

AN EVALUATION OF THE INTERMEDIATE REGION OF THE
REARRANGED LANGMUIR ISOTHERM FOR P ADSORP-
TION ON FIVE OKLAHOMA SOILS

By

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. REVIEW OF LITERATURES.	3
P Sorption in Acid Soils	3
P Sorption in Calcareous Soils	7
Effects of Organic Matter on P Sorption	9
Models of P Sorption	10
III. METHODS AND MATERIALS	15
IV. RESULTS AND DISCUSSION	19
V. SUMMARY AND CONCLUSION	38
LITERATURE CITED	40

LIST OF TABLES

Table	Page
I. Textural and Mineralogical Data for Five Oklahoma Soils	16
II. Chemical and Selected Physical Properties for Five Oklahoma Soils	17
III. Amount of P Sorbed (mg/g of soil)	20
IV. Regression Statistics for the Conventional and Rearranged Langmuir Equations	28
V. Slope (k) and Sorption Maxima (b) for Rearranged and Conventional Langmuir Equation	28
VI. Correlation Coefficients of b and k Values Correlated with Soil Characteristics for Conventional and Rearranged Langmuir Equation	35
VII. Multiple Regression Equations of b Using Significantly Correlated Soil Characteristics	37

LIST OF FIGURES

Figure	Page
1. Conventional Langmuir Isotherm for the Summit Soil	22
2. Conventional Langmuir Isotherm for the Ulysses Soil	23
3. Conventional Langmuir Isotherm for the Kingfisher Soil	24
4. Conventional Langmuir Isotherm for the Tipton Soil	25
5. Conventional Langmuir Isotherm for the Bowie Soil	26
6. Rearranged Langmuir Isotherm of the Summit Soil	27
7. Rearranged Langmuir Isotherm of Summit Overlaid with Data from Ashlock (1977)	30
8. Rearranged Langmuir Isotherm of Ulysses Overlaid with Data from Ashlock (1977)	31
9. Rearranged Langmuir Isotherm of Kingfisher Overlaid with Data from Ashlock (1977)	32
10. Rearranged Langmuir Isotherm of Bowie Overlaid with data from Ashlock (1977)	33

CHAPTER I

INTRODUCTION

Soil phosphorus (P) studies have been conducted for decades to answer questions concerning the apparent disappearance of this nutrient from available-to-plant forms. While much has been learned during this period, a full understanding has not been reached. To cope with the problem of P sorption, soil testing laboratories have used calibrated chemical procedures to make fertilizer recommendations to approach optimum yields. Although these procedures are well-suited for crop production, they are not suitable to estimate the rate of build up or total capacity for applied P without soil P fractionation and sorption studies.

In order to obtain the desired phosphate-soil relationships, the mechanism of retention, the quantity retained as a function of amount applied, and retention capacity are needed. A clear understanding is hard to obtain because these factors are a function of soil composition, such as amount and type of clay, iron (Fe), aluminum (Al), calcium carbonate, soil organic matter (OM), pH, surface area, and other characteristics of the soil.

In 1977 Ashlock used a Langmuir isotherm procedure in order to study P retention and release for 15 well-characterized Oklahoma soils. Five of these soils were selected for this study because of their diversity in physical and chemical characteristics. The purpose of this

study was to investigate the relationships between P sorption and soil characteristics with specific interest in the undefined transition region found by Ashlock (1977) and Syers et al. (1973) identified using the Rearranged Langmuir plotting technique.

CHAPTER II

REVIEW OF LITERATURE

If the mechanism of phosphate (P) sorption were completely understood, a more precise procedure for the determination of the available P and the P buffer capacity could be developed. This has been the design of Dickman and Bray (1941), Chang and Jackson (1957a), and others. Because so little is actually known about P sorption, there are conflicting ideas on the subject. The theories range from simple, monolayer adsorption to pure precipitation and almost every conceivable gradation between. One important factor, when considering P sorption, is the immediate environment of the phosphate ion. Brief discussions of P sorption mechanisms for acid and calcareous soils and organic matter (OM) along with sorption models are presented.

P Sorption in Acid Soils

In acid soils it is generally accepted that both clay and sesquioxides provide sorption sites for soil P. In pioneer work, with respect to P sorption in acid soils, Toth (1937) demonstrated that after removal of Fe-oxides from soil samples, the magnitude of sorption was markedly reduced. He concluded from this observation that Fe was an important factor in P sorption. This brought about numerous studies in this area (Kelly and Midgley, 1943; Struthers and Sieling, 1950). Kelly and Midgley (1943) believed the mechanism was an exchange of $\text{PO}_4^{=}$ for

hydroxyls forming Fe^{+3} hydroxyphosphates. Swenson et al. (1949) ran titrametric curves on Fe and Al and found, under normal acid soil pH, hydroxyphosphates were formed instead of simple Fe- and Al-P. Haseman et al. (1950b) found, through X-ray analysis, that simple Fe- and Al-P is converted to hydroxyphosphates of Fe and Al upon addition of OH^- . A major question remained at this point. Hydroxyphosphates of Fe and Al were formed under pure conditions, but what was the fate of P under soil conditions?

Kittrick and Jackson (1955a-c) used the principle of solubility products in order to understand what happened to P in soils. Under this principle P becomes insoluble due to a shift in the equilibrium concentration. This is characterized by the formation of relatively insoluble P, such as variscite and strengite, upon addition of soluble P. Chang and Jackson (1956b) felt that, due to the solubility product values obtained, Al- and Fe-P ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) should precipitate even in neutral solutions.

Lindsay et al. (1959) used purified variscite in a study to determine if variscite was the final soil product of added P. When $\text{Al}(\text{OH})_3$ was added to a solution of variscite and H_3PO_4 , equilibrium was reached in seven days. From this work, the pK_{sp} of variscite was determined to be 30.5. This was valuable information for comparing the solubility product of the pure variscite to soil P. They concluded that, under soil environmental conditions, products of higher solubility were formed, but postulated that upon aging, a variscite-gibbsite complex becomes important. Wright and Peech (1960), in a follow-up of this work, felt that a variscite-strengite isomorphous series was the end product. This is also supported by Cole and Jackson (1951).

Veith and Sposito (1977b) reacted o-phosphates of varying acidities with aluminosilicates, aluminum oxides, and hydrous aluminum oxides and found amorphous variscite and montebrazite by X-ray analysis. Their purpose was to eliminate questions as to whether or not variscite was a formation product of P sorption. They felt that the quantity of the reaction products is a function of H^+ concentration. Such was generally the case for both the Fe- and Al-silicates and oxides. With respect to Al-silicates, nearly 65% of the Al reacted within a 24-hour period. From this work and the work of others (Low and Black, 1948; Hemwall, 1957), it was found that Si concentration increased with time. They concluded that this rapid reaction could not be a simple surface phenomenon. Hsu (1964), however, concluded that the fast reaction was the result of surface adsorption. Hsu also proposed that in strongly acidic soils, Al would be present in large concentrations. It was presented without proof that rapid precipitation of $Al-PO_4$ would occur, but surface adsorption on amorphous $Al(OH)_3$ and Fe-oxides would dominate. Hsu also stated that adsorption might be considered a special case of precipitation.

Work has been done to evaluate the relative contributions of Al and Fe in P sorption. Williams et al. (1958) concluded correlation studies between P sorption and removal of Fe and Al from Scottish soils that P sorption was best correlated to aluminum. They used NH_4 -oxalate at pH 3.2 for their extracting solution. Bromfield (1965), on the other hand, found no conclusive correlation of P sorption and Fe and Al in Australian soils. In the same study, using a different extractant, Bromfield found P sorption was mostly due to acid-soluble Al and non-reducible Fe and not to the reducible Fe fraction.

The effect of clay minerals on P sorption is not conclusive. The controversy is between the theory of precipitation and exchange of P with the hydroxyl ion on clay surfaces. Kelly and Midgley (1943) felt that P sorption was due to "anion exchange". They found that additions of P to hydrated Fe-oxide, kaolinite, and soil suspensions produced an increase in pH which indicated the phosphate ion was exchanging with the hydroxyls. Prior work (Bradfield et al., 1935) suggests that sorption is due to precipitation of exchangeable Fe and Al, but Kelly and Midgley (1943) stated that the oxides were sufficiently hydrated to be susceptible to anion exchange. Low and Black (1950) found that dilute P solutions obeyed the Freundlich adsorption isotherm for kaolinite. They concluded this was a criteria for anion exchange. Kuo and Lotsi (1972) came to the same conclusion using Ca-saturated kaolinite.

The theory of anion exchange has gained less support than the precipitation theory. Coleman (1944) showed that there was an increase in pH after one month equilibration period, agreeing with the work of Kelly and Midgley (1943). Coleman also felt that the Fe and Al on the clay surfaces were responsible for sorption.

