

MOLECULAR STRUCTURE AND pH EFFECTS ON THE ADSORPTION OF 13 *s*-TRIAZINE COMPOUNDS ON MONTMORILLONITE CLAY

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ABSTRACT

The adsorption of 13 related *s*-triazine compounds on montmorillonite clay as influenced by pH and molecular structure was investigated. Adsorption isotherms for prometone on montmorillonite were determined at six pH levels. The maximum adsorption of all the compounds on montmorillonite was found to occur at a pH in the vicinity of the pK_A value of each compound. Substituent groups on the triazine ring were found to be related to the amount of adsorption which resulted. Mechanisms of adsorption were postulated and discussed.

INTRODUCTION

A number of investigators have determined that triazine compounds are adsorbed on montmorillonite clay. Factors such as pH (Frissel, 1961; Harris and Warren, 1964), salt concentration (Frissel, 1961), temperature (Harris and Warren, 1964; Weber *et al.*, 1965) and time of exposure (Weber, *et al.*, 1965) have been found to affect the amount of adsorption which takes place.

This paper concerns the effects of pH and molecular structure of 13 triazines on the adsorption of these compounds on montmorillonite clay. The main objective was to gain information on the mechanism or mechanisms of adsorption and to determine if the amount of adsorption of the compounds was related to chemical properties and/or molecular structures of the compounds.

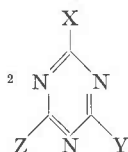
EXPERIMENTAL

Properties of organic compounds and clay. Analytical grade chemicals, supplied by the Geigy Chemical Corporation, were used. Chemical properties, names and structures of the compounds used are given in Table 1. All of the compounds behave as weak bases in aqueous solution. The compounds in order of basicity (the larger the pK_A values, the more basic) are hydroxy > methoxy > methylthio > chloro. The types of amino groups also appear to have an effect on basicity of the triazine compounds. For this series of compounds, the larger the amino groups, the more basic the compound; *i.e.*, tetraetatone > ipatone > trietatone > prometone > atratone > desmetone = simetone. The solubility in water data available on the compounds are not complete, but the following statements are made on the data available in Table 1. The chloro compounds are generally less soluble than the other compounds and, at least

TABLE 1. CHEMICAL PROPERTIES OF 13 *s*-TRIAZINE COMPOUNDS

No.	Common name ¹	Groups on triazine ring ²			Solu- bility ³ %	pK _A ⁴	U.V. absorption maximum
		X	Y	Z			mμ
1.	Desmetone*	OCH ₃	NHCH ₃	NHC ₃ H ₇	0.3500	4.15	217
2.	Simetone	OCH ₃	NHC ₂ H ₅	NHC ₃ H ₅	0.3200	4.15	217
3.	Atratone	OCH ₃	NHC ₂ H ₅	NHC ₃ H ₇	0.1800	4.20	217
4.	Prometone	OCH ₃	NHC ₃ H ₇	NHC ₃ H ₇	0.0750	4.28	218
5.	Triatone*	OCH ₃	NHC ₂ H ₅	N-(C ₂ H ₅) ₂	0.0040	4.51	223
6.	Ipatone	OCH ₃	NHC ₃ H ₇ ⁵	N-(C ₂ H ₅) ₂	0.0100	4.54	223
7.	Tetraatone*	OCH ₃	N-(C ₂ H ₅) ₂	N-(C ₂ H ₅) ₂	—	4.76	230
8.	Prometryne	SCH ₃	NHC ₃ H ₇	NHC ₃ H ₇	0.0048	4.05	222
9.	Ipatryne*	SCH ₃	NHC ₃ H ₇	N-(C ₂ H ₅) ₂	—	4.43	230
10.	Propazine	Cl	NHC ₃ H ₇	NHC ₃ H ₇	0.0009	1.85	222
11.	Ipazine	Cl	NHC ₃ H ₇	N-(C ₂ H ₅) ₂	0.0040	1.85	228
12.	Hydroxypropazine	OH ⁶	NHC ₃ H ₇	NHC ₃ H ₇	—	5.20	221
						~11.0	
13.	Hydroxyipazine	OH ⁶	NHC ₃ H ₇	N-(C ₂ H ₅) ₂	—	5.32	224
						~11.0	

¹ Names of asterisked compounds were designated by the author.



² Solubility data from manufacturer.

