Role of the Amido Group in Adsorption Mechanisms

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The quantitative adsorption of 52 structurally related N-phenylcarbamates, acetanilides, and anilines from 2% ethanol solutions was investigated for three solid adsorbents: nylon, cellulose triacetate, and cellulose. The influence of temperature, time, solubility, and solvent was studied. Nylon and cellulose triacetate adsorbed all chemicals, although the extent varied, while cellulose adsorbed none. Desorption studies indicated that adsorption occurred through hydrogen bond formation. Statistical analysis showed that the inverse relationship between solubility and adsorption accounted for 60% of the total variation in adsorption. A new regression line deviation technique was used to evaluate the effect of molecular configuration on adsorption in terms of tautomerism, chelation, induction, and steric hindrance. The results suggest that the preferred adsorption mechanism of the amido compounds from aqueous solution is via the adsorbate's imino hydrogen and the adsorbent's carbonyl oxygen. Should neither of these be available, alternative binding sites are utilized.

RELATIONSHIPS between molecular structure and adsorptive properties of pesticides constitute a fundamental problem in both soil residue and phytotoxic research. The relationships are influenced by the availability and the binding strength of the adsorption sites in both the adsorbent and adsorbate molecules. The adsorbent, whether it be plant or animal substrate or the organic fraction of the soil, possesses many different functional-group adsorptive sites. Prominent among these are the hydroxyl, carbonyl, and amido groups. Within the organism, phytotoxicity of the pesticide is often associated with adsorption by the proteinaceous portions of the cells, and in the soil, adsorption of pesticides is increased in proportion to increased organic matter content (15, 19). The amido group (-NHCO-) of the adsorbent, therefore, is a highly significant factor in the availability and effectiveness of pesticides. It seemed appropriate to investigate the quantitative adsorption of various chemicals on a pure, well classified substance that possessed this group. The adsorbent chosen was Nylon 66, which contains an ordered arrangement of amido groups similar to that found in proteins. To provide a comparison, cellulose and cellulose triacetate, representative of the functional groups of other organism and soil constituents, were included in this study.

Various N-phenylcarbamic acid esters and acylanilides (both of which also contain the amido group) are of commercial significance as herbicides. A number of these chemicals, containing a variety of substituent groups, were selected for quantitative adsorption studies from aqueous solutions on nylon, cellulose, and cellulose triacetate. For comparative purposes several anilines of similar structure were also investigated.

The objective of the present investigation was to determine the effect of molecular structure on the quantitative adsorption of N-phenylcarbamates and acetanilides on nylon, and thereby ascertain the role of the amido group in adsorption. Temperature at which adsorption occurs, time of equilibrium attainment, solubility of the carbamates in the solvent, and the particular solvent used may modify the amount of adsorption on nylon. Therefore, the influence of each of these factors on adsorption was determined.

Materials and Methods

The adsorbents used were Nylon 66 (Zytel-101, 80-mesh, E. I. du Pont de Nemours & Co.), cellulose triacetate (acetyl content by weight 43.2%, Eastman Chemical Products, Inc.), and cellulose (chromatography grade powder, Whatman). The solid chemical adsorbates were purified by repeated recrystallizations until a constant melting point was reached for each. The liquids were distilled.

Adsorption of Carbamates, Acetanilides, and Anilines by Nylon, Cellulose Triacetate, and Cellulose. Twenty-five milliliters of an aqueous 2% ethanol solution of each chemical was shaken with 0.5 gram of powdered adsorbent until equilibrium was reached. The concentrations of solute used were 1.0, 0.8, 0.6, and 0.4 × 10⁻⁴M.

The supernatant was removed by filtration through a small disk of Whatman No. 1 paper in a Gooch crucible. The concentration of the solution was determined by observing its absorbance on a Beckman Model DU spectrophotometer at the characteristic maximum absorbance wavelength of the chemical used, and comparing this value with a previously determined standard curve. The difference between the concentration of the added solution and the supernatant at equilibrium was taken as the amount of chemical adsorbed. An appropriate blank, consisting of all components except the chemical, was included in each determination.

Factors Influencing Extent of Adsorption. The minimum shaking time required for the attainment of equilibrium between the adsorbed chemical and the aqueous phase was determined by means of the above procedures for 6, 12, 24, and 48 hours of shaking.

The extent of adsorption of all the chemicals was determined at 26.5° C. in a temperature-controlled room. In addition, the quantitative adsorption of ten N-phenylcarbamates on nylon was determined at 10° and 50° C. by shaking in a constant temperature water bath.

The extents of adsorption on nylon of three carbamates [ethyl-N-phenylcarbamate, ethyl-N,N-diphenylcarbamate, and ethyl-N-(4-chlorophenyl) carbamate] from n-hexane and cyclohexane solutions were determined using the standard procedure. Similarly, solu-

tions of varying concentrations of ethyl-N-phenylcarbamate in water, 2% ethanol, 25% ethanol, and 50% ethanol were equilibrated with nylon and the adsorption isotherms obtained.

The maximum solubility of each chemical in 2% ethanol was determined at 26.5° C. by shaking an excess of the chemical in the solvent until a constant concentration had been obtained. The concentration was determined by filtering the supernatant and comparing the ultraviolet absorbance of the diluted liquid, at the characteristic wavelength of the chemical, with a standard curve of concentration vs. absorbance. The solubility of most of the carbamates in water was so low that the desired isotherms could not be established with water as a solvent. Therefore, the use of the arbitrary solvent, 2% ethanol, was necessary in all cases. In those cases where the chemicals were soluble in water, no difference in the quantitative adsorption could be detected with the use of either water or 2% ethanol as a solvent.

