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Adsorption of Oxamyl and Dimecron in Montmorillonite Suspensions[1]

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ABSTRACT

Adsorption of oxamyl and phosphamidon (Dimecron) was determined from dilute solutions of montmorillonite saturated with different cations, e.g., Li^+, Na^+, K^+, Cs^+, Fe^{3+}, and Al^{3+}. Adsorption of oxamyl was found to be greater than adsorption of Dimecron. The shapes of the isotherms depended on the exchangeable cations. The adsorption varied directly with the polarizing power of the exchangeable cation and inversely with changes in temperature, organic matter, and ionic strength up to 0.6, after which it became constant. The enthalpy changes (ΔH°) calculated from the temperature coefficient of the equilibrium constant showed that the process is exothermic. The adsorption of pesticides on montmorillonite gives rise to an entropy loss that is higher for trivalent cations. Various studies, e.g., infrared (IR) and x-ray, as well as thermodynamic parameters and Freundlich adsorption isotherms, revealed the existence of protonation or coordination (or both) between exchangeable cations of clay and oxygen of > C=0 group of the pesticides. However, desorption studies showed the presence of physical adsorption.

Additional Index Words: phosphamidon, adsorption isotherm, organic matter, pesticide adsorption.

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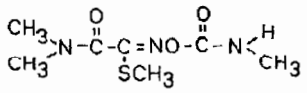
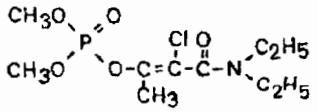
SOIL ADSORPTION AND RETENTION of pesticides have been shown to be influenced by pH, organic matter, clay content (17, 15), and, to a lesser degree, concentration of ions present in solution, temperature, and type of exchangeable cations present on clay surfaces (8).

The subject of clay-pesticide interaction has been extensively reviewed by Bailey and White (2) and Mortland (24). An organic chemical may be bound to the clay surface by strong ion dipole attraction (4), hydrogen bonding (19), coordination (26), ion exchange, protonation, and hemisalt formation (32). Clay minerals constitute one of the most important reactive surfaces of soil. Clay minerals have been found to possess reactive sites at the edges, corners, interlayers, and interlattice positions (20, 30).

Oxamyl [[methyl-2-(dimethylamine)-*N*-[(methylamino) carbonyl] oxy]-2-oxoethanimidothioate]], a formulation of DuPont deNemours and Co. (DuPont 1410 Nematicide), is a broad-spectrum nonionic pesticide suitable for the effective control of nematodes and other plant pests in soils and is used as a foliar spray (33, 14).



Dimecron {*O*[2-chloro-2-(diethylcarbamoyl)-1-methyl-vinyl] *O,O*-dimethyl phosphate}, a commercial formulation of phosphamidon registered by CIBA-Geigy Ltd., Basle, Switzerland, is used as a nematicide.



The purpose of this experiment was to determine the influence of temperature, organic matter, solution ionic strength, and exchangeable cations on the nature of the adsorption and desorption isotherms of oxamyl and Dimecron on Akli bentonite.

MATERIALS AND METHOD

Through treatment with 1*N* NaCl, a < 2-μ fraction of montmorillonite (bentonite sample from Akli in Rajasthan, India, member of the group beidellites) was purified by sedimentation and centrifugation and converted into Cl^--free Na-saturated clay using the Aldrich and Buchanan method (1). Homoionic suspensions of Li-, K-, Cs-, Fe-, and Al-montmorillonite were obtained from the Na form by the ion exchange technique. The pH of the suspensions was between 6.2 and 6.4. The concentrations of the suspensions varied from 15.5 to 13.6 g/L. The cation exchange capacity (CEC) of the clay determined by the Ganguli method was 720 μeq/g of clay (11). The total surface area determined by the Carter et al. method (7) was 690, 685, 675, 660, 645, and 640 m^2/g for the Na-, Li-, K-, Cs-, Fe-, and Al-montmorillonites, respectively.

