such low levels of dieldrin adsorption, sufficient distance exists between the high-energy edge adsorption sites that peripheral edge blocking would not occur and that dieldrin has the opportunity to diffuse into the interlamellar region. Yaron et al. (48) reported that aldrin adsorption reached equilibrium on a Wyoming montmorillonite in only 5 min. Their adsorption isotherm for the aldrin-montmorillonite system can be superimposed on that of the aldrin-kaolinite system. This data suggests that aldrin adsorbed only on the exterior surfaces of montmorillonite which accounted for the short equilibrium time. The short equilibrium adsorption times observed in the present study indicates that, as with aldrin and dieldrin, Dasanit was adsorbed only on the exterior surfaces of montmorillonite clay, irrespective of the saturating cation.

X-ray Diffraction Studies — Table 2 shows the d(001) spacings and Δ , the clearance space between structural sheets of montmorillonite, for the various treatments. These results were obtained using the first procedure outlined in the Materials and Methods section where the supernatant equilibrium solution was discarded after centrifugation and the Dasanit-clay mixture was resuspended in distilled water. Since some Dasanit could have desorbed under these conditions, a second set of slides was prepared

Table 2 - d(001) spacing of the various montmorillonite systems with and without adsorbed Dasanit under dry and moist conditions. Data obtained using method of complete replacement of equilibrium adsorption solution by distilled water [method (I)]

Cation	With Dasanit				Clay only			
	Dry *		Moist †		Dry *		Moist †	
	d(001)	$\Delta \ddagger$	d(001)	$\Delta \ddagger$	d(001)	$\Delta \ddagger$	d(001)	$\Delta \ddagger$
Mont §	10.64	1.0	11.62	2.0	10.64	1.0	11.18	1.6
Na-M	10.52	0.9	11.40	1.8	10.52	0.9	11.11	1.5
Li-M	11.94	2.3	12.52	2.9	11.62	2.0	12.27	2.7
Ca-M	12.18	2.6	15.31	5.7	11.94	2.3	15.23	5.6
Mg-M	12.27	2.7	14.97	5.4	12.27	2.7	14.97	5.4
Al-M	12.27	2.7	14.72	5.1	11.86	2.3	14.02	4.4
H-M	11.78	2.2	14.72	5.1	11.55	2.0	13.80	4.2
Pb-M	11.94	2.3	12.71	3.1	11.32	1.7	12.52	2.9
Cu-M	12.02	2.4	12.62	3.0	12.02	2.4	12.44	2.8
Fe-M	11.94	2.3	13.28	3.7	11.69	2.1	12.90	3.3

* Slides purged with dry nitrogen gas until d(001) spacings were constant (0.75 to 2-hours).

† Slides equilibrated at 40% relative humidity.

‡ $\Delta = d(001) \text{Å} - 9.6 \text{Å}$; the "clearance" space between structural sheets.

where sufficient supernatant equilibrium solution was retained for resuspension. The Δ values obtained by the second method were equal to or less than those values shown in Table 2. It is immediately apparent that there was no interlayer adsorption of Dasanit in the dry untreated, natural-montmorillonite and Na-montmorillonite systems. The Δ values for the remainder of the dry systems, with adsorbed Dasanit, range from 2.2 Å (H-montmorillonite) to 2.7 Å (Mg-, Al-montmorillonites). These values are equal to or slightly exceed the A values for the dry clay without Dasanit.

A stereomodel structure of Dasanit suggested that the maximum thickness of the molecule was in the order of 2.0 Å. Grim (25) stated that the van der Waals thickness of a methyl group is 4 Å, a somewhat larger figure. In their studies, Brindley and Hoffmann (9) have observed that the c-axis dimension of organic complexes in parallel orientation in interlayer spaces was 0.4 to 0.8 Å less than the sum of the van der Waals cross section of the organic molecules plus the thickness of the montmorillonite layer. They showed that this appreciable contraction occurred as a result of keying of the molecules into the surface structure. One must conclude from these results that the Δ value for interlayer methyl groups could not be much less than $4 - 0.8 = 3.2 \text{Å}$. Since the Dasanit molecule has a methyl group and two ethyl groups, it appears very improbable that there was any interlayer adsorption of Dasanit, based on the maximum observed value of 2.7 Å for the dry Mg- and Al-montmorillonite systems. Although this conclusion is in agreement with that for the adsorption rate data, it does seem surprising in view of the substantial polarity of the sulfoxide group and the large adsorption capacity for Dasanit by montmorillonite. Perhaps Dasanit quickly forms a stable hydrate in the presence of water molecules, creating an entity whose effective size is much larger, thereby preventing its entry into the interlayer spaces of the clay.