The extent of desorption was determined by first measuring the quantitative adsorptions of four carbamates, three acetanilides, and four anilines on nylon from $10^{-4}M$ solutions as described above. The nylon adsorbent was recovered after filtration of the supernatant, rinsed quickly with 2 ml. of solvent, placed in 25 ml. of solvent, and shaken for 24 hours. The solvent was then analyzed spectrophotometrically to measure the degree of desorption and the establishment of a new equilibrium.

Experimental Results

Equilibria were found to be attained in all cases within 24 hours of shaking. Adsorption isotherms of the amount of solute in micromoles adsorbed per gram of adsorbent, (x/m), as a function of the equilibrium concentration, c, were used to interpret all adsorptive results. For nylon and cellulose triacetate adsorption all chemicals at the concentrations used had linear isotherms passing through a zero intercept. These data fit the empirical Freundlich equation

$$x/m = Kc^{\frac{1}{n}} \qquad (1)$$

where x/m is the amount of solute adsorbed by a given weight of adsorbent, c is the equilibrium molar concentration, and K and n are specific constants for the system under consideration. Since the quantitative adsorption on nylon and cellulose triacetate resulted in straight lines, the value of n is 1 and the amount adsorbed is directly proportional to c. It was possible, therefore, to select an arbitrary equilibrium concentration (0.2 $\times$ $10^{-4}M$) and use the x/m value at this concentration as a single numerical expression of the adsorption equilibria. The expressions were designated as k values and are given in Table I (k_N for nylon and k_A for cellulose triacetate adsorption). The k values embrace all factors influencing adsorption from solu-

Table I. Solubility and Adsorption Constants for Carbamates, Acetanilides, and Anilines on Nylon and Cellulose Triacetate

Carbamate No.	Compound Name	Solubility (× 10⁻⁴M) in 2% Ethanol	$k_N{}^a$	$k_A{}^a$	$D_N{}^b$	$D_A{}^b$
	CARBAMATE DERIVATIVES					
1	Ethyl-N-methyl-N-phenyl	172	0.22	1.42	−0.01	−0.39
2	Ethyl-N-benzyl	121	0.49	2.03	0.07	−0.31
3	Ethyl-N-phenyl	96	1.03	3.68	0.26	0.02
4	Ethyl-N-ethyl-N-phenyl	78	0.25	1.83	−0.08	−0.63
5	Ethyl-N-(2-nitrophenyl)	71	0.90	3.25	0.18	0.10
6	N-Phenylglycine ethyl ester	64	0.16	0.83	−0.12	−1.17
7	Phenyl	28	0.40	0.58	−0.15	−1.92
8	Isopropyl-N-phenyl	16	1.16	4.95	0.02	0.77
9	Ethyl-N-(4-chlorophenyl)	9.6	5.70	14.70	1.66	2.43
10	Ethyl-N-butyl-N-phenyl	8.5	0.80	6.75	−0.35	−0.95
11	n-Butyl-N-phenyl	8.5	2.20	9.62	0.21	0.02
12	Ethyl-N-(4-nitrophenyl)	5.7	3.65	8.75	0.61	−0.80
13	Ethyl-N-benzyl-N-phenyl	2.9	1.85	12.65	−0.56	−0.85
14	Ethyl-N-(2,5-dichlorophenyl)	2.6	4.00	19.40	0.20	1.55
15	Ethyl-N-(2,3-dichlorophenyl)	2.5	3.65	27.90	0.02	4.86
16	Ethyl-N,N-diphenyl	1.7	1.02	9.10	−1.40	−3.94
17	Isopropyl-N-(2-methyl-5-chlorophenyl)	1.6	3.37	14.00	−0.51	−1.90
18	Methyl-N-(2,4-dichlorophenyl)	0.72	15.10	...	2.89	...
19	Isopropyl-N-(3-chlorophenyl)	0.50	9.00	8.45	−0.30	...
20	Isopropyl-N-(3,4-dichlorophenyl)	0.32	23.00	...	4.00	...

Acetanilide No.		ACETANILIDE DERIVATIVES				
1	N-Ethylacetanilide	2320	0.05	0.20	−0.01	0.04
2	4-Hydroxyacetanilide	1580	0.25	0.13	0.07	−0.01
3	Acetanilide	624	0.21	0.32	0.03	0.03
4	2-Chloroacetanilide	375	0.25	0.47	0.02	0.06
5	4-Aminoacetanilide	352	0.06	0.05	−0.06	−0.11
6	N-n-Butylacetanilide	167	0.23	0.89	−0.04	0.12
7	2-Nitroacetanilide	138	0.16	0.72	−0.08	0.07
8	2-Hydroxyacetanilide	32	0.26	0.15	−0.24	−0.44
9	N-Phenylacetanilide	31	0.26	1.59	−0.24	0.12
10	4-Chloroacetanilide	16	1.19	2.64	0.04	0.30
11	3,4-Dichloroacetanilide	12	6.05	6.83	1.81	1.85
12	4-Nitroacetanilide	11	1.02	2.18	−0.24	−0.06
13	4-Bromoacetanilide	11	1.73	3.30	0.05	0.39
14	2,5-Dichloroacetanilide	10	0.92	1.59	−0.31	−0.33