Adsorption experiments were conducted using 10 mL of the appropriate montmorillonite suspension in a large number of glass-stoppered tubes, adding various amounts of standard oxamyl or Dimecron solution (0–15 mL of 5,000 μg/mL of oxamyl and 7,500 μg/mL of Dimecron), and making up the volume to 25 mL with distilled water. The suspensions were shaken for 30 h in a constant-temperature water bath at 15 ± 0.5, 25 ± 0.5, and 35 ± 0.5°C. Preliminary kinetic measurements indicated that equilibrium was reached in < 27 h. Removal from the water bath was followed by centrifugation for 15 min at 1 500 × *g*, with the samples being kept at the same temperature as during the experiment and the supernatants estimated spectrophotometrically at 435 nm as copper-dithiocarbamate (27), Dimecron by modified method of oxamyl. The amount of pesticide adsorbed was obtained from the amount added minus that remaining in the supernatants.

The influence of the solution ionic strength was determined by equilibrating 15 mL of pesticide solution (5,000 μg/mL of oxamyl and 7,500 μg/mL of Dimecron), which was initially prepared in appropriate salt solutions of different electrolytes ranging from 0.00166 to 3*N* with 10 mL of the appropriate clay suspension at 25 ± 0.5°C. The amount of oxamyl adsorbed was calculated as cited above.

Adsorption in the presence of organic matter was investigated in another set of experiments by adding 50 or 100 mg of humic acid to each of the montmorillonite suspensions used for adsorption.

In the desorption experiments, 10 mL of oxamyl- or Dimecron-complexed clay suspensions were treated with water and 1 mL of 0.1*M* KCl or 0.05*M* $BaCl_2$, respectively. The volume was adjusted to 25 mL with distilled water and the samples shaken for 33 h. The oxamyl or Dimecron in solution was estimated as cited above.

All the experiments were conducted in duplicate with suitable reagent and clay blanks.

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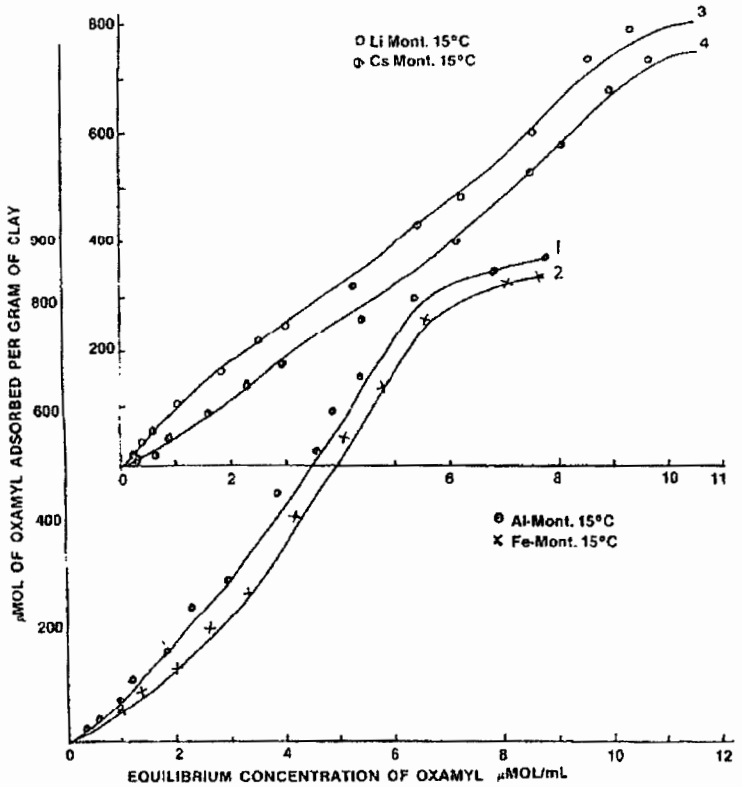


Fig. 1—Adsorption isotherms of oxamyl adsorption on montmorillonites.

X-ray and IR analyses of different cation-saturated clays and their complexed samples were performed as described elsewhere (28).

RESULTS AND DISCUSSION

The empirical Freundlich relationship can be used to describe the oxamyl or Dimecron adsorption results on montmorillonite. The linear form of this equation is

$$\log C = \log K + (1/N)\log C_e,$$

where C is the amount (μg/g) of pesticide-adsorbed clay, C_e is the equilibrium concentration in solution (μg/mL), and K and 1/N are constants. K is the amount adsorbed for a unit equilibrium concentration of pesticide, and 1/N is a measure of intensity of adsorption reflecting the degree of linearity of adsorption. The values are given in Table 1.