The most popular sorption mechanism was brought to light by Low and Black (1948). They found that the concentration of Si increased when P is applied to kaolinite. They hypothesized their findings to be a result of the solubility products principle because the clays decomposed. Hemwall (1957) suggested that, in order for this to be the case, Al must be observed in sufficient quantity, as supplied by the clay structure, and that there must exist a solubility product relationship between the added P and the clay. Kittrick and Jackson (1955c) showed additions of P to a kaolinite-variscite system produced an increase in variscite and

decomposition of kaolinite with no change in the solubility product of variscite. Later Low (1955) found, by titration methods, hydrogen-saturated clays were in reality H^+ -Al saturated clays with the Al arising from the clay structure. This same general mechanism of P sorption for montmorillonite, illite, and kaolinite was verified by Haseman et al. (1950a). They said fast and slow P sorption reactions needed further consideration. Hsu (1964) claims the rapid reaction is due to surface adsorption on a hydroxypolymer of Al and Fe. Hemwall (1957) believed that fast reaction is a precipitation of surface aluminum and the slower reaction is a process of clay decomposition. The structure dissociation of kaolinite was found to be the rate determining step in P sorption. Veith and Sposito (1977b) concluded that the P reaction with Al-SiO showed a slow approach to equilibrium which agreed with Hemwall's work.

In summarizing the literature of P sorption in acid soils, it is commonly felt that Al and Fe oxides are responsible for P sorption according to the solubility products principle with the Al and Fe coming from the clay surface or lattice. The less regarded mechanism of P sorption is anion exchange. This, perhaps, may be due to smaller observed amounts of P sorbed with ion exchange when compared to the solubility products theory.

P Sorption in Calcareous Soils

The amount of research on P sorption in calcareous soils appears to be significantly less than for acid soils. In considering the theories of P sorption in calcareous soils, researchers, as a whole, indicate there are two mechanisms. Cole et al. (1953) presented evidence that at

low phosphate concentrations, P sorption proceeded in a Langmuir-like reaction while at high phosphate concentrations, precipitation of insoluble Ca-phosphates occur. They felt the precipitate was a more soluble Ca-phosphate than hydroxyapatite or fluoroapatite, but that the apatites were the primary product over time. In 1955 Clark and Peech showed, through a solubility determination, that neither dicalcium phosphate or hydroxyapatite were in the soil or clay system studied. The equilibration period for their work was five months. Later Griffin and Jurinak (1974) used solubility criteria to show that hydroxyapatite was the principle end product of P application.

Kuo and Lotsi (1975) assumed that at low P concentrations sorption was monolayer adsorption because it followed Langmuir kinetics. They proposed the mechanism was a displacement of H_2O or anions from the clay surface.

The precipitation of Ca-phosphates at high phosphate concentrations, as found by Cole et al. (1953), proceeded much like the process for rain. A Ca nuclei forms the center of precipitation in perhaps a complex surface reaction with each layer of the precipitated P providing a new surface. Under this theory, P sorption may be limited by "impurities" on the surface or by an equilibrium between the solid and liquid phases.

Kuo and Mikkelsen (1979) found additions of Mg reduced P adsorption by $CaCO_3$. They theorized Mg displaces up to one-half of the Ca in the calcium phosphate crystal. They believed this displacement hinders nucleation of crystal growth of the phosphate precipitates. The role of clay in calcareous soils, therefore, is believed to be a source of Ca-nuclei or the surface for anion exchange.

Effects of Organic Matter on P Sorption

The literature on OM effect on P sorption and release is not always clear as to the nature of the organic matter, whether it is soil OM or crop residues or manure. The author, therefore, has tried to stipulate the nature of the OM where possible.

The addition of crop residues and manures has been observed to increase the solubility of soil phosphorus. Struthers and Sieling (1950) found addition of organic acids reduced the amount of fixed phosphates at various pH levels. Citric acid was the most active. The work of Dalton et al. (1952) and Stanford and Pierre (1953) support this theory. Dalton et al. (1952) believed that through decomposition of the organic matter, stable organometallic complexes of Al and Fe were formed and increased the solubility of P. Recently Earl et al. (1979) investigated the effects of citrate, tartrate, and acetate on P sorption in both soils and gels. They concluded the reduction in sorbed P is due to removal of Fe and Al at the soil surface. Meek et al. (1979) observed that heavy animal manure applications of soils greatly increased the NaHCO_3 -P fraction. They also observed P movement via the soil solution to a depth of 60 cm.

Doughty (1935) investigated the effects of soil OM on the P-fixing power of soil. He discovered the addition of H_2O_2 decreased the ability of the soil to fix P. He theorized that by oxidation, P is released from OM and saturates the fixing material.

Although many studies show organic matter additions increase P solubility, researchers have found positive correlations between OM and P sorption (Harter, 1969; Lopez-Hernandez and Burnham, 1974a; Holford

and Mattingly, 1975). Weir and Soper (1963) found humic acid extracts of soil OM form organometallic complexes with ferric-Fe on the non-carboxylic OH groups above pH 4.7. The Fe-organic complexes have the capacity to bind P against some exchange resins. Weir and Soper (1963) further found that the P associated with the Fe-OM complex were almost completely exchangeable with ^{32}P but only slightly available to plants.

Singh and Jones (1976) found that organic residues decreased P sorption after 30 days, but found that for a 75-150 day period, P sorption increased or decreased when the phosphorus content of the residue was $\leq 0.22\%$ or $> 0.31\%$ P, respectively. No mechanism was discussed.

The effect of humified clover extracted OM on P retention was found to be a function of mineral type by Perrott (1978). He found that Al/(Si + Al) mole ratios played an important role as to whether organic residue additions would depress or have no effect on P retention. When the Al/(Si + Al) ratio was high or low, a decrease in P retention occurred while a mineral of intermediate ratio produced no effect on P retention by organic additions. Perrott (1978) believed that in the latter case, organomineral complexes of the hydroxyaluminum species were formed which retained their ability to sorb P.

Models of P Sorption

In order to quantify P sorption, a number of kinetic models are employed. The value of the models depends upon their ability to predict or assess P sorption over a large range of soil conditions and P concentrations.

The most frequently used models are those of Freundlich (1926) and Langmuir (1918). The Freundlich equation, empirical of nature, fits a

large group of soils over a relatively large P concentration range. As pointed out by Olsen and Watanabe (1957), the disadvantage of the Freundlich equation (i) is in its inability to predict the maximum amount of phosphate that can be fixed in a given soil. For this reason, Olsen and Watanabe (1957) used the Langmuir equation (ii).

$$x/m = kC^{1/n} \quad (i)$$

where x/m = amount sorbed, C = activity of the ion in solution, and k and n are constants.

$$C/(x/m) = 1/kb + C/b \quad (ii)$$

where x/m and C are the same as above, b = sorption maximum, and K is a constant.

The Langmuir isotherm (ii) is based upon kinetic theory of gases. The assumptions are: (1) monolayer adsorption, (2) energy of adsorption is constant throughout the sorption process, and (3) the activity of the adsorbate is equal to the molarity. There is probably little error in making the third assumption at low concentration, but the (1) and (2) assumptions are apparently not met. Deviation from linearity is believed to be a direct result of the inaccuracy of assumptions 1 and 2 and desorbed ions in the equilibrium solution (Harter and Baker, 1977). Although the Langmuir equation has been found to fit linearly at < 14 $\mu\text{g/ml}$ (Olsen and Watanabe, 1957; Rennie and McKercher, 1959), curvilinear responses usually occur at higher concentrations.

One misuse of the Langmuir isotherm is to assume a linear plot is evidence of monolayer adsorption. Olsen and Watanabe (1957) warned against making assumptions about reaction mechanisms as they relate to

the isotherm. Veith and Sposito (1977a) showed that a statistically significant relationship was found between the isotherm and precipitation to support the warning of Olsen and Watanabe (1957). Veith and Sposito (1977a) concluded that unless pure adsorption can be proven as the sorption mechanism, the Langmuir equation can not be used to determine the nature of the mechanism.

Variations of the Langmuir equation were employed to bring about a linear relationship. Gunnary (1970) analyzed linear, quadratic, square root, and logarithmic variations of the Langmuir equation to find the best fit on a group of 24 soils. Gunnary (1970) found the square root function accounted for > 99% of the variance for the P sorbed on all soils tested. The calculated adsorption maximum was also increased up to 2.4 times when the square root function was employed.

Holford et al. (1974) believed that P sorption occurred on two types of surfaces of differing energies of sorption. They designed a two-surface equation (iii) to account for the curvilinearity.

$$x/m = \frac{k'b'C}{1 + k'C} + \frac{k''b''C}{1 + k''C} \quad (\text{iii})$$

where all terms have the same meaning as in (ii) except that the superscripts denote the differing surfaces.

Syers et al. (1973) used a curve splitting technique, normally referred to as the Rearranged Langmuir equation (iv), to resolve the plot into two linear portions. They found, however, that the plot would be better represented by three or more linear portions.

$$x/m = b - (x/m)/kC \quad (\text{iv})$$

In discussing the applicability of the Langmuir equation, Harter

and Baker (1977) felt that errors in the use of the equation were present as a result of not considering the effect of desorbed ions in solution.

Although the Langmuir equation has inherent drawbacks, perhaps the greatest value that can be obtained is the ability to determine sorption parameters (k and b). These parameters can be correlated with physical and chemical characteristics through least square methods. The value, then for variations of the Langmuir equation would be (1) a more quantitative picture of what happens to added phosphate and (2) more accurate sorption parameter measurements.