⁴ Determined by spectrophotometric titration according to methods of Dixon, Woodberry and Costa (1947) and Hirt, Schmidt, Strauss and Koren (1961).

⁵ In all cases, C₃H₇ is in the iso form.

⁶ These compounds probably exist in the keto form rather than the enol form.

for the methoxy compounds, it appears that the larger the amino groups, the less soluble the compound. Prometone is used as a postemergence, nonselective herbicide around industrial sites and noncropped areas. Prometryne and propazine are used to control weeds in cotton and sorghum, respectively. The remaining compounds are not presently available commercially.

Procedures. SPV Volclay bentonite (montmorillonite) from Wyoming¹ was dispersed in deionized water and the 0.2–2 μ fraction separated. The

¹ Supplied by the American Colloid Company, Chicago, Illinois.

suspension of bentonite was centrifuged to obtain thick pastes which were lyophilized (freeze-dried) to a dry state, mixed and stored in sealed glass containers. The C.E.C. (cation exchange capacity) of 0.847 me per gram was determined using Na as the saturating cation. A Beckman D.U. flame photometer was employed in determining the amount of Na in the solutions.

Clay samples of 2.50 mg were weighed into 250-ml glass beakers, deionized water added and the suspensions were thoroughly mixed. A stock solution of each *s*-triazine was added to each of the clay suspensions to give a total volume of 100 ml. Triazine concentrations, amounts of clay used and exposure times are included in the figures. The suspensions were stirred at room temperature for one hour, the pH was then measured and a portion of each was centrifuged to allow the clear supernatant to be analyzed for the solute left in solution. After analysis each of the samples was returned to its respective beaker and the pH adjusted with HCl for the acid phase samples (pH levels, 5, 4.5, 4, 3, 2 and 1) using a Beckman Research Model pH meter. The samples were then stirred for 20 minutes. Equilibrium was found to be attained in 10–15 minutes between each pH change. A portion of each sample was again centrifuged and the solute remaining in solution determined. A similar series of samples was prepared for the alkaline phase using NaOH to adjust pH. Concentrations of acid and base used ranged from 0.01 to 11.6 M and the total amount added for either acid phase (pH values 5.0 to 1.0) or alkaline phase (pH values 7.0 to 10.0) did not exceed 2 ml. The quantity of each triazine remaining in solution was determined spectrophotometrically at the respective ultraviolet wavelength maximum for each compound (Table 1). A Beckman DK-2 recording spectrophotometer equipped with a deuterium lamp was employed according to methods outlined by Willard, Merritt and Dean (1958). Standard curves were determined for each pH level at the wavelengths given in Table 1 and the amount of solute remaining in solution was also measured at the U.V. wavelength of the isosbestic point for each compound for check purposes. The isosbestic point is the wavelength at which the molecular and protonated species of the triazine molecules have the same molar absorption coefficients. Precision of pH measurement was ± 0.02 pH units. Blanks, clay plus acid or base and *s*-triazine standards were included with each run and reproducibility was within $\pm 4\%$. Duplicate samples were included at random and each experiment was run twice.

Spectrophotometric determinations of ionization constants (pK_A values) for the triazines were made according to the methods of Dixon, Woodbury and Costa (1947) and Hirt, Schmidt, Strauss and Koren (1961).

For studies employing extracting solutions, Na and prometone in the supernatant were determined as outlined above. Successive extractions of 20 ml each, exposed for 18 hours, were made on the clay samples with the following solution: deionized water, 0.1 M BaCl₂, and 0.01 N NaOH.

RESULTS

Effects of molecular structure and pH on adsorption. Previous investigations showed that prometone was readily adsorbed on montmorillonite clay at pH 6.0 in a 0.025 M Na phosphate buffer system (Weber *et al.*, 1965). Figure 1 contains an adsorption isotherm taken from this study. The curve represents the average values for isotherms made at 10° and 55° C.

Adsorption isotherms describing the adsorption of prometone on montmorillonite clay at several pH levels are given in Fig. 1. The lowest adsorption of prometone occurred at pH 8.5–9.5, which was the unadjusted series of samples.