The values of 1/N during oxamyl or Dimecron adsorption on Al- and Fe-saturated montmorillonites were more than unity, indicating an S type of isotherm (Fig. 1 and 2) (21). The values indicate that new sites become available to the solute as the adsorption occurs, whereas the values of the 1/N during adsorption of both pesticides on Li-, Na-, K-, and Cs-montmo-

Table 1—Freundlich adsorption isotherm constants of oxamyl and Dimecron adsorption at 15, 25, ad 35°C on montmorillonites saturated with different cations.†

Saturating cations	Oxamyl						Dimecron					
	$K \pm S$			$1/N \pm S$			$K \pm S$			$1/N \pm S$		
	15°C	25°C	35°C	15°C	25°C	35°C	15°C	25°C	35°C	15°C	25°C	35°C
Al^{3+}	601.3 (7.0)	572.2 (6.3)	541.1 (5.2)	1.320 (0.005)	1.280 (0.010)	1.200 (0.010)	542.2 (6.3)	520.0 (5.6)	501.1 (5.0)	1.200 (0.010)	1.160 (0.005)	1.130 (0.015)
Fe^{3+}	582.1 (7.1)	560.0 (6.3)	526.1 (5.1)	1.210 (0.005)	1.170 (0.005)	1.140 (0.005)	521.2 (6.2)	511.0 (5.1)	491.1 (4.9)	1.170 (0.010)	1.140 (0.002)	1.100 (0.005)
Li^{+}	575.1 (6.8)	550.2 (6.0)	516.6 (4.8)	0.820 (0.005)	0.800 (0.005)	0.780 (0.010)	511.2 (5.6)	500.9 (3.2)	483.2 (6.1)	0.810 (0.005)	0.790 (0.008)	0.775 (0.005)
Na^{+}	554.3 (6.6)	537.2 (5.3)	500.9 (4.9)	0.805 (0.005)	0.780 (0.005)	0.765 (0.005)	500.1 (3.9)	490.3 (4.3)	472.6 (6.0)	0.795 (0.003)	0.770 (0.005)	0.755 (0.003)
K^{+}	551.2 (6.3)	530.6 (5.2)	495.2 (3.2)	0.800 (0.002)	0.770 (0.010)	0.760 (0.005)	495.2 (7.2)	483.2 (2.0)	463.7 (3.9)	0.790 (0.002)	0.765 (0.002)	0.740 (0.010)
Cs^{+}	511.1 (6.2)	500.2 (3.1)	480.9 (3.0)	0.780 (0.010)	0.750 (0.010)	0.735 (0.005)	478.2 (6.0)	463.9 (3.2)	450.3 (4.1)	0.770 (0.005)	0.740 (0.010)	0.720 (0.006)

† The values in parentheses show standard error of estimate.