Olejnik et al. (36) found that a water content of 9% v/v was most favorable for kaolin intercalation by dimethyl sulfoxide. In the present study, an Fe-montmorillonite X-ray slide which had been equilibrated over P_2O_5 was coated with Dasanit, then scanned from 5° to $10^\circ 2\theta$. The d(001) spacing before and after Dasanit application remained constant, indicating no Dasanit penetration into the interlayer spaces. The slide was then exposed to a free water surface for 5 min and then re-scanned, but the d(001) spacing did not appreciably increase. It would appear that the surface film of Dasanit blocked the entry of water molecules to the interlayer region of the clay. Vivaldi et al. (45), in their study of DMSO-montmorillonite complexes, heated DMSO to at least 60°C to obtain vapor adsorption by the clay. At this temperature there would be a minimal amount of free water on the clay to compete with DMSO adsorption. This was not the situation in the present study for Dasanit adsorption in aqueous clay suspensions. They give no information regarding the possibility of DMSO adsorption by montmorillonite in an aqueous environment.

Another possible explanation for the X-ray results of Table 2 is that the Dasanit molecules migrated from the interlayer region to the exterior surfaces of the clay while drying the X-ray slides which resulted in small Δ values. As the drying process proceeded, the mass flow of water molecules to the exterior surfaces could transport the Dasanit molecules with them. In addition to this mass flow process, an additional driving force for molecular migration would be created by the drier exterior surfaces which would favor Dasanit adsorption. This migration of Dasanit would be partially opposed by interlayer surface attractive forces, specifically the cations. The magnitude of these forces would vary for the various clay saturations as indicated by the sequence of adsorption isotherms of Fig. 2, with the Fe-clay providing the greatest attraction and the Na and untreated, natural clays, the least. Although the small Δ values of Table 2 are consistent with the hypothesis of interlayer Dasanit migration, these results cannot be used to confirm its existence since it is not known whether Dasanit initially entered the interlayer spaces when the clay was highly hydrated while in suspension.

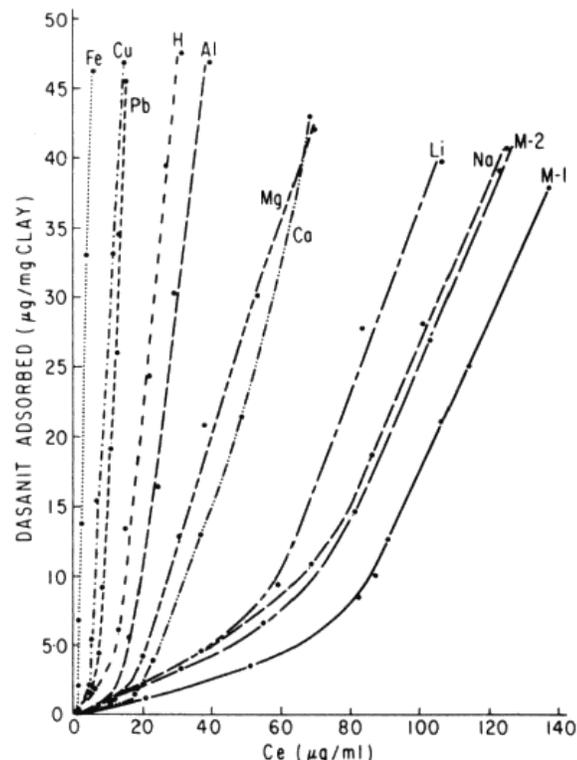


Fig. 2- Equilibrium adsorption isotherms for Dasanit on montmorillonite clay saturated with various cations. —1 refers to the untreated, natural montmorillonite; —2, the same clay suspension 10 months later.