In the systems where the dilute prometone and smaller clay samples were used (Fig. 2), the unadjusted samples had pH values of 6.2, as compared to the more concentrated systems where the pH ranged from 8.5 to 9.2. The higher pH resulted primarily from the larger amounts of montmorillonite clay used in the suspensions, and only slightly from the effects of the higher concentrations of prometone used. The clay adsorbed

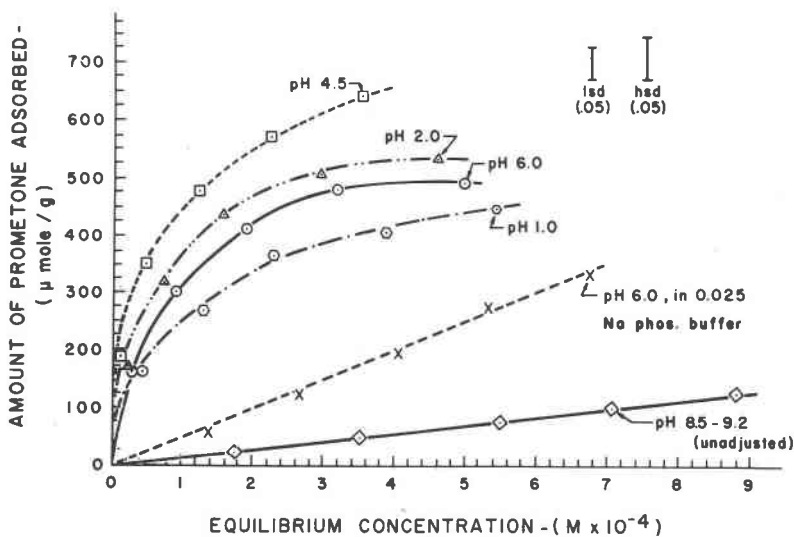


FIG. 1. Adsorption isotherms for prometone on montmorillonite clay at five pH levels (prometone concentrations of 0, 2, 4, 6, 8 and 10×10^{-4} M used with 100 mg of clay and an exposure time of 20 minutes for each pH change)

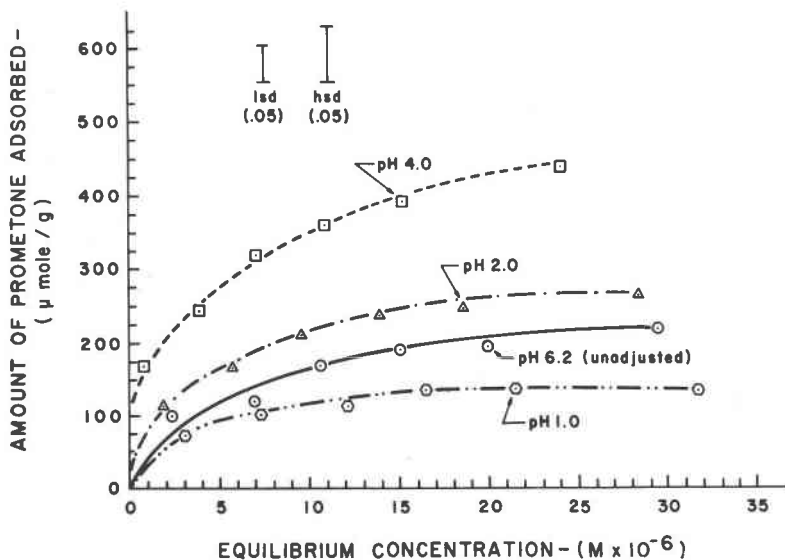


FIG. 2. Adsorption isotherms for prometone on montmorillonite clay at four pH levels (prometone concentrations of 0, 5, 10, 15, 20, 25 and 35×10^{-6} M used with 2.5 mg of clay and an exposure time of 20 minutes for each pH change)

proportionately more prometone per gram, at the same pH, in the concentrated system as compared to the dilute system (*i.e.*, for pH 2.0 at a concentration of 10×10^{-4} M added, compare 550 μ mole per gram adsorbed in the concentrated system as compared with 250 μ mole per gram adsorbed in the dilute system where 1/40 as much prometone and clay were used). Changes in pH had a greater effect on the amount of prometone adsorbed in the dilute system than in the more concentrated system.

Similar adsorption isotherms were obtained for propazine, prometryne and hydroxypropazine which indicated the same adsorption mechanisms were probably involved for all of the compounds.

Adsorption studies were performed using a constant amount of prometone and varying clay sample sizes. Adsorption isotherms similar to those of Figs. 1 and 3 were obtained.