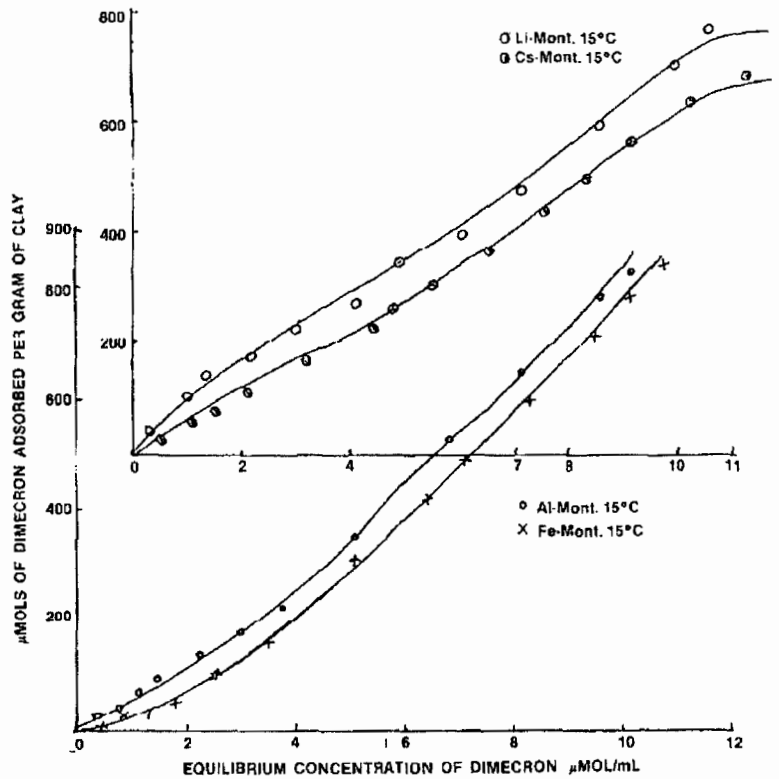


Fig. 2—Adsorption isotherms of Dimecron adsorption on montmorillonites.

rillonites were less than unity, indicating a convex, or *L* type of isotherm (Fig. 1 and 2 and Table 1) (13). This kind of isotherm may arise because of minimum competition of solvent for sites on the adsorbing surface. The slope of the isotherm steadily decreases with a rise in solute concentration, because vacant sites become less accessible with the progressive covering of the surface. The curvilinear isotherm suggests that the number of available sites for the adsorption becomes a limiting factor. Results of this type have been reported elsewhere (21). Table 1 also shows that in general oxamyl adsorption is greater than Dimecron adsorption, which is supported by the values of *K* and 1/N as well.

Adsorption of oxamyl or Dimecron follows the order (Table 1) Al-clay > Fe-clay > Li-clay > Na-clay > K-clay > Cs-clay. It indicates that the adsorption of both pesticides decreases as the polarizing power of the exchangeable cation decreases. Higher adsorption during Al- and Fe-clay suspension may be attributed to its polarizing ability by increasing the acidity of inner layer water, as suggested by Yariv et al. (35). The values of 1/N and *K* (Table 1) also supported the above inferences, and similar results have been reported by Stutzmann and Siffert (31). An increase in temperature from 15 to 35°C results in a decrease of adsorption for both pesticides, but the effect is less in Dimecron. A decrease in adsorption may be attributable to two factors: (i) a change in the energy of adsorption or weakening (or both) of van der Waal's forces of attraction between the pesticide and clay surface (16), causing a decrease in physical adsorption (31); and (ii) a change in solubility of pesticides with a change in temperature. Similar results have been reported by Farmer and Aochi (9) and Harris et al. (16).

Figures 3 and 4 show that adsorption of oxamyl or Dimecron on Al-, Fe-, Li-, Na-, K-, and Cs-montmorillonites decreases progressively as more humic acid is added. It may be caused by preferential adsorption of organic matter on clay surfaces linked through exchangeable cations on the clay and ionized carboxyl groups in humic acid (clay-M-00CR) (18).

Adsorption experiments for oxamyl or Dimecron were carried out at ionic strengths ranging from 0.005 to 1.5. The results show that adsorption of pesticides decreases as ionic strength increases up to 0.6, after which it becomes constant (Table 2). The adsorption of oxamyl or Dimecron apparently is affected more where the saturating ions are Al^{3+}, Fe^{3+}, or Li^{+} rather than Na^{+}, K^{+}, or Cs^{+}. Decreasing adsorption with increasing ionic strength (0.0–0.6) ranged from 29.0 to 30.3% for oxamyl and 28.5 to 30% for Dimecron (Table 2). Decreasing adsorption with increasing ionic strength may be caused by (i) competition of oxamyl or Dimecron with increasing amounts of cations for sites (29), (ii) decrease in activity of the pesticide in solution as the ionic strength increases (12), and (iii) formation of a nonadsorbable metal-pesticide complex in solution (28).

Desorption results (Table 3) indicate that part of the oxamyl or Dimecron adsorbed on Li-, Na-, K-, Cs-,

Table 2—Adsorption of oxamyl or Dimecron on montmorillonites saturated with different cations at several ionic strengths (of appropriate salt) at 25°C.