Adsorption-Desorption Studies—Equilibrium adsorption isotherms for Dasanit on the various cation-saturated montmorillonite systems (Fig. 2) are similar to the Type III isotherm of Brunauer et al. (10) for the Van der Waals adsorption of gases by solids, or to the Class "S" isotherm as defined by Giles et al. (23). One example of a Type III adsorption isotherm was reported by Reyerson and Cameron (39) for bromine vapor adsorption onto silica gel. Similar isotherms for water adsorption by porous carbon (16) and protein adsorption by silica gel (33) have also been reported.

There are several features of the Dasanit isotherms distinct from either Type III or Class "S" isotherms: (i) There are two distinctly separate regions of each isotherm a curvilinear segment at lower equilibrium concentrations followed by a linear segment at higher concentrations. The extent of the curvilinear lower segment and the slope of the upper linear segment are related to the nature of the saturating cation; (ii) If the equilibrium concentrations in Fig. 2 (C_e) are converted to relative saturated concentrations (C_e/C_o) by dividing C_e by the maximum water solubility of Dasanit (1910 $\mu\text{g/ml}$ at 23C, as determined in this laboratory), most of the isotherms shown lie entirely below $C_e/C_o = 0.073$ ($C_e = 140 \mu\text{g/ml}$). With most Type III isotherms involving physical adsorption of gases on solids, the steep segment of the isotherm occurs as the relative pressure, P/P_o , approaches unity. The transposition of the Dasanit isotherms towards the ordinate axis suggests strong physical adsorption energies approaching those for chemisorption. In the case of the Fe-montmorillonite system, the removal of Dasanit from solution was about 99% complete over the concentration range studied, resulting in an isotherm similar to that for a positively charged molecule (23, 47), which is a chemisorption process.

The nature of Dasanit isotherms at equilibrium concentrations greater than those shown in Fig. 2 is not well established. Because of the limited water solubility of Dasanit, the upper practical working limit of the presorption concentration was near 750 $\mu\text{g/ml}$. The upper datum point shown in each isotherm in Fig. 2 was established using a presorption Dasanit concentration near 700 $\mu\text{g/ml}$. An attempt to extend the isotherms was made by adding 30 ml of Dasanit solution directly to 450 mg of freeze-dried montmorillonite. Adsorption values obtained were up to 25% larger than would be expected by mixing equal volumes of clay suspension and Dasanit solution as in Fig. 2, and produced a linear isotherm up to a presorption concentration of 1,500 $\mu\text{g/ml}$. The presence of presorbed water molecules decreased clay adsorption capacity for Dasanit from that obtained when Dasanit and water molecules were simultaneously added to dry clay.

Perhaps the most interesting aspect of these isotherms is the dramatic effect that various saturating cations have on both shape and position of the isotherms. With the exception of the Pb and H isotherms, the sequence of the isotherms, i.e. relative positions of the linear segments, can be approximated by considering the magnitude of the product of the valence and atomic weight of the saturating cations (Table 3). The H-montmorillonite was probably a H/Al system and consequently the H isotherm reflects this fact by its proximity to the Al isotherm. There is no apparent explanation for the position of the Pb isotherm, other than Pb is the only Group IV element whereas the remainder of the cations are either transition elements or alkali earth metals. This technique also reverses the sequence of the Na and Li isotherms and places the Ca isotherm considerably above the Mg isotherm, instead of an almost identical position, as in Fig. 2. Probably a third factor such as the nature of the hydration water shell of these cations must also be considered in predicting this sequence. Weed and Weber (47) and Peterson et al. (38) have related the adsorption of organic cations on micas and vermiculites, respectively, to the nature of the water structures associated with the saturating cations, Ca and Mg.

It is of interest to compare the isotherms M1 and M2 for the untreated, natural clay. The only known difference between these isotherms is that the clay in M2 had aged in suspension for about 10 months following the

generation of the M1 isotherm, resulting in an apparent increase in adsorption capacity. During the aging process, some aluminum would be released from the crystal lattice of the clay into solution (31), a portion of which would migrate to exchange positions on the clay surface. The presence of aluminum on the exchange complex, as shown by the Al-montmorillonite isotherm, would increase the adsorption capacity for Dasanit, thereby accounting for the increased Dasanit adsorption of M2 over M1.