Olsen and Watanabe (1957) used the sorption maxima (b) to correlate P sorption with soil characters by linear regressions. They obtained an equation relating P sorption with ethylene glycol retention. Syers et al. (1973) found that in Brazilian soils, phosphate sorption was best correlated with exchangeable Al. Lopez-Hernandez and Burnham (1974a) found high correlations between P sorption and extractable Al and Fe in well-drained British soils and high correlation with soil OM in poorly-drained soils. Holford and Mattingly (1975) found low energy sorption was best correlated to soil OM while high energy sorption was correlated best to dithionite soluble Fe in calcareous soils. Harter (1969) found soil OM, Clay %, Al and Fe content, and pH correlated with P sorption. Lopez-Hernandez and Burnham (1974b) found that pH was not correlated within a mixed group of soils while correlation was observed with a group of pedologically similar soils differing mainly in pH. They found increases in pH significantly decreased P retention.

Correlations are used as an attempt to quantitatively relate mechanisms. A high correlation does not, necessarily, identify a specific sorption mechanism.

CHAPTER III

METHODS AND MATERIALS

Five soil types, representing some of the major soils in Oklahoma, were selected from the soils used by Ashlock (1977) because of their range of chemical and physical characteristics. The soils included in this study were Summit clay loam (Vertic Argiudolls), Ulysses loam (Aridic Haplustolls), Kingfisher silt loam (Udic Argiustolls), Tipton loam (Pachic Argiustolls), and Bowie sandy loam (Plinthic Paleudults). The soil characteristics used were determined by and taken from Ashlock (1977) which includes textural and mineralogical data (Table I) and chemical and selected physical properties (Table II).

One-gram samples were weighed into 50 ml plastic centrifuge tubes and equilibrated with 25 ml of one of seven P solutions for 24 hours on a horizontal shaker. The treatments used were 0, 400, 600, 700, 800, 900, 1000 ug P/g of soil. The P solutions were adjusted to pH 7 with 4 N KOH. After the equilibration period, the samples were centrifuged at 1500 rpm for ten minutes and the supernatant solution removed. The supernatant was analyzed for P concentration by the Murphy and Riley procedure (1962; Watanabe and Olsen, 1965) on a Turner spectrophotometer, fitted with a Fisher concentration computer. The amount of P sorbed per gram of soil was determined from the difference between the final and original solution concentrations multiplied by the volume of solution. All soils and all treatments were run once per day for 16 days.

TABLE I
TEXTURAL AND MINERALOGICAL DATA FOR
FIVE OKLAHOMA SOILS*

Soil Type	Order	Percent Composition				
		Sand	Silt	Clay	Course Clay	Fine Clay
1 Summit CL	Mollisol	26	40	34	M-V,I,K,Q,C	M-V,k
2 Ulysses L	Mollisol	34	46	20	I,K,Q	M-V,I,k
5 Kingfisher Sil	Mollisol	34	52	14	M-V,I,k,Q	M-V,I
9 Tipton L	Mollisol	44	44	12	m-v,I,K,Q	M-V,i
13 Bowie SL	Ultisol	58	36	6	M-V,K,Q	M-V,k

Capital letters - medium - strong peaks
Lower case letters = weak - medium peaks

M = montmorillonite
I = illite
K = Kaolinite

Q = quartz
M-V = montmorillonite - vermiculite interstratification
C = chlorite

*From Ashlock, 1977.

TABLE II
 CHEMICAL AND SELECTED PHYSICAL PROPERTIES
 FOR FIVE OKLAHOMA SOILS[†]

Soil Type	pH (1:1)	C.E.C. ¹	P.P.M.	P	Surface area m ² /g soil		Ex ² Al	% CaCO ₃	% Fe ₂ O ₃	% OM	% ³ Al
			Bray	Total	23°C	500°C*					
1 Summit CL	6.4	27.36	2.5	432	150	54	0.00	1.75	2.54	6.55	0.12
2 Ulysses L	7.9	19.30	6	316	138	49	0.00	1.81	0.70	1.55	0.05
5 Kingfisher SiL	5.2	7.71	27	204	51	10	0.28	0.53	1.14	0.85	0.06
9 Tipton L	8.1	13.11	37	253	61	19	0.25	1.84	0.42	0.89	0.03
13 Bowie SL	5.2	3.44	9	80	10	2	3.95	0.07	0.35	2.58	0.11

¹C.E.C. = expresses in me/100g.

²ExAl = exchangeable Al expressed in me/100g.

³% Al was determined by extracting Al by the Na-citrate procedure of Frink (1965).

*Determined after saturation with K⁺ and heated at 500°C for 4 hours.

[†]from Ashlock, 1977

The collected data were then statistically evaluated by analysis of variance and regression procedures with the Statistical Analysis System (SAS) program.

The model of regression was the Rearranged Langmuir equation (iv).

The linear regression parameters, slope, and intercept were correlated with the soil properties listed in Table II.

CHAPTER IV

RESULTS AND DISCUSSION

The amount of P sorbed by the selected soils is given by treatment in Table III. Amounts sorbed were significantly different (0.05 level) by treatment for each soil excepting treatments C and D for Ulysses, D and E for Tipton, and E and F for Bowie soils. Lack of significance in Ulysses is believed to result from random error of the analysis. The changes in Tipton and Bowie soils were opposite to treatment concentration and unexpected. These two soils have been cultivated and fertilized for many years and sampling variability or non-uniform distribution of residual P from fertilization could produce error of this nature. A possible solution may be to use larger samples in an attempt to minimize effects of localized residual P from previous fertilizations.

All selected soils show a significant regression model as P treatment concentration increased. The amount of P sorbed in Summit, Ulysses, and Kingfisher soils was highly correlated to treatment P level ($R^2 > 0.90$) and sorption in Tipton and Bowie soils less well correlated ($R^2 > 0.70$). Reasons for lower R^2 values for Tipton and Bowie soils is thought to be related to sample size and high dilution requirements for P determination possibly causing a magnification of errors.

Sorption isotherms were made to evaluate P sorption parameters. The P sorption parameters were correlated with measured soil characteristics. The Conventional Langmuir equation (equation ii) isotherm

TABLE III
AMOUNT OF P SORBED (mg/g of soil)

Soil Type	Phosphorus Treatments (mg/g soil) ¹						Regression Analysis	
	B 400 ¹	C 600	D 700	E 800	F 900	G 1000	R ² *	CV [†]
Summit	219.7	262.5	284.4	307.1	323.6	349.5	0.962	2.89
Ulysses	100.6	124.7	129.5	150.9	156.2	180.5	0.903	5.94
Kingfisher	89.3	102.1	110.4	128.2	133.2	164.3	0.902	6.30
Tipton	59.9	76.4	88.8	85.2	93.4	113.2	0.713	11.54
Bowie	89.3	101.9	118.2	122.1	120.9	157.9	0.731	10.11

¹The following treatments were used in the study:

Treatment	mg P/ml	ml used	Total mg P/g soil
A	0	25	0
B	16	25	400
C	24	25	600
D	28	25	700
E	32	25	800
F	36	25	900
B	40	25	1000

*R² refers to the regression coefficient

[†]CV refers to the coefficient of variation

graphs are shown in Figures 1 through 5, one for each of the five selected soils.

Ballaux and Peaslee (1975), Syers et al. (1973), and Ashlock (1977) found non-linearity in Conventional Langmuir isotherm plots at high P concentrations as also indicated in Figures 1 through 5 at the higher P treatments used in this study. Statistically, the plots show significant regression (Table IV) suggesting the possibility that this region is a third linear region with the exception of the Tipton soil. Although the regression models are significant for most soils, the R^2 values (Table IV) show that only the Summit soil is linear ($R^2 = 0.96$) when judged by an arbitrary standard that the R^2 values should exceed 0.80. As discussed by Syers et al. (1973), these "linear" regions are indicative of different P sorption sites having different maximum sorption capacities and sorption rates.

Figure 6 depicts the data in the Rearranged Langmuir form (equation iv) for the Summit soil. As seen in this graph, it appears that this region might be characterized by a smooth curve even though the regression model is significant.