Ionic strength	Saturating cation	Amount of oxamyl adsorbed	Amount of Dimecron adsorbed
		μmol/g	
I = 0.000	Al^{3+}	856	811
	Fe^{3+}	839	781
	Li^{+}	822	773
	Na^{+}	790	754
	K^{+}	780	740
	Cs^{+}	752	721
I = 0.006	Al^{3+}	830	802
	Fe^{3+}	802	763
	Li^{+}	792	751
	Na^{+}	761	732
	K^{+}	742	716
	Cs^{+}	722	702
I = 0.018	Al^{3+}	800	783
	Fe^{3+}	767	750
	Li^{+}	772	726
	Na^{+}	726	703
	K^{+}	711	692
	Cs^{+}	700	681
I = 0.054	Al^{3+}	722	700
	Fe^{3+}	702	682
	Li^{+}	681	663
	Na^{+}	661	630
	K^{+}	643	625
	Cs^{+}	632	613
I = 0.09	Al^{3+}	682	659
	Fe^{3+}	671	636
	Li^{+}	652	620
	Na^{+}	633	601
	K^{+}	621	588
	Cs^{+}	610	572
I = 0.27	Al^{3+}	660	630
	Fe^{3+}	642	603
	Li^{+}	629	587
	Na^{+}	613	572
	K^{+}	600	555
	Cs^{+}	582	543
I = 0.54	Al^{3+}	602	580
	Fe^{3+}	589	562
	Li^{+}	573	551
	Na^{+}	563	541
	K^{+}	546	526
	Cs^{+}	531	506
I = 0.6, 1.2, 1.8	Al^{3+}	600	577
	Fe^{3+}	585	553
	Li^{+}	572	550
	Na^{+}	561	539
	K^{+}	545	525
	Cs^{+}	530	505

Al-, and Fe-montmorillonites can be desorbed by water or solutions of inorganic salts. The desorption was greater for oxamyl than with Dimecron. More of the pesticide was desorbed by salt solution than by the distilled water. This may be attributable to (i) a coagulation effect on dispersed solids due to a decrease in the electrical double layer at the interface solution-dispersed clay particle (34) and (ii) a flucculation effect resulting from polymer bridges between the mineral particles in suspension (6). The results of desorption (17–41%) indicate that appreciable adsorption of oxamyl or Dimecron occurs by ionic interactions at crystal edge and crystal basal surfaces.

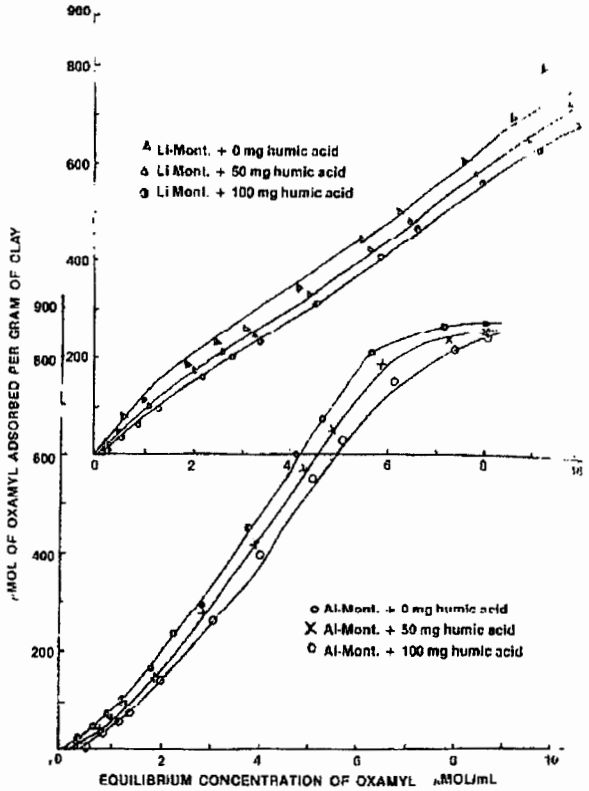


Fig. 3—Adsorption of oxamyl on montmorillonites in presence of 0, 50, and 100 mg of humic acid.

The above conclusions are also supported by thermodynamic parameters, i.e., standard free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes, with the thermodynamic equilibrium constant (K_d) calculated by the Biggar and Cheung method from the adsorption curves (5). The values are given in Table 4.