The influence of pH on the adsorption of the *s*-triazine compounds by montmorillonite clay was very similar for all compounds (Fig. 3-5). The amount of each compound adsorbed increased as the pH of the solution was lowered, until an adsorption maximum was reached. Lowering the pH still further resulted in releasing a portion of each of the compounds into solution. The maximum adsorption of each compound by the montmorillonite clay occurred in the vicinity of the pK_A value of the particular compound. The seven methoxy compounds and the two methylthio

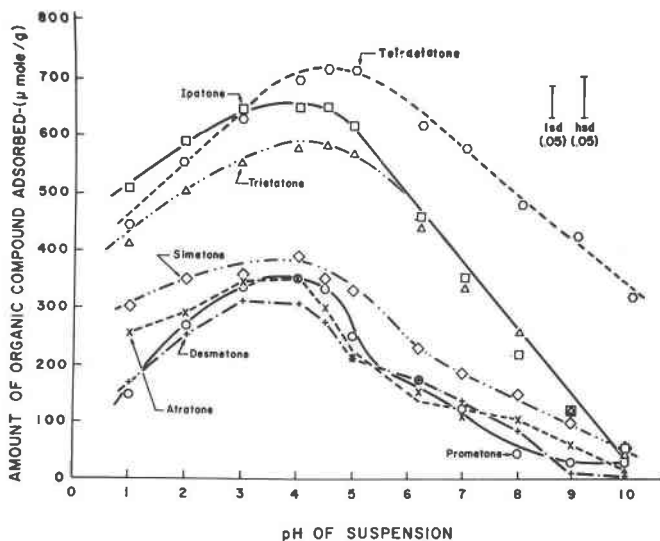


FIG. 3. Effect of pH on the adsorption of seven methoxy-*s*-triazines on montmorillonite clay (concentrations of $25 \times 10^{-6} \text{ M}$ of each compound were used with 2.5 mg of clay and 20 minutes exposure time between each pH change)

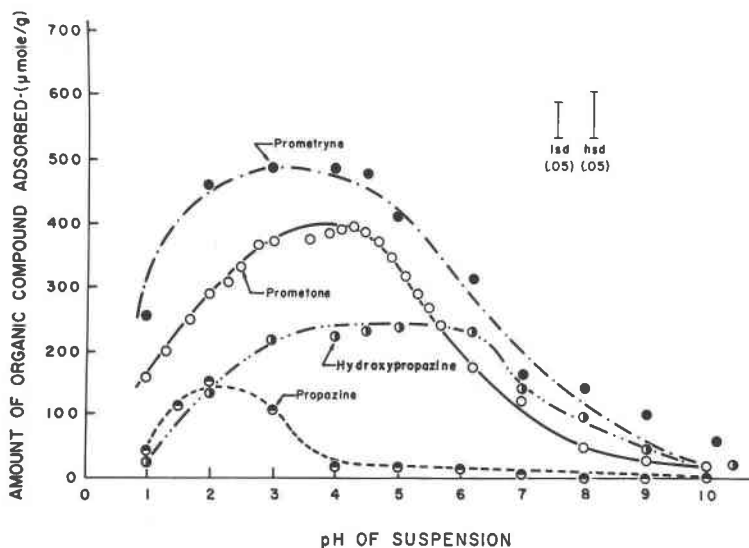


FIG. 4. Effect of pH on the adsorption of four related *s*-triazines [4,6-bis(isopropyl-amino) series] on montmorillonite clay (concentration of $25 \times 10^{-6} \text{ M}$ of each compound was used with 2.5 mg of clay and 20 minutes exposure time between each pH change)