Table V contains the sorption parameters, sorption maxima (b) and slope (k) for both Conventional and Rearranged Langmuir equations for the area under investigation. The parameters are based on statistically significant regressions but not necessarily linear. In all cases the sorption maxima is larger and the slope decreased when calculated by the Conventional Langmuir equation compared to the Rearranged Langmuir equation. The regression coefficients (R^2) were improved by employing the Conventional Langmuir as a regression model for all soils using data from the region under investigation (Table IV). An evaluation of the

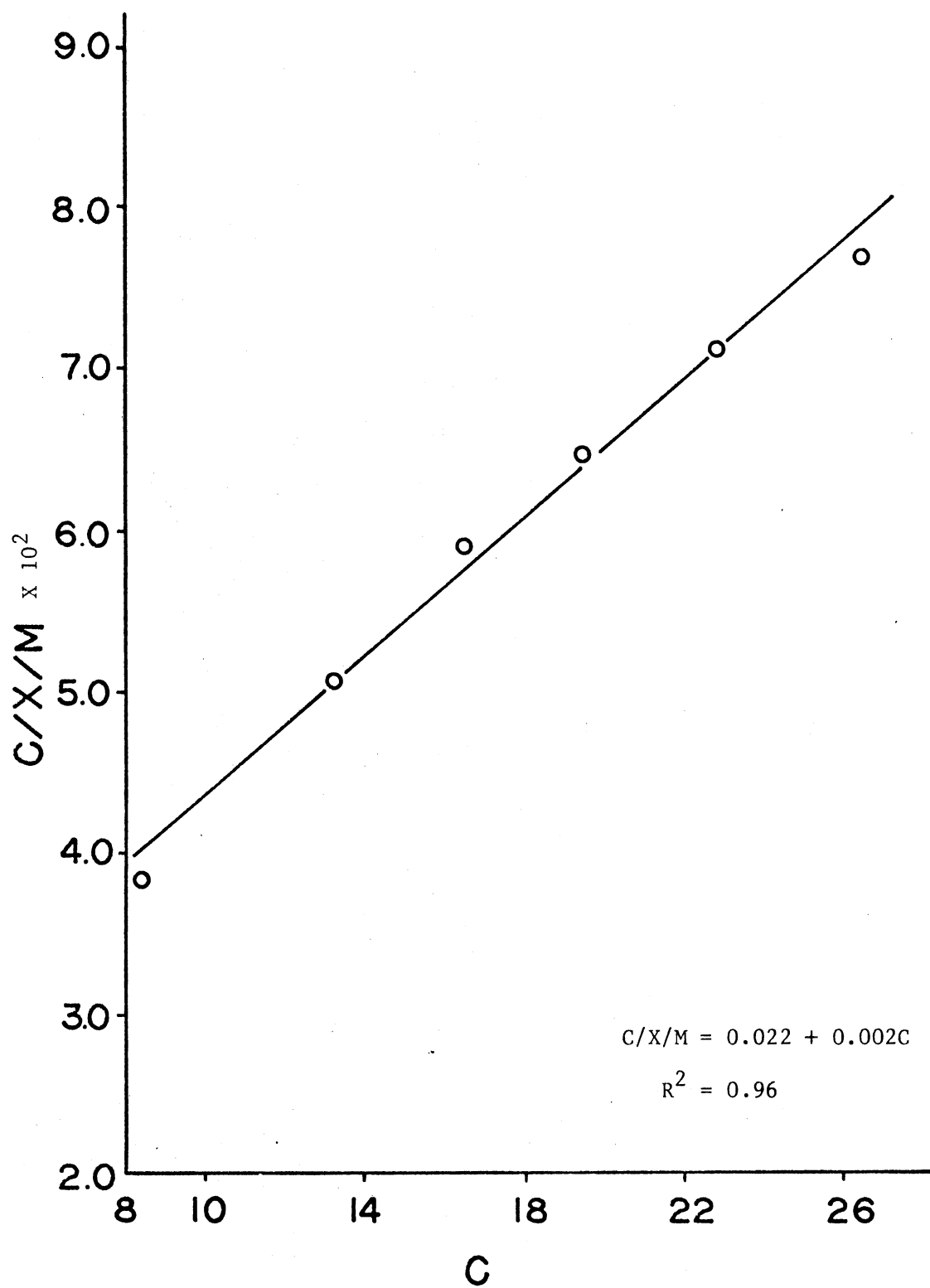


Figure 1. Conventional Langmuir Isotherm for the Summit Soil.

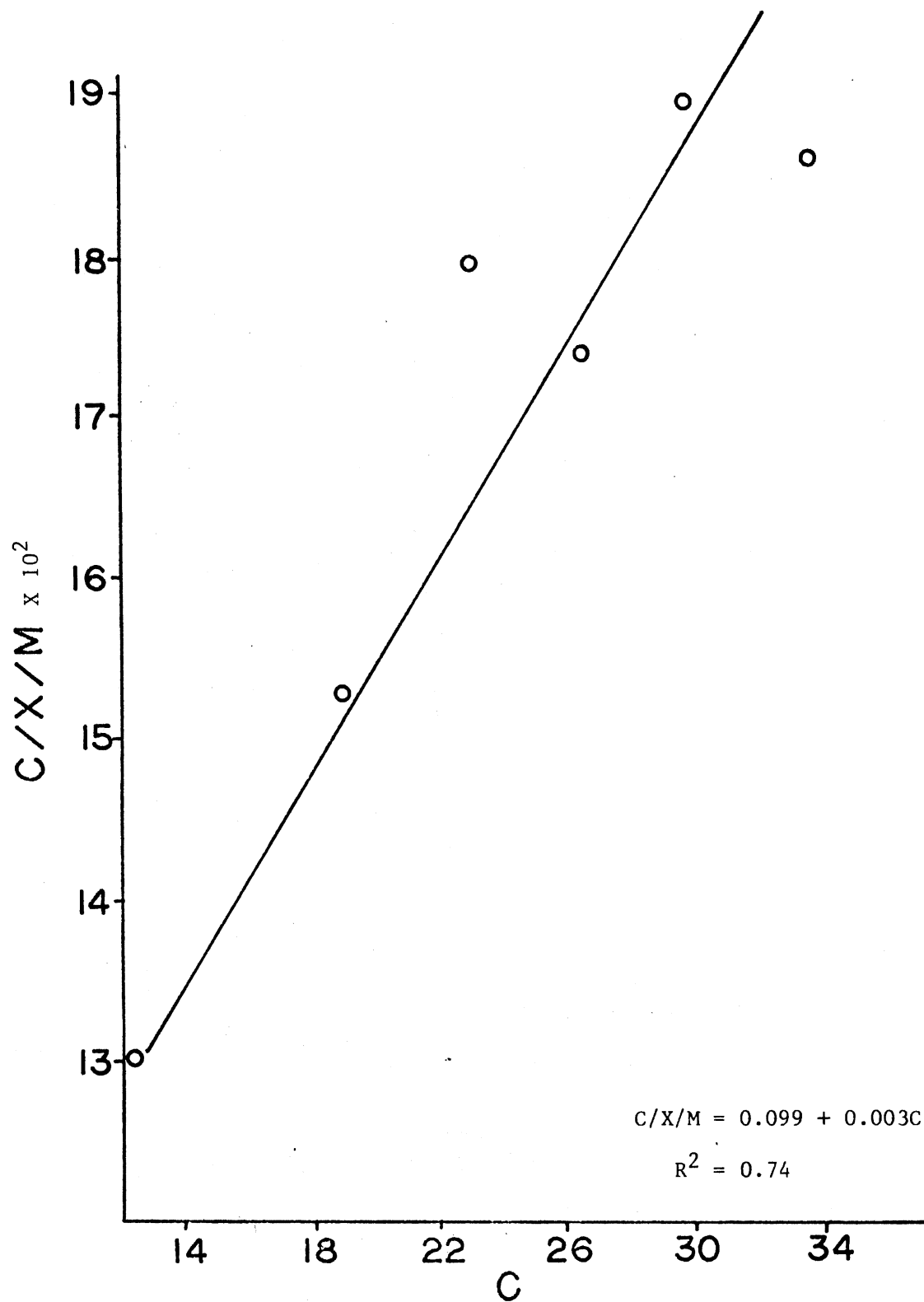


Figure 2. Conventional Langmuir Isotherm for the Ulysses Soil.