Aniline No.		ANILINE DERIVATIVES				
1	Aniline	4450	0.07	0.27	−0.01	−0.04
2	2-Methylaniline	1670	0.10	0.44	−0.02	−0.09
3	4-Methylaniline	1240	0.05	0.50	−0.05	−0.11
4	N-Methylaniline	560	0.24	0.92	−0.02	−0.10
5	4-Chloroaniline	520	0.68	3.31	0.15	0.84
6	2-Chloroaniline	450	0.55	1.94	0.09	0.25
7	N-Ethylaniline	250	0.32	1.10	−0.06	−0.28
8	2-Nitroaniline	103	0.91	2.84	0.03	−0.06
9	N,N-Dimethylaniline	95	0.52	2.12	−0.34	−0.94
10	2,3-Dichloroaniline	85	3.45	7.20	1.00	1.58
11	3,4-Dichloroaniline	52	4.32	10.20	1.21	2.39
12	2,5-Dichloroaniline	49	3.78	11.20	0.97	2.76
13	4-Nitroaniline	38	1.10	3.40	−0.19	−0.64
14	N-n-Butylaniline	16	1.42	6.55	−0.53	−0.58
15	2-Nitro-4-chloroaniline	9	3.70	7.80	−0.12	−1.30
16	2,4-Dinitroaniline	5	1.94	5.65	−1.51	−3.69
17	N-Benzylaniline	4	3.46	19.48	−1.22	1.22
18	N-Phenylaniline	3	16.50	24.00	3.42	1.70

^{a} k_N, k_A. Values of N at equilibrium concentration of 0.2 $\times$ $10^{-4}M$.
^{b} D_N, D_A. Deviations from regression line for nylon and cellulose triacetate, respectively.

tion: the properties of the adsorbate, adsorbent, and solute; and the equilibria among them; solute-solvent, solute-adsorbent, and solvent-adsorbent.

Cellulose powder adsorbed none of the chemicals from solution. Nylon and cellulose triacetate adsorbed each of the carbamate, acetanilide, and aniline derivatives, although the percentage varied. The k values for these adsorption data may be used to compare the relative adsorption from solution of two or more chemicals on the same adsorbent, or of any one chemical on both adsorbents.

In general, as the solubility of a series

of related compounds decreases, the adsorption on a well classified adsorbent increases (4). The influence of molecular structure on the adsorption process can be better understood if the influence of structure on solubility can be evaluated. The extent of the latter relationship was determined by subjecting the solubility and k value data (Table I) to a statistical analysis. The log of the solubility, S, can be treated as a function of the log of the adsorption k values (k_N for nylon, k_A for cellulose triacetate), giving Equation 2 for adsorption on nylon:

$$\log k_N = \log Z_N + b_N \log S \quad (2)$$
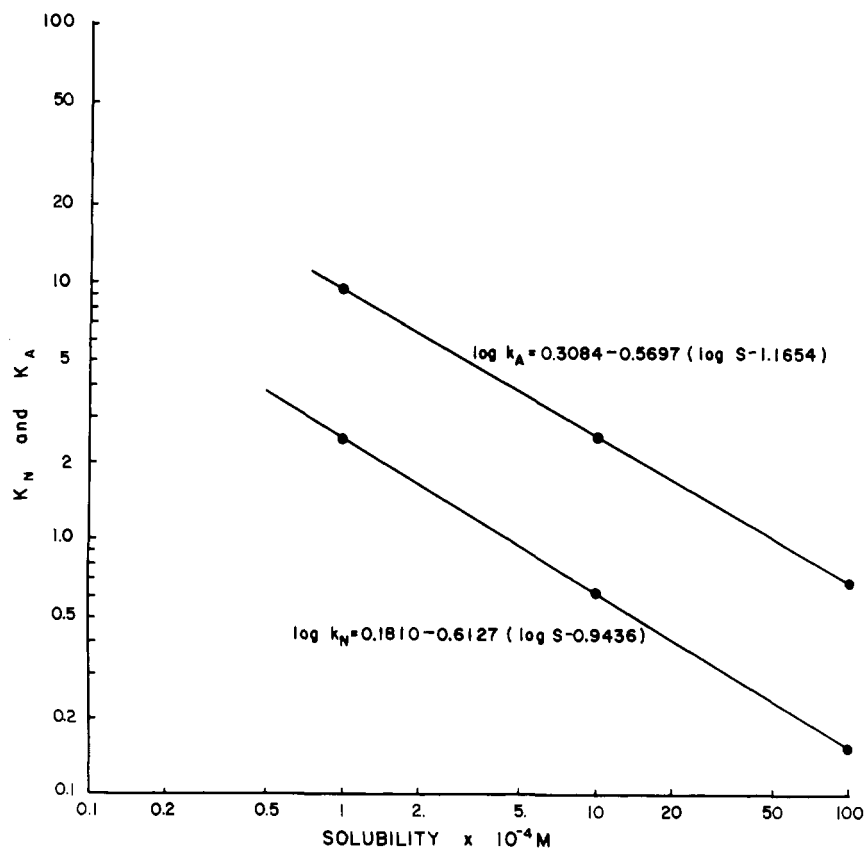
Figure 1. Lines of regression, estimated by least square method, for log k_N and log k_A on log solubility for N-phenylcarbamates
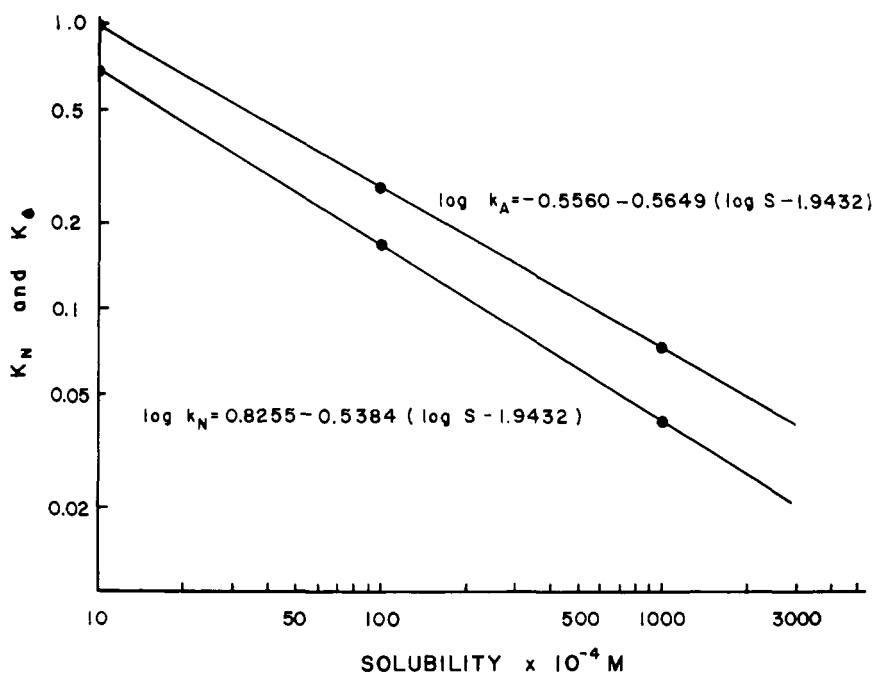