Figure 3 shows the effect of the Dasanit/clay ratio on the extent of Dasanit adsorption. The total amount of clay was varied from 15 mg/ml (20 μg Dasanit added/mg clay) to approximately 0.25 mg/ml (1,200 μg Dasanit added/mg clay). Optimum Dasanit adsorption occurred at clay suspension concentrations less than 0.30 mg/ml, or at Dasanit/clay ratios exceeding 1,000 μg added/mg clay. The maximum adsorption value shown for the Fe-montmorillonite is 354 $\mu\text{g/mg}$ clay, or 35.4% by weight. This large adsorption value is more characteristic of protein adsorption by clays (28) or adsorption by organic adsorbents (40). However, German and Harding (21) have shown that montmorillonite exhibits a very high adsorption capacity for immiscible alcohols ($>C_4$) and a moderate adsorption capacity for alcohols with chain lengths $<C_4$. All isotherms in Fig. 2 were constructed using a clay suspension concentration of approximately 30 mg/ml (15 mg/ml after dilution with an equal volume of Dasanit solution) except for the H-montmorillonite. This suspension was so viscous that it was impossible to exceed 23.8 mg/ml.

Table 3 — The sequence of the isotherms as predicted by the product of valence and atomic weight of the saturating cation

Cation	Valence	Atomic weight	Product	Predicted sequence	Observed sequence
Fe	3+	55.8	167.4	1	1
Cu	2+	63.5	127.0	2	2
Pb *	2+	207.2	414.4		
H †	1+	1.0	1.0		
Al	3+	26.9	80.7	3	3
Mg	2+	24.3	48.6	5	4
Ca	2+	40.1	80.2	4	4
Li	1+	6.9	6.9	7	5
Na	1	23.0	23.0	6	6

* Pb (II) is in Group IV A, whereas the other cations are either transition elements or alkali earth metals.

† H-montmorillonite is probably H/Al-montmorillonite.

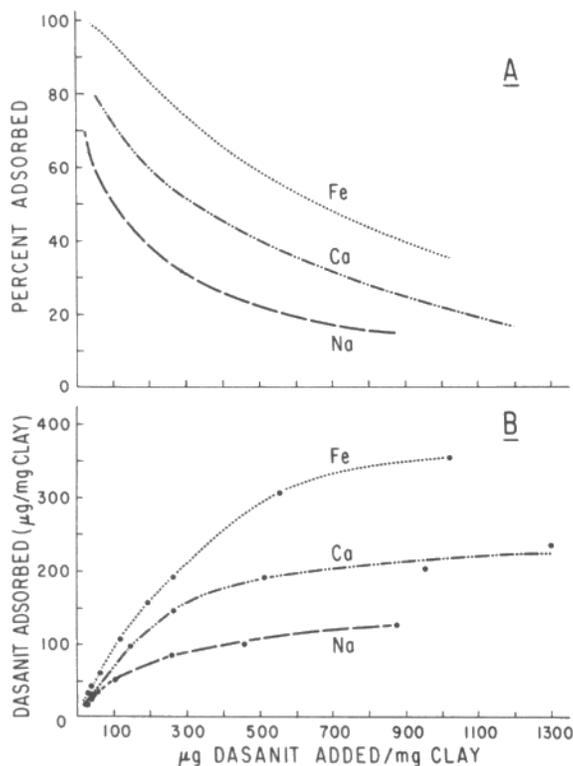


Fig. 3 — Dasanit adsorption on Fe-, Ca-, and Na-montmorillonite as a function of Dasanit/clay ratio. Presorption Dasanit concentrations = 9000 µg (constant); total volume = 30 ml (constant). The curves in Fig. 3A were drawn from the curves best fitting the data points in Fig. 3B.

to accommodate four Dasanit molecules, disregarding the effects of steric hindrances.

The great variation in the position and shape of the adsorption isotherms in Fig. 2 is attributable to several factors:

(i) The nature of the cation-Dasanit interaction—Farmer and Mortland (20), in their studies of pyridine adsorption by montmorillonite, and Bowman et al. (8), in their studies of malathion adsorption by montmorillonite, have demonstrated that at high moisture contents H bonding with the cation hydration water was favored, and only at low moisture conditions did direct complex formation with cations occur. Unless the sulfoxide group of Dasanit replaced cation hydration water, it is improbable that a direct complex between Dasanit and the cations occurred in the clay suspension. It is probable that a H bonded water bridge formed between the sulfoxide group and the exchangeable cation. Over the concentration range studied there was no cation-Dasanit complex of fixed molar ratio. However, this might be expected since the highest adsorption point on the Fe isotherm (Fig. 2) gave a molar ratio of only 2.31 whereas theoretical calculations suggest a maximum ratio of approximately 4 (for monolayer coverage).