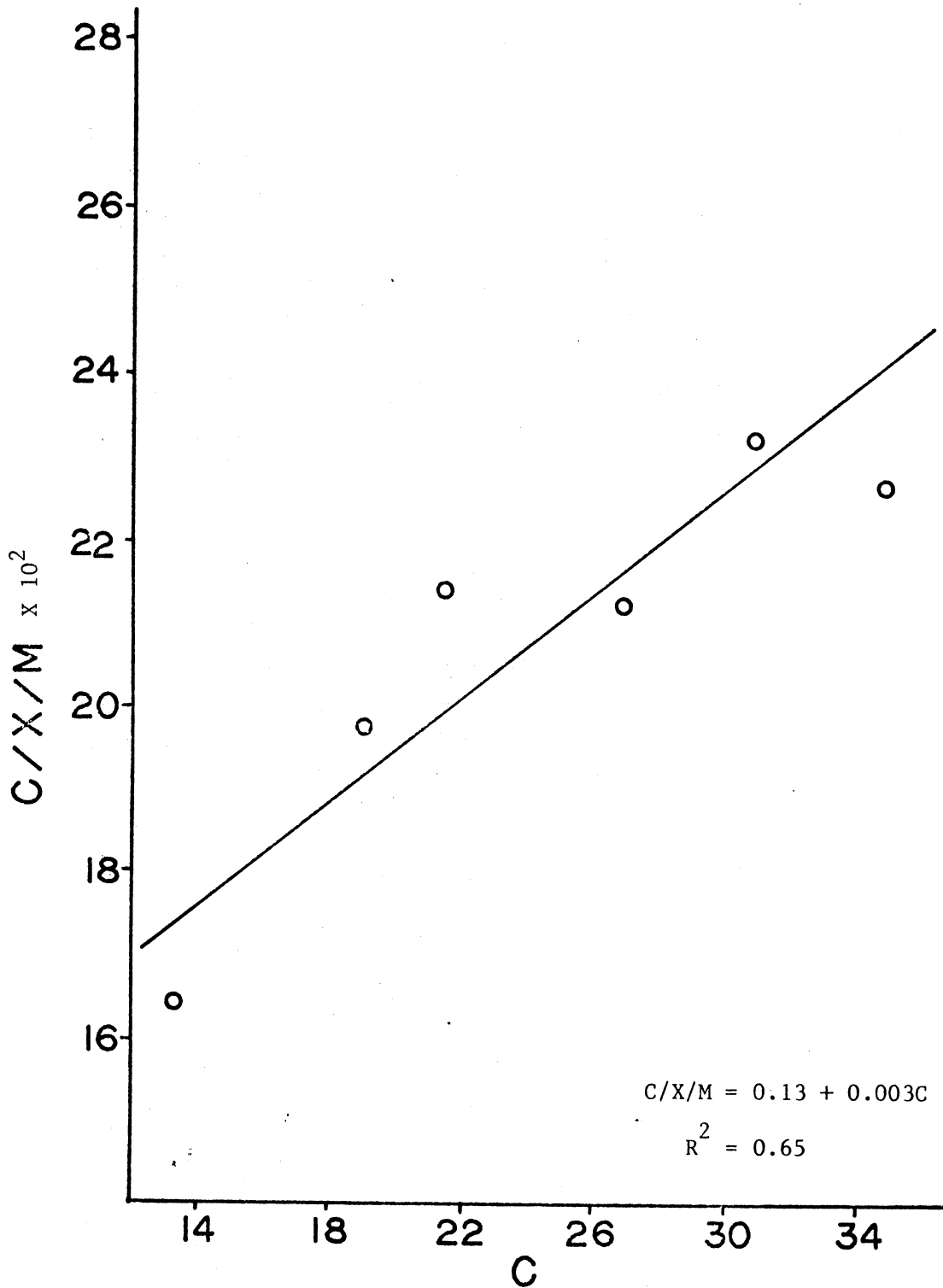


Figure 3. Conventional Langmuir Isotherm for the Kingfisher Soil.

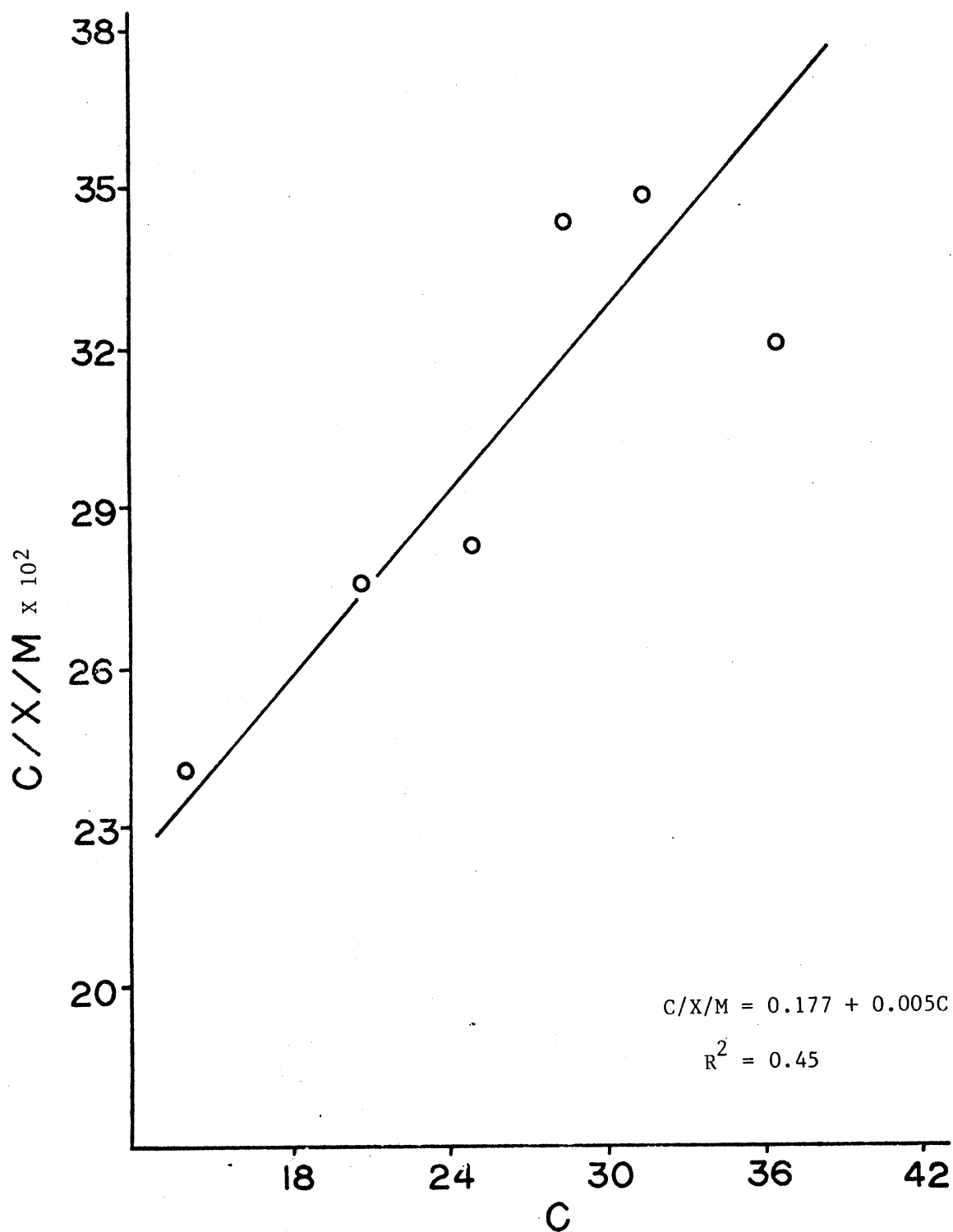


Figure 4. Conventional Langmuir Isotherm for the Tipton Soil.

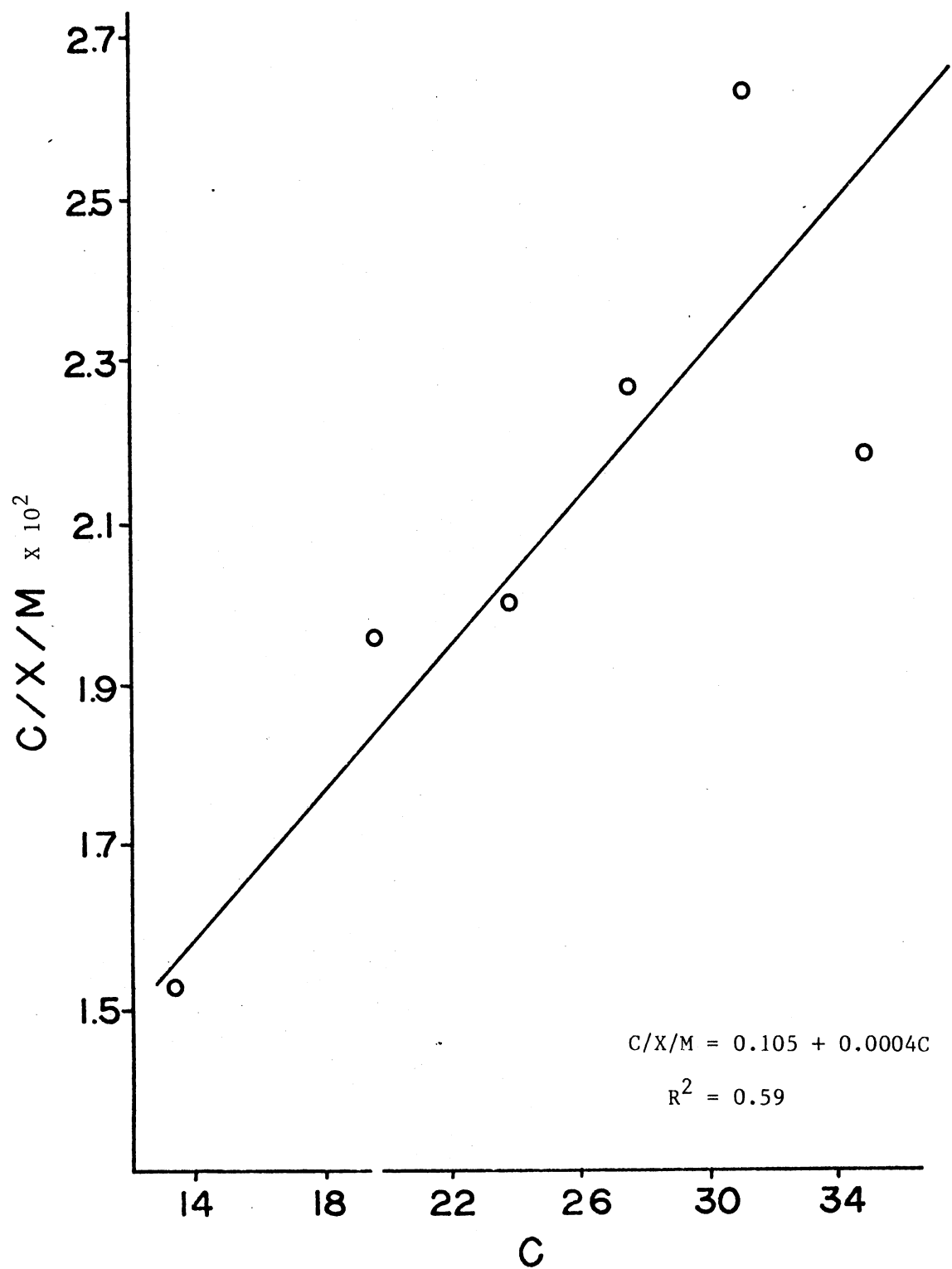


Figure 5. Conventional Langmuir Isotherm for the Bowie Soil.