Figure 2. Lines of regression, estimated by least square method, for log k_N and log k_A on log solubility for acetanilides

and for adsorption on cellulose triacetate:

$$\log k_A = \log Z_A + b_A \log S \quad (3)$$

Log Z and b (Table II) are constants relevant to each adsorption system. By use of standard regression techniques (18) the fraction of the sum of squares of deviations from the mean log k which can be attributed to the linear regression function of log k and log S, can be expressed as a single function, r^2 (Table II). Regression lines (Figures 1, 2, and 3) for the three families of chemicals on the two adsorbents show similar slopes, b, which fact indicates that for an increment in solubility there are approximately equal changes in the adsorptions of carbamates, acetanilides, and anilines as a whole, and that the natures of the bonding mechanisms are similar for the three families of compounds on nylon and cellulose triacetate.

The regression function, r^2, numerically indicative of the inverse correlation between the solubility of a compound and its adsorption on the solid adsorbents can be used as a predictive value for adsorption. Further, use of the r^2 function can be strengthened by incorporating in each of the above equations a factor representing the relative adsorption k values of a chemical on the other adsorbent. The logarithmic forms of the resulting equations are:

$$\log k_N = \log Z_N + b_N \log S + c_N \log k_A \quad (4)$$

$$\log k_A = \log Z_A + b_A \log S + c_A \log k_N \quad (5)$$

The values of Z, b, and c for the three families of chemicals on nylon and cellulose triacetate were obtained by data substitution and the respective values of R^2 (the modification of r^2 caused by the added factor) were determined (Table II). There was a marked increase from r^2 to R^2 in all cases, and, as in r^2, the R^2 values for the anilines were decidedly higher on both nylon and cellulose triacetate than were those of the carbamates and acetanilides.

In general, therefore, if the solubilities of several members of certain families of chemicals and their k adsorption values on cellulose triacetate are known, the quantitative adsorption on nylon can be predicted.

The regression lines, as a measure of the inverse relationship between solubility and adsorption, account for about 60% of the variation in adsorption among the members of a chemical family as a whole. If the graphical position of a single carbamate (log solubility vs. log k_N) is plotted on the regression figure of all the carbamates (Figure 1), the vertical deviation, D, of the point from the line gives a measure of those factors influencing adsorption above and beyond solubility. The deviations (D_N for nylon and D_A for cellulose triacetate) are

Table II. Statistical Values for Linearization by Regression Methods of Relationship between Solubility, S, and Quantitative Adsorption, k

Value	Basis of Determination	Carbamates	Acetanilides	Anilines
		NYLON		
r^2	k_N on S	0.5760	0.6319	0.7673
R^2	k_N on S and k_A	0.8191	0.7785	0.9492
$\log Z_N$	Constant	−0.1810	−0.8255	−0.4374
b_N	Constant	−0.6127	−0.5384	−0.6322
		CELLULOSE TRIACETATE		
r^2	k_A on S	0.6588	0.5986	0.8047
R^2	k_A on S and k_N	0.8544	0.7585	0.9573
$\log Z_A$	Constant	0.3084	−0.5560	0.0995
b_A	Constant	−0.5697	−0.5649	−0.5396

Table III. Effect of Temperature on Adsorption Equilibria of Various Carbamates between Nylon and Solution Phase

Carbamate Derivative	k_N Value[a]		
	10° C.	26.5° C.	50° C.
Ethyl-N-phenyl	1.03	1.03	1.03
Isopropyl-N-phenyl	1.16	1.16	1.16
Ethyl-N-methyl-N-phenyl	0.22	0.22	0.22
Ethyl-N-ethyl-N-benzyl	0.25	0.25	0.25
Ethyl-N-benzyl-N-phenyl	1.33	1.85	1.85
Ethyl-N,N-diphenyl	0.66	1.02	1.02
Isopropyl-N-(3-chlorophenyl)	9.00	9.00	9.00
Ethyl-N-(2-nitrophenyl)	0.75	0.90	0.90
Ethyl-N-(4-nitrophenyl)	3.65	3.70	3.70
Ethyl-N-(2,3-dichlorophenyl)	3.70	3.70	3.70

[a] Value of N at $c = 0.2 \times 10^{-4}M$.

designated as positive if the log k value of a chemical is higher than the predicted regression line value at the solubility of the compound, and as negative if lower (Table I). The 40% (approximately) of adsorption variation not accounted for by solubility must be due to specific steric or electronic differences among the chemicals. The differences influence the adsorption binding sites to a different extent and thereby affect the amount of adsorption. The effects are above and beyond the possible influences of the same steric and electronic effects on the solubility of the chemical. The D values obtained from the regression analysis represent a measure of deviation from the predicted adsorption-solubility relationship. No prior example has been found in the literature for the use of this technique as an aid in relating the molecular structure of a chemical to its quantitative adsorption.