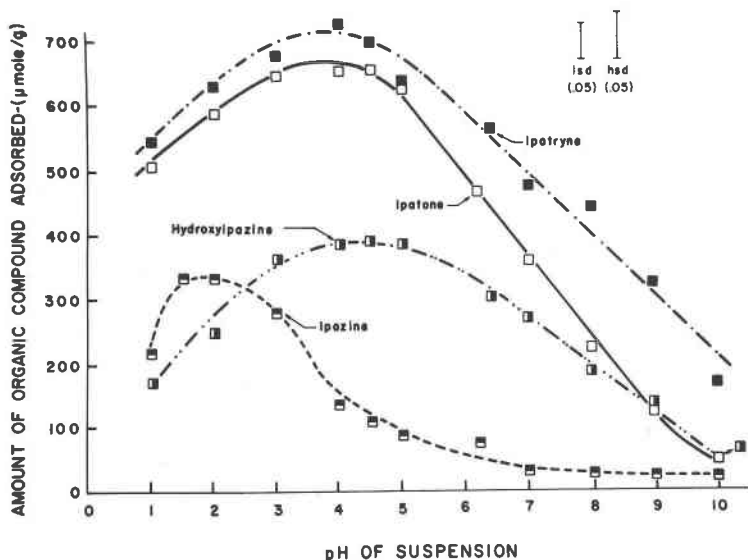


FIG. 5. Effect of pH on the adsorption of four related *s*-triazines (4-isopropylamino-6-diethylamino series) on montmorillonite clay (concentration of 25×10^{-6} M of each compound was used with 2.5 mg of clay and 20 minutes exposure time between each pH change)

compounds, with pK_A values ranging from 4.05 to 4.76, reached a maximum adsorption at pH 4.0–4.5, while the chlorinated compounds, with pK_A values of 1.85, reached a maximum adsorption at pH 2.0, and the hydroxy compounds, with pK_A values 5.20 and 5.32, reached the maximum adsorption at pH 5.0–6.0 (Table 1, Fig. 3–5).

Figure 3 contains the effect of pH on the adsorption of seven methoxy-*s*-triazines on montmorillonite. The compounds differed in molecular structure in the 4 and 6 positions (Table 1). The adsorption isotherms are grouped into two different patterns. Tetraetaton, ipatone and trietaton, represented by the upper three curves, were adsorbed in much greater amounts than simetone, atratone, prometone and desmetone, represented by the lower four curves. The compounds in the three upper curves have dialkylamino groups in the 4 and 6 positions, while the compounds in the lower curves have only one alkyl group in each of the 4 and 6 positions. It appears that the greater the number of alkyl groups in favor of H on the N atoms in the 4 and 6 positions, the greater the compound is adsorbed by the clay.

Table 1 shows that the substitution of an alkyl group for a H atom in the 4 or 6 positions increases the basicity, pK_A value, of the methoxy-*s*-triazine compounds. The order of decreasing adsorption and pK_A value,

at pH 4.0, is as follows:

Compound:	tetraetone>	ipatone>	trietatone>>	simetone=
pK _A value:	4.76	4.54	4.51	4.15
	atratone=prometone=desmetone			
	4.20	4.28	4.15	

Figure 4 illustrates the effects of pH on the adsorption on montmorillonite of four similar *s*-triazines which differ in molecular structure in the 2 position only; *i.e.*, the 4,6-isopropylamino series. A comparison of the maximum amount of each compound adsorbed on the montmorillonite shows prometryne>prometone>hydroxypropazine>propazine.

Figure 5 contains the effects of pH on similar series of compounds which differ in 2 positions; *i.e.*, the 4-isopropylamino-6-diethylamino series. A comparison of the maximum amounts of each compound adsorbed on the montmorillonite shows ipatryne>ipatone>hydroxyipazine>ipazine. It is concluded from these two series of compounds (Figs. 4, 5) that the compounds with methylthiol ($-\text{SCH}_3$) groups in the 2 position are adsorbed in greater amounts than comparable compounds with methoxyl ($-\text{OCH}_3$), hydroxyl ($-\text{OH}$) and chloro ($-\text{Cl}$) groups, respectively.

Effects of pH and sodium on prometone adsorption. An adsorption study was performed to determine the effect of pH on the adsorption of prometone and the displacement of Na on montmorillonite clay. Table 2 shows the increase of Na which occurred in the solutions containing prometone. The increase in Na displaced by prometone amounted to 18.1 and 24.6 μmoles at pH levels of 4.0 and 6.0, respectively. At the other pH levels considerably lesser amounts of Na were displaced. When the clay samples were extracted with deionized water, slightly larger amounts of Na were removed from the samples which had not been subjected to prometone. Extraction of the clay samples with 0.1 M BaCl_2 removed considerable amounts of Na from the clay samples which had not been subjected to prometone and only small amounts of Na from the prometone-clay systems, with the exception of the pH 8.5 prometone-clay system. The total amount of Na displaced from all of the clay samples was very similar. The results indicate that at pH levels where prometone was present in the protonated form, it exchanged for Na on the clay surface. At very low pH levels, H effectively replaced the Na on the clays in both the prometone and no prometone systems. The 0.1 M BaCl_2 effectively replaced the remaining Na not replaced by either prometone or H. In the pH 8.5 systems neither the molecular prometone nor deionized water replaced Na from the montmorillonite clay. The 0.1 M BaCl_2 effectively removed Na from the clay in these systems.