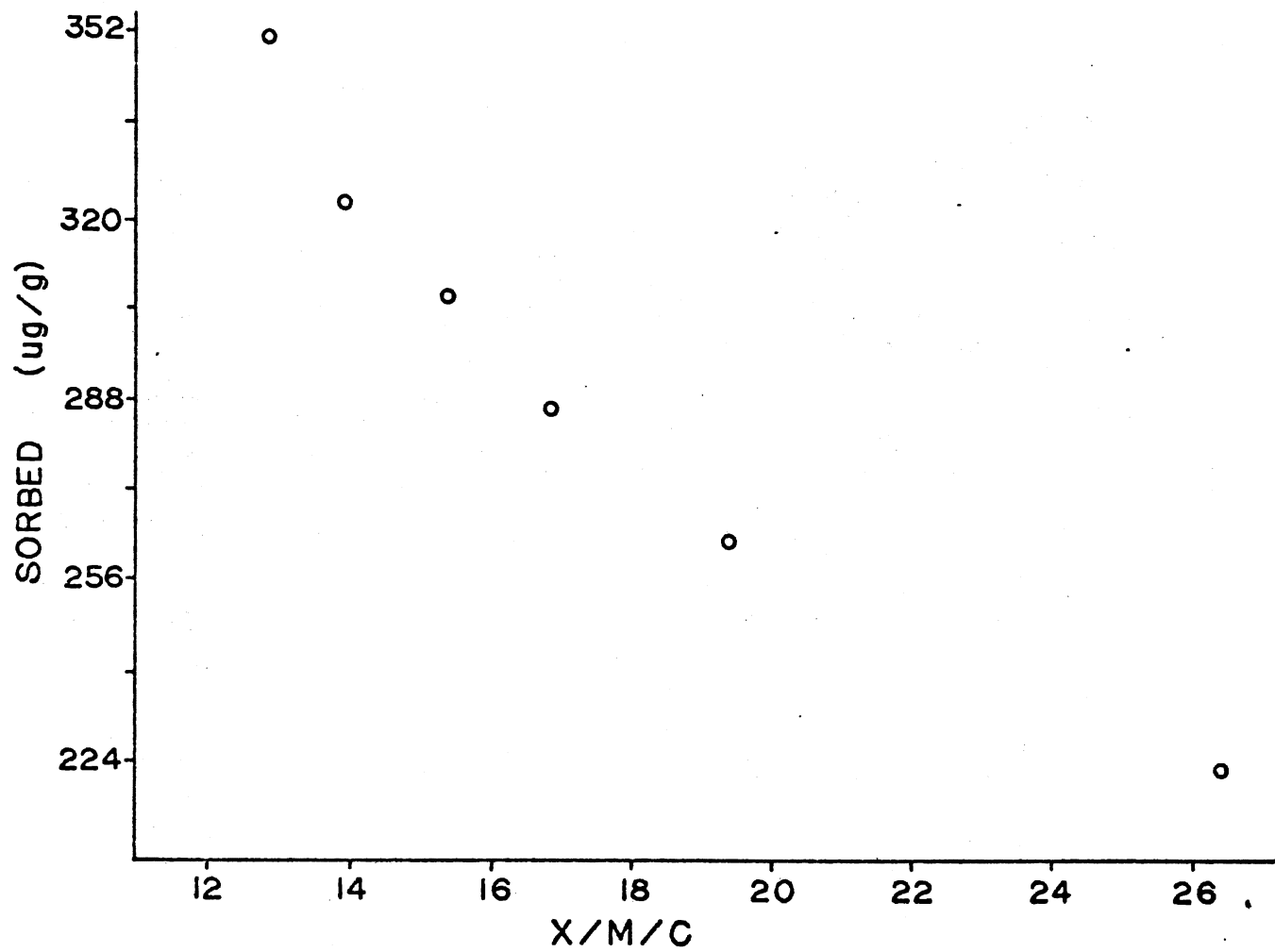


Figure 6. Rearranged Langmuir Isotherm of the Summit Soil.

TABLE IV
REGRESSION STATISTICS FOR THE CONVENTIONAL
AND REARRANGED LANGMUIR EQUATIONS

Soil	Conventional Langmuir		Rearranged Langmuir	
	OSL [*]	R ² [†]	OSL	R ²
Summit	0.0001	0.96	0.0001	0.79
Ulysses	0.0001	0.74	0.0001	0.43
Kingfisher	0.0001	0.65	0.0001	0.33
Tipton	0.0001	0.45	0.07	0.03
Bowie	0.0001	0.59	0.0001	0.16

*OSL signifies observed significance level

†R² signifies regression coefficient

TABLE V
SLOPE (k) AND SORPTION MAXIMA (b) FOR REARRANGED
AND CONVENTIONAL LANGMUIR EQUATION

Soil	Rearranged		Conventional	
	k	b	k	b
Bowie	0.10	166.17	0.04	239.98
Tipton	0.17	105.73	0.03	207.14
Kingfisher	0.05	210.95	0.024	323.29
Ulysses	0.05	253.82	0.03	344.29
Summit	0.12	434.71	0.10	470.89

high and low energy sorption regions from the work of Ashlock (1977) substantiates this observation. It appears that the Conventional Langmuir equation is a better model of P sorption than the Rearranged Langmuir equation. The value of the Rearranged Langmuir equation appears to be in its ability to split curves into regions of different "sorption sites."

Syers et al. (1973) and Ashlock (1977) found the Rearranged Langmuir isotherm could not be satisfactorily resolved into two linear regions for some soils and thus suggesting a possible third region in the transition zone investigated in this study. Figures 7 through 10 contain the Rearranged Langmuir isotherm plots from the work of Ashlock (1977) overlaid with the data of this study for all soils except Tipton. The Summit soil (Figure 7) has three distinct P sorption sites. The same general condition seems to occur for the Ulysses and Kingfisher soils although these intermediate regions were shorter and difficult to evaluate.

It appears from Figure 10, the Bowie soil has only two linear regions eventhough the b and k values are different than Ashlock (1977) observed for this soil. At this point, the lack of singularity in b and k values for both studies can only be attributed to random error. The Tipton soil isotherm contained a large amount of error and is not depicted here.

The Summit soil was the only soil studied that could be classified with certainty as having a third distinct linear region corresponding to a separate sorption site. A possible explanation for this observation is in the soil characteristics listed in Table II. The Summit soil has a high OM content. Although not significantly correlated at the 0.05