The effect of temperature on the k values for various carbamates and nylon is shown in Table III. Generally, the adsorption of chemicals on soils decreases with an increase in temperature (2), although Harris and Warren (11) found no difference in the adsorption of certain herbicides on muck at 0° and 50° C. In the present study no difference was found in adsorption at the three temperatures used, except where the imino hydrogen of the carbamate is replaced with a phenyl or benzyl group or where the 2-nitro group, capable of intramolecular hydrogen bonding with the imino hydrogen, is present on the phenyl ring. Each of these three chemicals had the same amount of adsorption at 26.5° and 50° C., but less adsorption at 10° C. Investigations of temperature-adsorption relationships are being continued.

Three carbamates, ethyl-N-phenylcarbamate, ethyl-N,N-diphenylcarbamate, and ethyl-N-(4-chlorophenyl)carbamate, were not adsorbed on nylon from either n-hexane or cyclohexane solutions, in which the chemicals are very soluble. The k_N values for these nonpolar solvents would be zero. The isothermal adsorptions on nylon using varying concentra-

tions of ethyl-N-phenylcarbamate in water, 2% ethanol, 25% ethanol, and 50% ethanol reveal that as the alcoholic content of the aqueous solvent increases substantially the extent of adsorption decreases. The k_N values of 1.03, 1.03, 0.31, and 0.05, respectively, can be inversely correlated with the fact that the solubility of the carbamates increases as the ethanol content of an aqueous solution increases. Frissel (6) noted, similarly, that in the presence of 50% ethanol, the adsorption of simazine by soils is negligible.

All 11 of the chemicals subjected to desorption tests were desorbed by the pure solvent in varying amounts from nylon and cellulose triacetate (Table IV).

Discussion

The two types of quantitative adsorption values which were determined for the 20 carbamates, 14 acetanilides, and 18 anilines differed in that solubility was incorporated in the k values but not in the D values. K values represent a dynamic situation similar to that found under field conditions, where the soil ad-
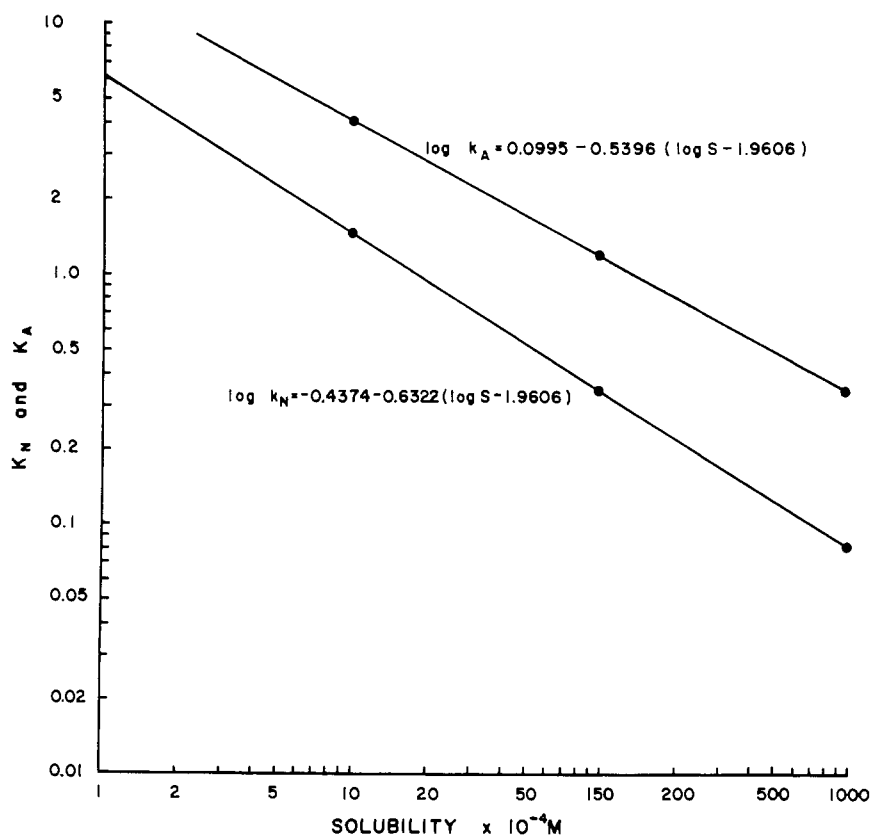

Figure 3. Lines of repression, estimated by least square method, for log k_N and log k_A on log solubility for anilines

$\log k_A = 0.0995 - 0.5396 (\log S - 1.9606)$

$\log k_N = -0.4374 - 0.6322 (\log S - 1.9606)$

Table IV. Adsorption and Desorption (of Amount Adsorbed) of Various Carbamates, Acetanilides, and Anilines from 2% Ethanol Solutions by Nylon and Cellulose Triacetate