TABLE 2. EFFECT OF pH ON THE ADSORPTION OF PROMETONE AND THE DISPLACEMENT OF SODIUM AND THE EFFECT OF SEVERAL EXTRACTING SOLUTIONS ON DISPLACING SODIUM FROM 100 mg SAMPLES OF MONTMORILLONITE CLAY

pH of solution	Amount of prometone adsorbed ¹	Amount of Na in solution	Diff. in Na	Amount of Na displaced from mont. ²				Total Na displaced
				With H ₂ O ₂	Diff.	With 0.1 M BaCl ₂	Diff.	
1.0	0	39.3		0.2		0.2		39.7
1.0	45.0	40.6	1.3	0.2	0.0	0.2	0.0	41.0
2.0	0	40.6		0.3		1.3		42.2
2.0	59.5	41.5	0.9	0.2	0.1	0.2	1.1	41.9
4.0	0	24.9		1.4		11.8		38.1
4.0	70.0	43.0	18.1	0.3	1.1	0.3	11.5	43.6
6.0	0	14.1		2.8		21.2		38.1
6.0	53.2	38.7	24.6	1.1	1.7	2.0	19.8	41.8
8.5	0	8.0		4.4		26.0		38.4
8.5	14.5	14.1	6.1	3.0	1.4	22.3	3.7	39.4
	Std. error =	0.5		0.3		0.3		
	lsd (.05) =	1.4		0.8		0.8		
	hsd (.05) =	2.0		1.2		1.2		

¹ In all cases 100 μ moles of prometone were added to the 100-ml solutions.

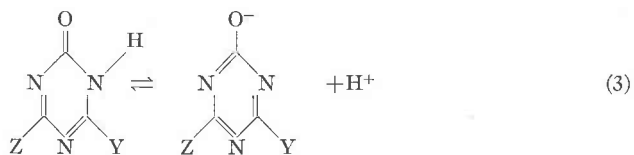
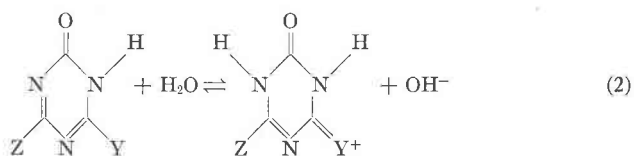
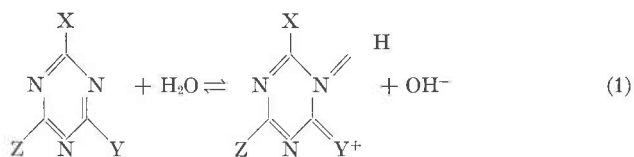
² Successive extractions of 20 ml each exposed for 18 hours.

Effects of several extracting solutions on displacing adsorbed prometone. The amount of prometone removed by the various extraction solutions was also determined for the prometone-clay systems. Table 3 shows the amount of prometone displaced from the montmorillonite clay by the various extracting solutions. Deionized water removed 25.5% of the prometone from the montmorillonite clay system at pH 8.5. Lesser amounts were removed from the clay at lower pH levels. The 0.1 M BaCl₂ removed considerably more prometone from the pH 2.0 and 4.0 clay systems, but the percentage removed was very similar for all samples. The 0.01 N NaOH removed the largest amounts of prometone from the clay samples of any of the extracting solutions. The largest amount of prometone was removed from the pH 4.0 level clay system, but the per cent prometone removed from the clay was very high for all samples. The total prometone extracted from the montmorillonite clay by the vari-

ous extracting solutions ranged from 63.6 to 92.1%. The amount removed increased with the increase in pH of the prometone-clay system.

DISCUSSION

Adsorption mechanisms. It has been deduced, from recent investigation by Boitsov, Finkel'shtein and Petukov (1962), that the methoxy-, methylthio- and chloro-*s*-triazine compounds became protonated according to equation (1), while the hydroxy compounds probably associated according to equation (2) and dissociated according to equation (3).



The pK_A values are given in Table 1 and are utilized in this paper, rather than pK_B values because of the relationship of pH and pK_A .

It was postulated in previous studies (Weber *et al.*, 1965) that prometone present primarily in the molecular form at pH 6.0 was adsorbed by montmorillonite by H-bonding or through polar adsorption forces. This molecular adsorption is depicted in equation (4) below.