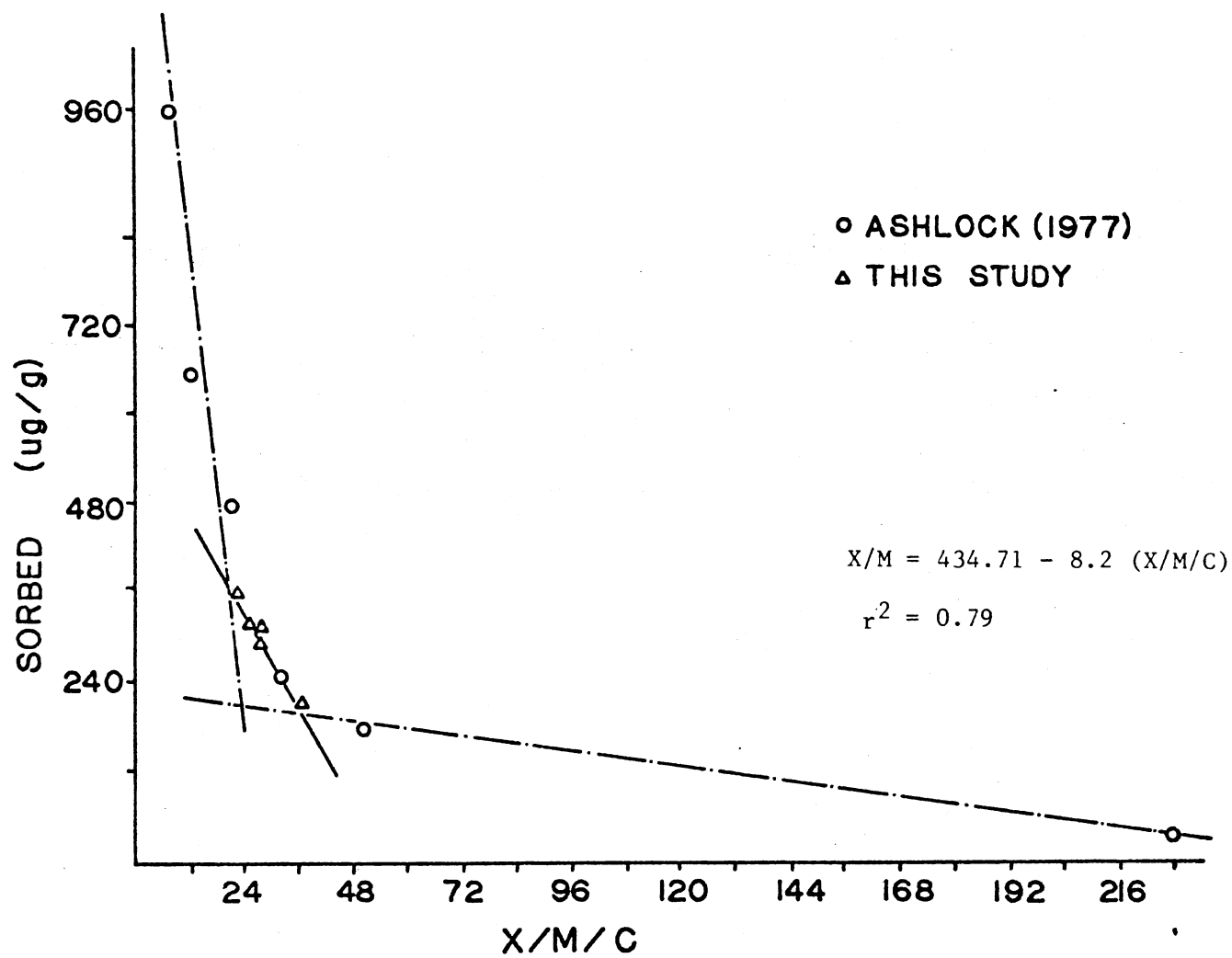


Figure 7. Rearranged Langmuir Isotherm of Summit Overlaid with Data from Ashlock (1977).

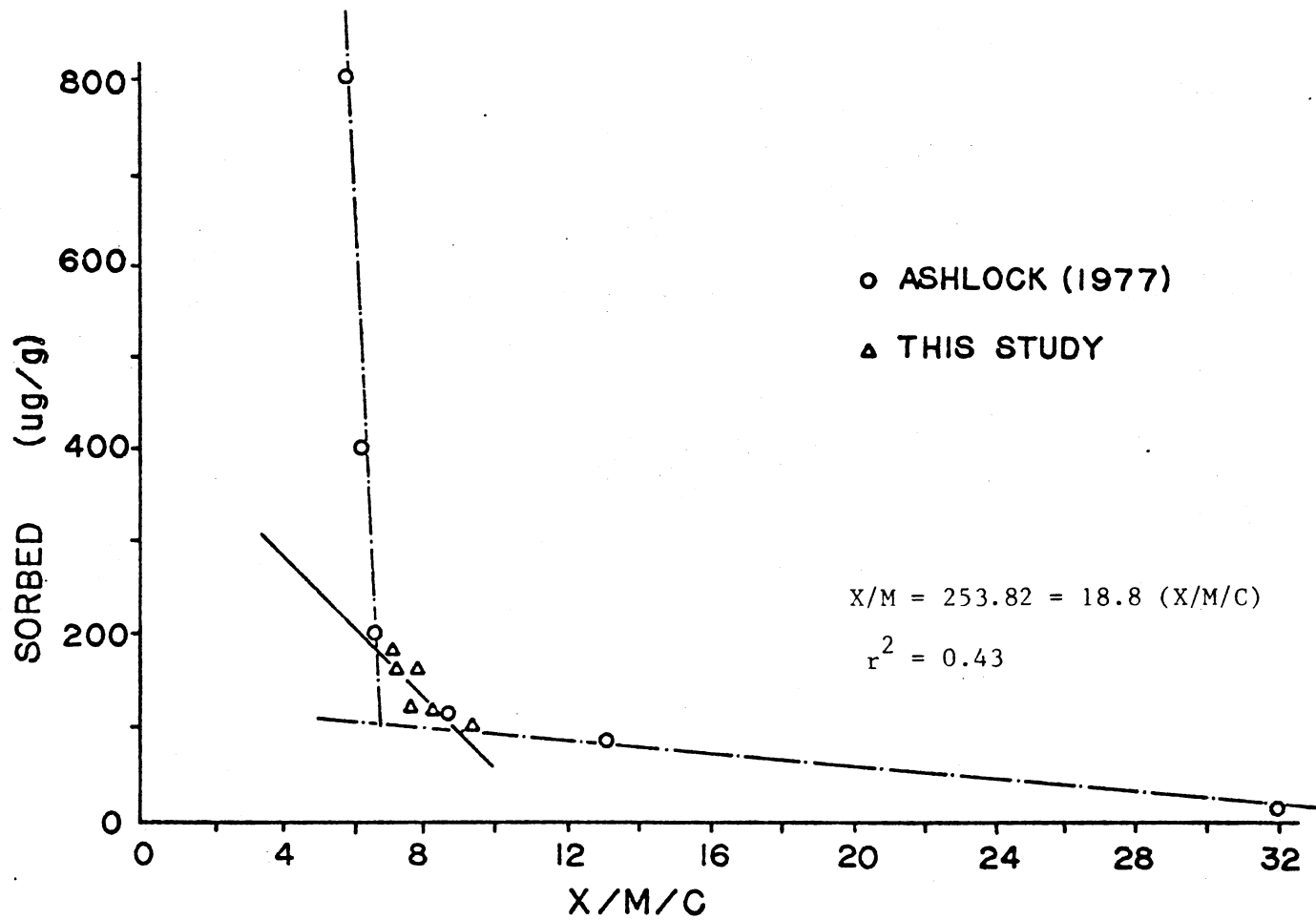


Figure 8. Rearranged Langmuir Isotherm of Ulysses Overlaid with Data from Ashlock (1977).

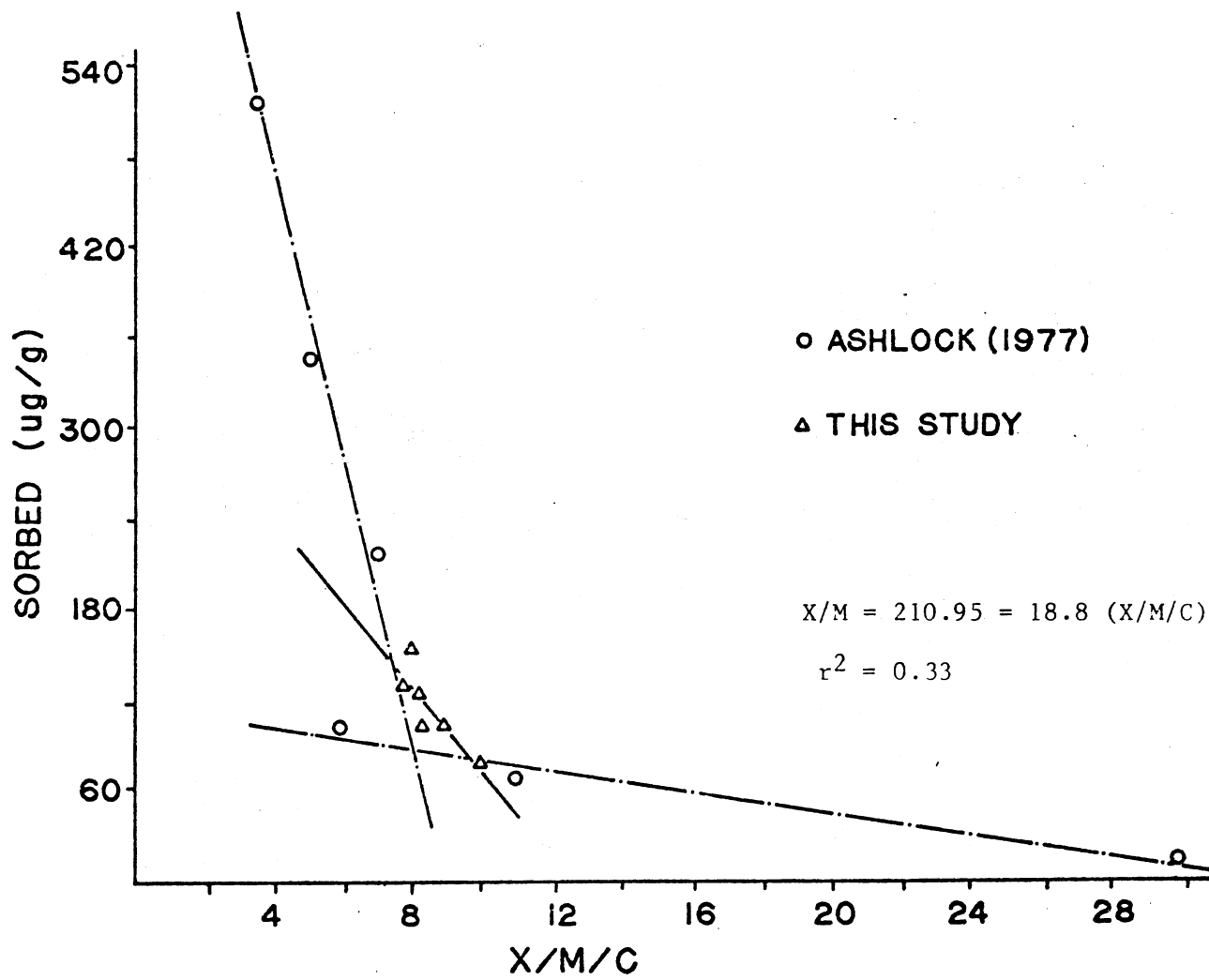


Figure 9. Rearranged Langmuir Isotherm of Kingfisher Overlaid with Data from Ashlock (1977).