Adsorbate	Nylon, %		Cellulose Triacetate, %	
	Adsorbed	Desorbed	Adsorbed	Desorbed
Ethyl-N-phenylcarbamate	48.5	45.7	48.6	38.3
Ethyl-N-ethyl-N-phenylcarbamate	17.3	82.4	15.6	80.5
Ethyl-N,N-diphenylcarbamate	49.5	44.5	50.4	20.7
Ethyl-N-(4-chlorophenyl)carbamate	82.0	15.8	82.4	8.9
2,5-Dichloroacetanilide	46.3	53.0	46.2	51.4
3,4-Dichloroacetanilide	84.5	12.2	84.6	5.6
N-ethylacetanilide	3.4	50.0	1.0	100.0
Aniline	8.7	76.3	7.2	77.0
N-ethylaniline	24.0	83.0	22.9	84.3
N-benzylaniline	76.1	19.6	76.8	8.8
N-phenylaniline	92.8	4.5	93.8	2.2

sorbed phase is in equilibrium with the dissolved phase. Changes in concentration caused by a loss of solvent or solute bring about the establishment of new equilibria. D values, obtained by the use of the regression technique, represent the amount of adsorption attributed to factors other than solubility. The principal variable factor remaining in the adsorption process is the difference in the molecular structures of the chemicals. This difference, with its accompanying steric and electronic influences, causes modifications in the strength of possible adsorption bonds. Therefore, a correlation of the adsorptive capacity of the various chemicals with their molecular structure should be possible. Although the factors influencing adsorption are interrelated, an explanation of the adsorptive results obtained in this investigation is first given as a function of each factor separately.

Steric Effects. The three most probable bonding sites between nylon and a carbamate having an imino hydrogen atom are shown in Figure 4.
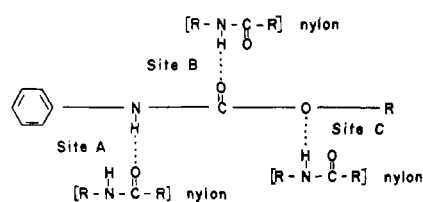

Figure 4. Probable bonding sites between nylon and N-phenylcarbamates

Because of free rotation about single bonds it is possible for the R group of alkyl-N-phenylcarbamates to block the carbonyl oxygen, the ether oxygen, or the imino hyrogen (7). Table I reveals that not only chain length but also bulkiness of the ester R group decreases the amount of adsorption of the N-phenylcarbamates on nylon and cellulose triacetate. Steric hindrance is also observed in carbamates and acetanilides having a benzyl or phenyl group instead of a normal alkyl group attached to the

imino nitrogen. The N-substituent can shield the carbonyl oxygen of carbamates or acetanilides or the ether oxygen of the carbamate. N-Alkyl-substituted anilines also have lower D_N and D_A values, in general, than the unsubstituted analogs.

Intramolecular Bonding. Certain ortho substituents on the phenyl ring adjacent to the imino nitrogen of carbamates and acetanilides can form intramolecular hydrogen bonds with the imino hydrogen, thereby preventing its engagement in intermolecular hydrogen bonding. Both ethyl-N-(2-nitrophenyl) carbamate and 2-nitroacetanilide are capable of intramolecular hydrogen bonding and both have lower D_N values than the nonnitrated compounds. The D_A values of the nitrated compounds are higher than those of the nonnitrated compounds, indicating that chelative effects are less significant when cellulose triacetate is the adsorbent.

Intramolecular hydrogen bonding is not a factor in adsorption of the anilines which have two amino hydrogen atoms.

Tautomeric Effects. Tautomeric character in the molecule enhances its ability to form hydrogen bonds via both the imino hydrogen and the carbonyl oxygen (14). Barker et al. (7) found intermolecular association bonds to be markedly strengthened in compounds containing an amide group as compared with isomers in which the -NH- and -CO- groups are separated by a methylene group. Two isomeric compounds, N-phenylglycine ethyl ester and ethyl-N-benzylcarbamate, were included in the adsorption study to observe the effect of such tautomeric character. The carbamate capable of tautomerism (ethyl-N-benzylcarbamate) proved to be adsorbed in the greater amount on both nylon and cellulose triacetate. Tautomerism can be expected to exist for all the other carbamates investigated (except the N,N-disubstituted ones) and for similar acetanilides. The extent of bonding in carbamates and acetanilides depends on the enol content of the equilibrium mixture. The ratio of keto to enol form of each chemical is a function of the nature

of the groups attached to each side of the amido group and to the solvent used. Chemicals having side groups which enhance tautomeric character were adsorbed to a greater extent than those having no or little such character. That the latter were adsorbed at all, however, indicates that there are potential adsorptive sites on the molecule other than the imino hydrogen of the amido group. Aniline and its derivatives do not have tautomeric structures.

Resonance Effects. In N-phenylcarbamates the net effect of resonance interaction of the nitrogen atom with the phenyl ring and the COOR group generally leads to a decrease in electron density about the nitrogen atom and an increase in its acidity. The combined effect of the two groups leads to a greater stability of the molecule and a loosening of the proton bond, and this in turn results in the formation of stronger hydrogen bonds with proton-attracting groups of the adsorbent. The same reasoning can be applied to the various acetanilides. Resonance in the carbamates also leads to a high electron density on the carbonyl oxygen and enhances its hydrogen bond-forming potential with the imino hydrogen of the nylon. Although phenylcarbamate ($NH_2COO-C_6H_5$) contains a phenyl ring, its structure does not lead to resonance forms. A comparison of its D_N and D_A values with those of N-phenylcarbamates indicates the influence of resonance on the adsorptive process.

Inductive Effects. Cluett (5) found that different alkyl groups in the R position of the phenylureas ($C_6H_5-NHCONHR$) had little effect on the dissociation of the imino hydrogens if other substituents were the same. In view of the structural similarity between phenylureas and N-phenylcarbamates, the inductive effects of the R groups in the latter would also appear to be ineffective, particularly when related to steric effects. However, the phenyl ring, particularly if it contains electronegative groups such as nitro and chloro, causes, in general, a negative inductive effect. The resulting loosening of the N-H bond and increased hydrogen bond formation (13) and adsorption are reflected in larger positive D_N and D_A values. The positive inductive and steric effects of an o-methyl group and its lack of influence in the five-position are reflected in the lower D_N and D_A values of compounds so substituted.