The question arises as to whether Dasanit can protonate in an aqueous clay suspension. Indeed the proximity of the Fe isotherm to the adsorption axis bears a definite similarity to an exchange isotherm for a cation (23, 47). However, the fact that the slopes of the isotherms gradually decrease from the Fe- to the Na-montmorillonite systems suggests that the adsorption mechanism is the same for all the systems, but with a gradation of adsorption energies from Fe- to Na-montmorillonite. The shape and position of the lower valence (Ca, Mg, Li, Na) isotherms are not indicative of protonated species adsorption. There appears to be no positive evidence that Dasanit existed as a protonated species in this study.

(ii) The effect of the saturating cation on the aggregation state of the clay—German and Harding (21) found that the degree of flocculation of the clay suspension was controlled by the exchangeable cation. Sodium tended to disperse the clay particles whereas Ca flocculated them. They pointed out that flocculated systems contain intercrystalline porous regions, and that in Ca-clay, the particles are arranged such that water can be trapped in voids between them. These regions become potential sources of space where adsorbate may be concentrated due to phase separation. They showed that addition of Na ions to an equilibrated Ca-montmorillonite-n-heptanol complex dispersed the hydrophobic flocs, releasing heptanol to the bulk solution. Perhaps the substantial differences in adsorption capacity of the untreated natural, Na, and Li systems from the other systems in Fig. 2 can be partially attributed to flocculation effects.

(iii) The effect of the limited water solubility of Dasanit—German and Harding (21) observed that the water solubility of alcohols had an important effect upon their adsorption by montmorillonite. When the solubility limit was exceeded, the isotherm changed from

Thus in comparing the H-montmorillonite isotherm with the Al-montmorillonite isotherm, the greater efficiency of adsorption by the lower suspension concentration of H-clay must be taken into consideration. This would position the H-isotherm closer to the Al-isotherm for equal suspension concentrations which is to be expected since H-clays revert to H-Al systems.

Total surface area determinations of the 10 cation-saturated montmorillonites, using the method of Carter et al. (12), gave values ranging from 680 m²/g for Cu-clay to 845 m²/g for Na-clay, the differences being ascribed mainly to the cations themselves. According to Grim (25), the external surface area of montmorillonite is only 15—20% of the total surface area. The average total surface area of the 10 montmorillonite systems studied was 735 m²/g, and thus the external surface area was estimated to be near 130 m²/g. Using the value of 90 Å²/Dasanit molecule, as suggested by a stereomodel, the value of 354 µg adsorbed/mg Fe-clay (Fig. 3) gives a surface area occupied by Dasanit to be 622 m²/g clay which is equivalent to 4.8 monolayers of Dasanit on the external surface of the montmorillonite. One monolayer of adsorbed Dasanit on the external surface would correspond to 73.7 µg/mg clay. Thus there was less than one Dasanit mono-layer adsorbed on the exterior surface of all montmorillonite systems in the isotherms of Fig. 2.

The CEC of the montmorillonite was determined to be 99 meq/ 100 g. This value corresponds to 1.98 X 10²⁰ trivalent cations/g clay. Using the maximum observed adsorption value of Dasanit (Fig. 3) of 354 µg/mg Fe-clay, the Dasanit / Fe(III) molar ratio was 3.49. If Dasanit adsorbed only on the exterior clay surface, then this molar ratio would increase to 17.5, since approximately 20% of the CEC occurs on the exterior clay surface (25). The highest Dasanit / Fe(III) molar ratio for external surface adsorption observed in the Fe-isotherm of Fig. 2 was 2.31. The average surface area associated with each Fe(III) ion was calculated to be 735 / 1.98 = 372 Å², a sufficient area

the Langmuir type to the S-type, and the adsorption capacity dramatically increased. Dasanit is partially miscible with water and its behavior is probably analogous to n-pentanol or n-hexanol adsorption on montmorillonite (21).