Preliminary studies further showed that the adsorption of prometone increased with a decrease in pH and it was postulated that this resulted from the protonation of prometone according to equation (5) and the adsorption of the monovalent prometone cation according to equation (6). The pK_B of equation (5) is 9.72 (14–4.28) as written, but pK_A is used in the discussion since it is directly comparable to pH. The increased adsorption at lower pH levels as illustrated in Figures 1 through 3 confirms the higher adsorption of the protonated prometone. The phenomena of reaching an adsorption maxima at approximately the pK_A value and then decreasing at lower pH levels has previously been attributed to competition by H. Equation (7) was thus included to illustrate that

TABLE 3. EFFECT OF SEVERAL EXTRACTING SOLUTIONS ON REMOVING PROMETONE ADSORBED ON 100 MG SAMPLES OF MONTMORILLONITE CLAY AT FIVE pH LEVELS

pH of solution at adsorption	Amount of prometone adsorbed ¹	Amount of prometone extracted from mont. ²						Total prometone extracted	
		With H ₂ O		With 0.1 M BaCl ₂		With .01 N NaOH			
		μmole	%	μmole	%	μmole	%	μmole	%
1.0	45.0	0.52	1.1	9.10	20.2	19.05	42.3	28.67	63.6
2.0	59.5	0.76	1.3	12.45	20.9	28.40	47.7	41.61	69.9
4.0	70.0	2.12	3.0	13.31	19.0	39.70	56.7	55.13	78.7
6.0	53.2	4.22	7.9	9.27	17.4	31.00	58.3	44.49	83.6
8.5 (unadj.)	14.5	3.70	25.5	3.00	20.7	6.65	45.9	13.35	92.1
Std. error =	1.2	0.10		0.10		0.10			
lsd (.05) =	3.5	0.25		0.25		0.25			
hsd (.05) =	5.2	0.50		0.50		0.50			

¹ In all cases 100 μmoles of prometone were added to the 100-ml solutions.

² Successive extractions of 20 ml each, exposed for 18 hours.

relatively high concentrations of H⁺ ions may compete with the prometone cations for sites on the clay. Similar results were obtained by McLaren *et al.* (1958) while studying the adsorption of proteins on montmorillonite. These workers attributed the low adsorption of proteins by montmorillonite at low pH to competition by H for sites on the clay surfaces.

Recent adsorption studies employing freshly prepared H(Al)-montmorillonite showed no significant change in the solution pH upon addition of prometone. Large amounts of prometone were adsorbed by the clay, however. This shows that prometone can associate with H which is bound to the clay surface. When organic cations were employed in the same manner as prometone, a large decrease in pH resulted, indicating that the organic cations had exchanged for H on the clay surface. Because of these studies, equation (8) has been included to illustrate that prometone may be adsorbed on the clay by direct association with H on the clay surface. The association of prometone and H at the clay interface is undoubtedly more complex than these preliminary studies reveal, however.

The presence of other ions in the prometone-clay systems has an effect on the amount of prometone adsorbed. This is illustrated in comparing the adsorption isotherms of Fig. 1 at pH 6.0. In the presence of 0.025 M Na phosphate buffer, less prometone was adsorbed than was the case at pH 6.0 in the absence of the buffer. Table 2 indicates that more Na was

displaced from the montmorillonite clay in the prometone-clay system as opposed to the clay solutions containing no prometone. Table 3 illustrates that 0.1 M BaCl₂ and 0.01 N NaOH were very effective in displacing adsorbed prometone on the montmorillonite clay. It is postulated that BaCl₂ displaced prometone primarily through cation exchange of protonated prometone by Ba²⁺ ions. The displacement of prometone from montmorillonite by NaOH was probably a combination of converting the protonated prometone to the molecular form by the higher pH, hence making it less tightly adsorbed, and also replacement of protonated prometone by the Na⁺ ions.

Equation (9) has been added to illustrate that cations other than H⁺ may compete with the prometone cations for sites on the clay.



where: P=molecular prometone, Na-M and H-M represent sodium- and hydrogen-montmorillonite clay, respectively; HP⁺=protonated prometone; P-(Na-M) = prometone physically bound to montmorillonite; and (Cation)ⁿ⁺=cations other than H⁺, such as Ba²⁺, Na⁺, etc., with valence "n."