The electron-withdrawing effects of phenyl and substituted phenyl rings are not as obvious in the acetanilides and the adsorption values obtained cannot be explained on the basis of inductive effects alone. The relatively high positions of N-ethyl and N-n-butyl acetanilides indicate that adsorption must occur in these two chemicals by some mechanism other than hydrogen bonding through

the imino hydrogen, possibly through the carbonyl oxygen or a hyperconjugated hydrogen of the methyl group. Of interest is the decreasing D_N adsorption order of the following acetanilide derivatives: 4-OH, 4-Br, 2-Cl, 4-NH$_2$, 2-NO$_2$, 4-NO$_2$, and 2-OH. On the basis of inductive, steric, and chelation factors, this adsorption order seems to have no definite pattern. The D_A order of 4-Br, 4-Cl, 2-NO$_2$, 2-Cl, 4-OH, 4-NO$_2$, 4-NH$_2$, and 2-OH seems to reflect the influence of the same factors more logically, except for the low position of the 4-NO$_2$ compound and the reversed positions of the 4-Br and 4-Cl acetanilides.

Inductive effects explain, generally, the relative acidity of the imino hydrogen of various anilines when arranged in decreasing order of adsorption.

Relation to Biological Activity. Many N-phenylcarbamates, acylanilides, phenylureas, and polycyclic ureas are phytotoxic to plants. Phytotoxicity may result from the binding of the herbicide molecule with receptor sites at or near the active centers in the chloroplasts by means of hydrogen bonds (16).

A comparison of the adsorptive results obtained here with the phytoactivity of the same chemicals is complicated by the difference in the complexity of the two systems involved. While the adsorptive situation in this investigation is relatively simple, biological systems have many adsorptive sites.

Nevertheless, several similarities can be noticed in the adsorption patterns. The 3,4-dichlorocarbamates (9) and 3,4-dichloroanilides (12) are among the most effective plant growth inhibitors and are found here to have high D values. Replacement of the imino hydrogen of ethyl-N-phenyl-carbamate with an ethyl, phenyl, or benzyl group results in a loss of inhibition of the photochemical activity of isolated chloroplasts (16). The same substitution results in a lowering of the D_N and D_A adsorption ratings from those of the parent compound.

The lack of adsorption of the chemicals considered here on cellulose suggests that herbicides having similar structures could travel unadsorbed through cellulosic plant tissues until more reactive sites were reached.

Desorption. The fact that all the chemicals investigated in the desorption work, whether having an imino hydrogen or not, were desorbed to some degree from nylon indicates that the bonds between the compounds and the nylon were not chemical in nature. The ease of desorption, plus the fact that van der Waals attractions between an adsorbate in aqueous solution and an adsorbent are relatively minor when the stronger hydrogen bonds can be formed, indicates that bond formation in all cases investigated here is by hydrogen-bonding mechanisms.

The desorption results (Table IV) suggest that those herbicides which have a greater degree of adsorption on amido and carbonyl adsorbents are released from soil in far lesser amounts as new equilibria are reached by removal of the unadsorbed portions. Herbicides adsorbed to a lesser degree have little reserve action, most of the herbicide being available immediately, and most of that adsorbed coming off quickly. Herbicides adsorbed to a great extent come off slowly and therefore should have an extended residual action.

Adsorption Mechanism of Nylon. The evidence suggests that adsorption of N-phenylcarbamate and acetanilide molecules on nylon can proceed, therefore, by either of two main mechanisms: (1) hydrogen bond formation between the imino hydrogen of the carbamate or acetanilide and the carbonyl oxygen of the nylon, or (2) hydrogen bond formation between the carbonyl oxygen of the carbamate or acetanilide and the imino hydrogen of the nylon. In a single system, adsorption is probably proceeding by both mechanisms, the extent of each depending on the structure of the adsorbate involved.

The greater aliphatic nature of the nylon molecule than the carbamate or acetanilide molecules (with their many resonating forms) would favor the nylon carbonyl oxygen having a greater electron density than the carbamate or acetanilide oxygen, and would indicate that mechanism 1 would be the more probable. However, should the imino hydrogen of the adsorbate be sterically blocked or chelated with an ortho group on the phenyl ring, or should an alkyl or aryl group be substituted for it, then adsorption would probably proceed by mechanism 2.

At least three other mechanisms may contribute to the total amount of adsorption. In a single system at equilibrium the statistical percentage of the three contributions is small. However, if the two main mechanisms above are blocked, the extent of the participation of each of the three latter mechanisms becomes greater. First, the enolized form of the chemical can bond to the nylon's carbonyl oxygen atom. The fact that carbamates and acetanilides exist in aqueous solution mostly in the keto form because of the polarity of the solvent and the nonplanar configuration of the molecule resulting from steric forces diminishes this possibility (10). Second, a hydrogen bond can form between the imino hydrogen of the nylon and the ether oxygen of the carbamate (3). This mechanism is of less significance because of the relatively low electron density of the ether oxygen and the steric hindrance of its attached alkyl group. Third, bonding is possible between electronegative groups, such as nitro or chloro, in the para position of the phenyl ring of either carbamates or

acetanilides, and the imino hydrogen of the nylon.