Table 3—Desorption of oxamyl or Dimecron from pesticide-clay complexes in micromoles per gram of clay by water, 0.1*M* KCl, and 0.5*M* $BaCl_2$ at 25°C.

Saturating cation	Amount of pesticide adsorbed		Amount of pesticide desorbed by water		Amount of pesticide desorbed by KCl		Amount of pesticide desorbed by $BaCl_2$	
	Oxamyl	Dimecron	Oxamyl	Dimecron	Oxamyl	Dimecron	Oxamyl	Dimecron
	μmol/g							
Al^{3+}	856	811	180	92	343	172	340	169
Fe^{3+}	839	781	164	95	330	160	336	160
Li^{+}	822	773	170	87	310	152	303	148
Na^{+}	790	754	172	82	326	143	321	139
K^{+}	780	740	160	80	302	136	308	131
Cs^{+}	752	720	152	76	296	120	290	122

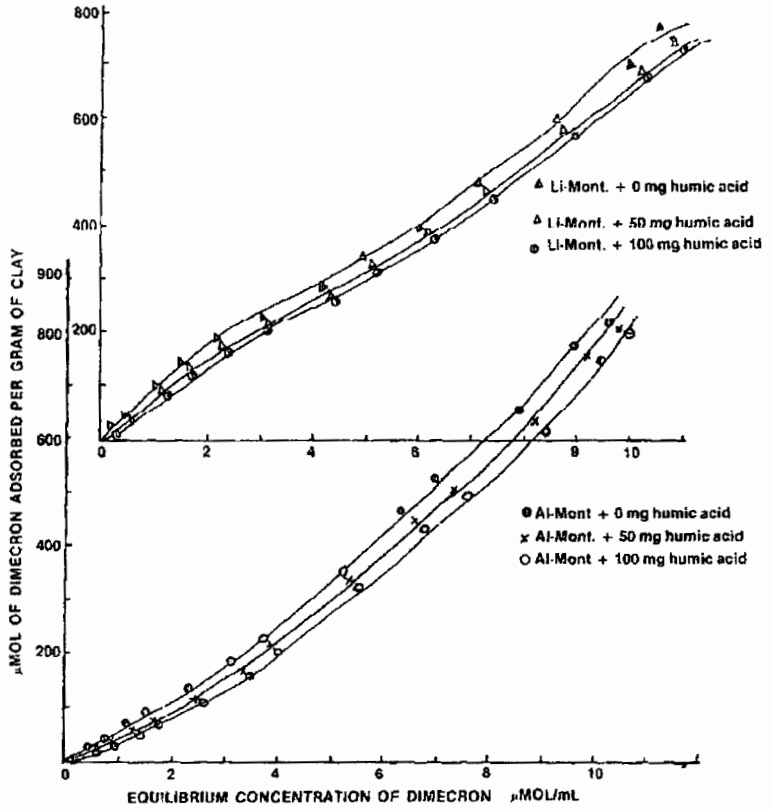


Fig. 4—Adsorption of Dimecron on montmorillonites in presence of 0, 50, and 100 mg of humic acid.

The values of K_o (Table 4) have been found to be higher than unity (i.e., oxamyl or Dimecron has a high preference for montmorillonite surface), and they decrease in the order Al- > Fe- > Li- > Na- > K- > Cs-montmorillonites, confirming my earlier deductions regarding the order of adsorption. The values of K_o also decrease as the temperature increases.

The values of $\Delta G°$ are negative at all three temperatures and increase with a rise in temperature, pointing toward the spontaneity of reaction, with a greater affinity of montmorillonite for oxamyl or Dimecron. The values of $\Delta G°$ show that for both pesticides the driving forces of the reaction, the strength of adsorption, and the degree of order attained during the adsorption reaction are Al- > Fe- > Li- > Na- > K- > Cs-montmorillonites.