The curvilinear lower segment of the isotherms may be ascribed to competitive effects of Dasanit molecules attempting to displace presorbed water molecules. As a result of intermolecular attractive forces, each adsorbed Dasanit molecule facilitates the adsorption of succeeding Dasanit molecules. The extent of this lower segment is an expression of the influence of the saturating cations upon the relative competitiveness of Dasanit molecules and surface adsorbed water molecules. At equilibrium concentrations above the bend in each isotherm, a constant partitioning of Dasanit occurs between solid and liquid phases producing a linear segment whose slope is strongly influenced by the saturating cation. Kipling (30) has stated that the extent of adsorption increases as the solubility limit is approached, and appears to become asymptotic to a line parallel to the adsorption axis. MacRitchie (33) ascribed a similar rapid increase in Bovine Serum Albumin adsorption on hydrophobic silica to interfacial coagulation, analogous to capillary condensation in gas adsorption.

Figure 4 shows the percent desorption of Dasanit for several montmorillonite systems as a function of presorption concentration. The desorption data were obtained by diluting the equilibrium adsorption mixtures with an equal volume of distilled water (30 ml) rather than replacing the equilibrium supernatant solution with distilled water. This approach more closely parallels the situation in natural aqueous environments where desorption usually occurs by dilution rather than by complete replacement of the equilibrium solution. The sequence of the four curves is the same as observed in Fig. 2 for the adsorption isotherms. Those clays showing the greatest adsorption capacity exhibited the least desorption (on a percentage basis). This data suggests that the differences in Dasanit adsorption capacity were largely due to differences in adsorption energies of the various cation-clay systems.

There was a negligible amount of conversion of Dasanit to its sulfone in any part of this study. Since the recoveries of Dasanit were always close to 100%, there also was no significant hydrolysis. In contrast to the rapid conversion of Dasanit to its sulfone in soil, under field conditions and in the laboratory (27), montmorillonite clay appears to retard this process in aqueous systems.

CONCLUSIONS

The present study of the adsorptive behavior of Dasanit in montmorillonite suspensions has demonstrated the following facts:

- (i) Dasanit, although possessing a polar sulfoxide group, does not appear to adsorb on the interlayer surfaces of montmorillonite. Consequently it is rapidly removed from aqueous solution by montmorillonite, reaching equilibrium in less than 15 min.
- (ii) Dasanit exhibits an adsorption isotherm similar to Type III or Class S isotherms where there appears to be no maximum adsorption value up to presorption concentrations approaching its water solubility.
- (iii) There appear to be three major factors which determine the adsorption capacity of the various montmorillonite systems and the nature of their isotherms: the nature of the cation-Dasanit interaction, the effect of the saturating cation on the aggregation state of the clay suspension, and the effect of the limited water solubility of Dasanit. There are indications that the bonding mechanism may involve a H bonded water bridge between the sulfoxide oxygen of Dasanit and the exchangeable cation.
- (iv) The saturating cation also affects the desorption tendencies of Dasanit in montmorillonite suspension. There appears to be an inverse relationship between the adsorption capacity and the desorption tendencies of the various systems studied. Further desorption studies and the movement studies of Dasanit in clay and soil systems are warranted.

An important practical implication emerging from this study involves the effect of iron content of soil on Dasanit bioactivity. A bioassay study has been undertaken involving Dasanit bioactivity in a mineral soil treated with FeCl_3 . Preliminary results have shown the bioactivity of Dasanit to be significantly reduced by the presence of iron in the soil.

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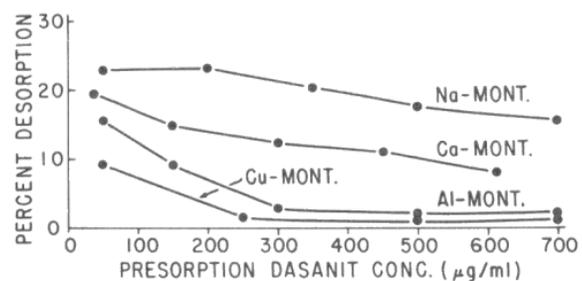


Fig. 4 — Percent desorption of Dasanit from various cation-saturated montmorillonite suspensions as a function of pre-sorption concentration.

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