The amount of prometone adsorbed at each pH level is determined by the equilibrium constants of all reactions involved. Since all of the triazine compounds used in these studies exhibited similar adsorption effects, it seems probable that the adsorption mechanism for all these compounds on montmorillonite was similar.

The possibility of the organic compounds forming bonds with Al³⁺ and/or Al hydrous oxides in or associated with the clay lattice is not included in this discussion.

Molecular structural effects on adsorption. The greater adsorption exhibited by the methoxy-*s*-triazine compounds containing dialkylamino groups in the 4 and 6 positions as compared to those containing only one alkyl group in each of the 4 and 6 positions is probably a composite of two factors. Replacement of an alkyl group for a H atom in the 4 or 6 positions results in an increase in basicity. This is probably because of the lower electronegative character of the alkyl groups as compared with hydrogen. The more basic compounds are probably adsorbed in greater amounts because a larger portion of the molecules are in the protonated form at each pH level. In addition to the higher basicity of the compounds with dialkylamino groups in the 4 and 6 positions, there is the

possibility that the larger molecular size and/or greater number of possible binding sites of these compounds adds to their greater adsorption on montmorillonite clay. Work by Finkel'shtein and Boitsov (1962) indicates that the *s*-triazine ring N atoms carry a partial negative charge and the X, Y and Z groups retain partial positive charges. The adsorption of the molecular species of the *s*-triazine compounds may therefore be through a H- or dipole-ionic bond with the O in the silicate lattice of the clay.

The effect of basicity and molecular structure of the *s*-triazine compounds on their adsorption by montmorillonite clay is evident in comparing the results of Figs. 4 and 5. For both series the order of decreased adsorption for comparative compounds differing only in the 2 position was: $-\text{SCH}_3 > -\text{OCH}_3 > -\text{OH} > -\text{Cl}$. The large differences in the amount of adsorption of the various compounds on montmorillonite cannot be accounted for in terms of basicity alone since the hydroxy compounds, which have the largest pK_A values, are adsorbed less than the methoxy and methylthio compounds. All of the compounds are adsorbed as cations at pH levels in the vicinity of their respective pK_A values. The bonding is probably through positive charges on the 4 and 6 positions illustrated in reactions 2 and 3. Other forces are probably also contributing to the adsorption. Adsorption of the molecular species of these compounds is probably by bonding of the partial positively charged 2, 4 and 6 groups to the negatively charged O in the silicate lattice of the clay. The methylthio-*s*-triazines are adsorbed in greater amounts than the methoxy compounds possibly because of the larger atomic size of S in relation to O, which may allow for better orientation on the silicate surface. Molecular species of the hydroxy compounds are probably adsorbed through partial positive charges at the 4 and 6 positions only, since the carboxyl O in the 2 position would normally retain a slight negative charge. Molecular adsorption of the chloro compounds was not significant in the case of propazine, and the small amount which occurred for ipazine probably also took place through partial positive charges on the 4 and 6 positions only. All of the 4-isopropylamino-6-diethylamino compounds were adsorbed in greater amounts than the respective 4,6-isopropylamino compounds, indicating again that the compounds with more alkylamino groups are adsorbed stronger than compounds with less alkylamino groups.

SUMMARY AND CONCLUSIONS

These studies showed that the adsorption of each of the 13 *s*-triazine compounds on montmorillonite clay increased with a decrease in pH to approximately the vicinity of the respective pK_A values for each compound. A further lowering of the pH resulted in some desorption of each

of the adsorbed *s*-triazine compounds. Sodium ions were found to be displaced by prometone at pH levels where prometone was in the protonated form. BaCl₂ and NaOH solutions were found to displace large amounts of prometone depending on the pH of prometone-clay system. Adsorption of prometone by montmorillonite clay was attributed to molecular adsorption at high pH and a combination of coulombic (cation exchange) forces and direct association with H on the clay surface at low pH. A combination of these adsorption mechanisms was postulated to have occurred at all pH levels.

The *s*-triazine compounds with dialkylamino groups in the 4 and 6 positions were found to be adsorbed in larger amounts on montmorillonite than compounds with monoalkylamino groups in these positions. The methylthio-*s*-triazine compounds were adsorbed in greater amounts by montmorillonite than were the methoxy-, hydroxy- and chloro-*s*-triazine compounds, respectively. The amount of each compound which adsorbed on the montmorillonite clay depended on the pH at which the compound became protonated; *i.e.*, the pK_A value, and on the molecular structure of the compound.

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