The negative values of overall adsorption heat ($\Delta H°$) (which is the net result of enthalpy change, molecular diffusion, and repulsion between adsorbed molecules and desorption of solvent) indicate the exothermic nature of reaction with a strong binding of pesticide molecules on the clay surface. The values of $\Delta H°$ also

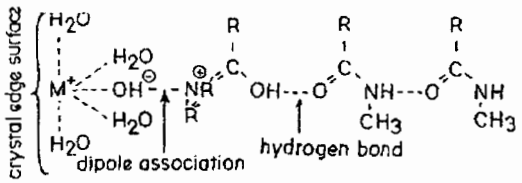
Table 4—Thermodynamic parameters for oxamyl and Dimecron adsorption on montmorillonites saturated with different cations at 15, 25, and 35°C.†

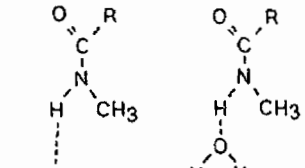
Pesticide	Saturating cation	Equilibrium constant K_o			$\Delta G°$, kJ/mol			$\Delta H°$, kJ/mol	$\Delta S°$, J/mol-degree
		15°C	25°C	35°C	15°C	25°C	35°C		
Oxamyl	Al^{3+}	2366	1561	1088	−18.64	−18.25	−17.89	−29.38 ± 0.20	−37.31 ± 0.02
	Fe^{3+}	2184	1432	971	−18.45	−18.04	−17.65	−29.94 ± 0.14	−39.91 ± 0.02
	Li^{+}	2001	1302	965	−18.27	−17.97	−17.60	−27.90 ± 0.52	−33.40 ± 0.04
	Na^{+}	1946	1332	949	−18.17	−17.86	−17.59	−26.51 ± 0.34	−29.40 ± 0.30
	K^{+}	1832	1288	929	−18.01	−17.77	−17.53	−24.88 ± 0.05	−23.85 ± 0.01
	Cs^{+}	1703	1199	879	−17.85	−17.60	−17.39	−24.29 ± 0.26	−22.40 ± 0.03
Dimecron	Al^{3+}	2273	1523	1049	−18.54	−18.19	−17.84	−25.81 ± 0.03	−34.63 ± 0.01
	Fe^{3+}	2031	1377	961	−18.27	−17.94	−17.62	−27.60 ± 0.08	−32.38 ± 0.02
	Li^{+}	1965	1349	943	−18.20	−17.89	−17.57	−27.11 ± 0.14	−30.95 ± 0.01
	Na^{+}	1872	1306	931	−18.07	−17.81	−17.54	−25.82 ± 0.06	−30.95 ± 0.01
	K^{+}	1798	1270	913	−17.98	−17.74	−17.49	−25.03 ± 0.10	−24.47 ± 0.01
	Cs^{+}	1642	1178	864	−17.76	−17.36	−17.34	−23.71 ± 0.03	−20.67 ± 0.01

† (±) Standard error of estimate.

show that the adsorption occurs through covalent bonding mechanisms (22). The values of entropy change ($\Delta S°$) during the interaction of oxamyl or Dimecron on montmorillonites is negative, indicating that there is no configurational change and that complexes of clay-pesticide are stable. Association, fixation, or immobilization of the pesticide molecule as a result of adsorption resulted in the loss of the degrees of freedom of the pesticide molecule, producing negative entropy effects.

The above inferences indicate that oxamyl and Dimecron may be adsorbed because of coordination or protonation (or both) (25, 5, 10, 3), hydrogen bonding and dipole association, or van der Waal's forces as follows:





where R′ = H or C_2H_5 and R″ = CH_3 or C_2H_5.

An examination of IR spectra show that the bands at 1670, 1690, and 1380 cm^{-1} in oxamyl assigned for > C=O stretching, > C=N stretching, and C-N vibrations, respectively, are shifted to 1645, 1710, 1390 cm^{-1}; 1650, 1700, 1395 cm^{-1}; 1650, 1695, 1390 cm^{-1}; 1660, 1700, 1385 cm^{-1}; and 1660, 1695, 1390 cm^{-1} during oxamyl interaction on Al-, Fe-, Li-, Na-, K-, and Cs-montmorillonites, respectively. These shifts indicate the coordination or protonation (or both) as carbonyl oxygen with shifting of the double bond toward nitrogen (23, 26). Similar results are obtained during Dimecron interaction. The shifts of bands are from 1665 to 1650 cm^{-1} (> C=O stretching), 1690 to 1705 cm^{-1} (C=N stretching), and 1385 to 1400 cm^{-1} (C-N stretching vibration). X-ray data show an expansion of 0.30 to 0.35 nm in the basal thickness on complexing of different cation-saturated montmorillonites with oxamyl or Dimecron, indicating a flat orientation of the intercalated oxamyl or Dimecron in monomolecular layers with formation of complexes at the basal surface.