On the other hand, anilines can hydrogen-bond to the amide group of nylon only via the chemical's hydrogen atom and the nylon's carbonyl oxygen. Since there are always some free carboxylic acid end groups present in the nylon polymeric chain, some of the aniline molecules can react with these. Zytel-101 has a ratio of 200 amide groups to each carboxyl group, and although comparisons within the aniline family are unaffected by the presence of the carboxyl groups, comparisons of the adsorption of anilines with the other families must be modified accordingly.

Adsorption Mechanisms on Cellulose Triacetate. The similarity between regression line slopes, the magnitude of k values, and the direction of deviation of D values for nylon and cellulose triacetate indicate the similar influence of solubility and molecular configuration on the adsorptive process. However, unlike nylon, cellulose triacetate has no strong proton-donating group. Therefore, the most probable hydrogen-bonding mechanism of the acetate with those chemicals having an imino or amino hydrogen atom is through its carbonyl oxygen atom, the point of greatest electron density. A lesser possibility is through the ether oxygen of the acetate group. However, carbamates and acetanilides possessing no imino hydrogen are also adsorbed by the acetate, the carbamates to a lesser degree than the regression-expected values and the acetanilides to a greater degree. The most logical explanation for this action is the formation of a hydrogen bond between the acetate's carbonyl oxygen atom and a hyperconjugated hydrogen atom of the terminal alkyl group of the carbamate or acetanilide.

Cellulose Adsorption. The total lack of adsorption of any of the 52 chemicals on cellulose could hardly have been because of the inaccessibility of reactive sites. The hydrogen-bonding sites of the hydrophilic cellulose, however, are highly hydrated (3), and the chemicals cannot preferentially displace the water molecules. Similar results have been obtained by Sherburne and Freed (17) for the adsorption of 3-(p-chlorophenyl)-1,1-dimethylurea on cotton and by Giles, Jain, and Hassan (8) for the adsorption of dyes on cellulose. Geissbühler, Haselback, and Aebi (7) noted the marked adsorption of an experimental herbicide, N' - (4 - chlorophenoxy)phenyl - N,N-dimethylurea, on both humus soil and cellulose. However, this compound is probably attached by means of van der Waals forces, since its structure more closely resembles that of vat dyes than those considered here. According to Vickerstaff (20), such dyes must have long, planar structures with several critically spaced adsorptive sites if ad-

sorption on cellulose by means of physical bonds is to occur.

Conclusions

The results of this investigation indicate that studies of the mechanism of adsorption on well defined adsorbents can be useful in explaining the relationships between pesticide activity and chemical structure. The systematic variations in the molecular structure of the organic chemicals investigated show clearly which sites in the molecule can be involved in adsorptive processes, how various substituents may influence the extent of adsorption, and that the mechanisms operate preferentially. These observations were made possible only by first accounting for the relationship between solubility and adsorption. The results may be projected to an explanation of other studies in which a specific adsorption site is presumed to be operative, such as in the investigation of the inhibition by herbicides of the functioning of certain plant tissues or in the study of the adsorption of herbicides by certain soil fractions.

Only two of the chemicals investigated [isopropyl - N - (3 - chlorophenyl)carbamate and isopropyl-N-phenylcarbamate] have been used as commercial herbicides. The phytotoxicity of compounds cannot be evaluated therefore by their relative quantitative adsorption on a few adsorbents. Adsorption data, such as those presented here, may at present best

be used to study the adsorptive relationships between herbicides and the soil environment and to evaluate this relationship in terms of the availability of the herbicide to the plant.

In the final analysis, complex structure-activity relationships, the sum of which mediate a herbicide's phytotoxic activity, may be presumed to involve a number of types of adsorptive sites, each of which imposes its own limiting features on the final expression of the relationship. Such complex systems can be understood only as the successive types of adsorptive sites involved in a given process are identified and the adsorption mechanisms clarified.

Acknowledgment

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HERBICIDES IN LEGUMES

Absorption, Translocation, and Residue Content of n-Propyl-1-C¹⁴-N,N-di-n-propylthiolcarbamate in Legumes

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THE absorption, translocation, and residue content of ethyl-N,N-di-n-propylthiolcarbamate (EPTC) and n-propyl-N-ethyl-N-n-butylthiolcarbamate (PEBC) in several plant species have been reported (2–4, 7). This paper describes a similar study for n-propyl-1-C¹⁴-N,N-di-n-propylthiolcarbamate (R-1607) in peanut and soybean plants.

Methods and Materials

Nineteen peanut seeds, variety North Carolina 4X, and 28 soybean seeds, variety Lee, were planted in each 25-

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pound freezer tin containing Newberg silty loam soil, and grown under greenhouse conditions. Twelve pots were used for each crop, divided into three groups of four pots each. The first group was used as a control and the second and third groups were treated with R-1607-C¹⁴ at the rate of 1 and 4 pounds per acre, respectively. Uniform application was achieved by dissolving 33.2 μc. of R-1607-C¹⁴ (2.21 mg.) for the 1-pound rate and 2.21 mg. R-1607-C¹⁴ plus 6.64 mg. of carrier R-1607 for the 4-pound rate in 100 ml. of distilled water and applying as a small stream from a plastic squirt bottle to the soil surface of each pot. The temperature of the greenhouse was maintained at 80° C. during the day and

70° C. at night. The daylight was supplemented with Sylvania VHF Gro-Lux fluorescent lights for 14 hours a day.

During the early stages, plants were harvested by digging up the entire plant, but during the latter part of the experiment, when the root system became too large to dig, the plants were cut off at the ground. Five peanut plants or ten soybean plants were harvested at each interval. The harvested plants were dissected into foilage, stem, roots, cotyledons, seeds, and seed pods. The plant parts were then weighed, dried in a vacuum oven at 60° C., and ground in a Wiley Micromill.

Unchanged R-1607 residue was extracted from a portion of the ground