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Kinetics of Nonexchangeable Potassium Release from Two Coastal Plain Soils[1]

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ABSTRACT

The kinetics of nonexchangeable-K release using H-saturated resin were investigated on Kalmia (fine-loamy, siliceous, thermic Typic Hapludults) and Kennansville (loamy, siliceous, thermic Arenic Hapludults) soil profiles from the Coastal Plain of Delaware. Calcium-saturated soil samples were equilibrated with H-saturated resin from 0.5 to 960 h. Equilibrium in K release in both soil profiles was attained in about 960 h. The kinetics of K release were evaluated using the Elovich, parabolic diffusion law, first-order diffusion, and zero-order equations. The first-order diffusion equation described the K-release kinetics best as evidenced by the highest correlation coefficient (r) and the lowest value of the standard error of the estimate (SE). The parabolic diffusion law also described the data satisfactorily indicating diffusion-controlled exchange. The zero-order and Elovich equations did not describe the data well as shown by higher SE values than those found with the first-order diffusion and parabolic diffusion law equations. Nonexchangeable-K release rate coefficients (k_2) ranged from 1.20 to 2.2 $\times 10^{-3}$ h^{-1} in the Kalmia soil and from 1.5 to 2.9 $\times 10^{-3}$ h^{-1} in the Kennansville soil. The magnitude of the k_2 values suggested low rates of nonexchangeable-K release from the two soils.

Additional Index Words: **first-order diffusion kinetics, diffusion-controlled exchange, Elovich equation.**

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NONEXCHANGEABLE K is released to the exchangeable form when levels of exchangeable and soil solution K are decreased by plant uptake and leaching (Jackson, 1964; Sparks et al., 1979; Sparks, 1980). Schmitz and Pratt (1953) found that while 47% of the variation in corn (*Zea mays* L.) yield percentage was due to exchangeable soil K levels, 88% was ascribed to the quantity of nonexchangeable and exchangeable K.

The release rate of nonexchangeable K from micas (Mortland, 1961; Reed and Scott, 1962; Scott, 1968; Feigenbaum et al., 1981) and from vermiculite (Mortland and Ellis, 1959) is diffusion controlled. Mortland (1958) investigated the kinetics of K release from biotite and found that the release rate was first-order using a batch technique and zero-order with a miscible displacement method. Mortland and Ellis (1959), using 0.1*N* NaCl as an extractant, found the release of nonexchangeable K from vermiculite was first order. Using HNO_3 extraction at 301 and 311K, Huang et al. (1968) showed that K release was first order for biotite, microcline, muscovite, and phlogopite. The rate coefficients were in the order biotite > phlogopite > muscovite > microcline. Using a H-saturated resin, Feigenbaum et al. (1981) found that relative rate coefficients based on the parabolic diffusion equation averaged 0.40 for muscovite particles.

While there are data on the kinetic reactions between solution and exchangeable forms of K in soils (Sparks et al., 1980a and 1980b; Sparks and Jardine, 1981; Sparks and Rechcigl, 1982), there are few reports in the soil chemistry literature on the kinetics of nonexchangeable-K release from soils. Accordingly, the objectives of this study were: to investigate the kinetics of nonexchangeable-K release using a resin technique, and to employ various kinetic equations to describe nonexchangeable-K release from two Atlantic Coastal Plain soils.

MATERIALS AND METHODS

Soil samples were taken at 0.15-m depth increments from 0 to 0.90 m of a Kalmia sandy loam (fine-loamy, siliceous, thermic Typic Hapludults) and a Kennansville loamy sand (loamy, siliceous, thermic Arenic Hapludults) from Delaware. These soils were chosen because anomalous crop responses to applied K were previously noted (Sparks and Liebhardt, 1982). The soil samples were air-dried and gently ground to pass through a 2-mm sieve in preparation for laboratory analyses.

Soil Characterization Analyses

Soil pH was determined using a 1:1 water-to-soil ratio, and organic matter was estimated using a modified Walk-

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