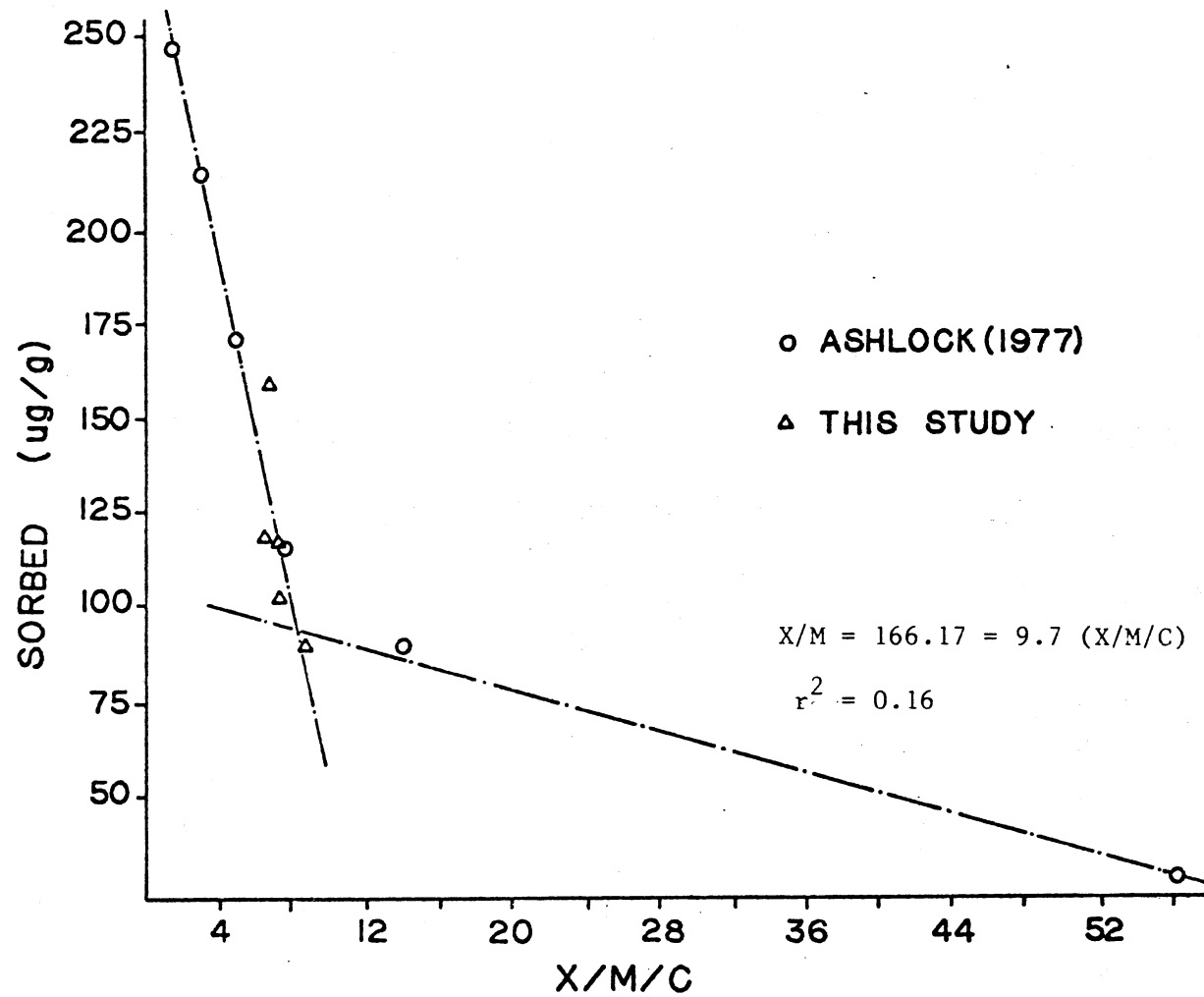


Figure 10. Rearranged Langmuir Isotherm of Bowie Overlaid with Data From Ashlock (1977).

level to sorption parameters in the region studied, OM may still play an important role in P sorption in this region. This soil also has a comparatively high Fe_2O_3 content which may account for a major reaction surface in this region. The Tipton soil, which exhibited the least significant linear response, has a relatively low OM and Fe_2O_3 content. The other soils, which have better statistical linear responses than the Tipton soil but not to the extent of the Summit soil, have OM and/or Fe_2O_3 contents of intermediate values. The percent Al, CEC, and surface area are also relatively high for the Summit soil which may help account for this linear region. It is proposed that the third linear region found in the Summit soil is due to the Fe_2O_3 and OM fractions with the other characteristics playing minor roles.

The sorption parameters b and k of the Conventional and Rearranged Langmuir equations were correlated with soil characteristics (Tables II and III) to help identify those soil characteristics best associated with P sorption in the intermediate region studied. The correlation of b and k values to soil characteristics is based on the premise that all soils have a significantly linear intermediate region. This premise is used only to help identify those soil characteristics that provide a major portion of sorption sites in the intermediate region. The correlation coefficients are listed in Table VI. The Conventional Langmuir equation sorption parameters show significant r values for Fe_2O_3 and Clay content at the 0.05 level and OM content at the 0.10 level for b and Fe_2O_3 , OM, and Clay content at the 0.05 level for k . Ferric Oxide, OM, and Clay content are significantly correlated to b (0.05 level) for the Rearranged Langmuir equation data, while the k value is not significantly correlated to any soil characteristic. Although more intuitive

TABLE VI
 CORRELATION COEFFICIENTS OF b AND k VALUES CORRELATED
 WITH SOIL CHARACTERISTICS FOR CONVENTIONAL
 AND REARRANGED LANGMUIR EQUATION

	Conventional		Rearranged	
	b	k	b	k
pH	-0.11	-0.13	-0.11	0.37
C.E.C.	0.79	0.70	0.80	0.13
SA	0.80	0.55	0.77	-0.12
HSA	0.77	0.59	0.77	-0.06
ExAl	-0.47	-0.11	-0.36	0.04
CaCO ₃	0.33	0.26	0.32	0.34
Fe ₂ O ₃	0.93*	0.87*	0.93*	-0.02
OM	0.77 [†]	0.99**	0.87*	0.20
% Al	0.52	0.77	0.63	-0.04
Sand	-0.83	-0.45	-0.74	0.24
S.H.	0.04	-0.50	-0.13	-0.47
Clay	0.93*	0.80	0.93*	-0.01

[†]Indicates significance at the 0.10 level.

*Indicates significance at the 0.05 level.

**Indicates significance at the 0.01 level.

than statistical from this correlation data, this helps to support the belief that Fe_2O_3 and OM content are the major contributors of sorption sites in the intermediate region.

In an attempt to quantify the effect of soil characteristics on the sorption maxima (b) multiple regression equations were constructed using only the significant soil characteristics for data from both isotherm models (Table VII). The multiple regression equation for the Rearranged and Conventional isotherm data were significant at the 0.10 level.

TABLE VII
 MULTIPLE REGRESSION EQUATIONS OF b. USING SIGNIFICANTLY
 CORRELATED SOIL CHARACTERISTICS

Source	OSL*	R ² †	C.V.**	Regression Equation
Conventional Langmuir equation data	0.10	.90	14.4	$\hat{Y} = 178.16 + 53.77(\% \text{ Fe}_2\text{O}_3) + 4.86(\% \text{ Clay})$
Rearranged Langmuir equation data	0.10	.91	23.2	$\hat{Y} = 67.92 + 70.64(\% \text{ Fe}_2\text{O}_3) + 5.44(\% \text{ Clay})$

*OSL signifies observed significance level

†R² signifies regression coefficient

**C.V. signifies coefficient of variation

CHAPTER V

SUMMARY AND CONCLUSION

In order to investigate P sorption in the undefined intermediate region of the Rearranged Langmuir equation plots from Ashlock's work, five important Oklahoma soil series were selected for this study. Samples were equilibrated with different P treatments in an attempt to discover the nature of P sorption in the intermediate region and perhaps, identify the soil characteristics responsible. The following conclusions were reached from this study.

1. All soils showed significant differences in the amount of P sorbed due to increasing P treatment concentration, except treatments C and D for Ulysses, D and E for Tipton, and E and F for Bowie soils (Table III, p. 20). The unexpected decrease in amount of P sorbed in these treatments of the Tipton and Bowie soils is believed to be due to sampling error associated with non-uniform distribution of residual P from past fertilization.

2. Langmuir Adsorption isotherm was distinctly linear for the Summit soil in the intermediate region. Use of the Conventional Langmuir equation for the intermediate segment improved the regression statistics over the Rearranged Langmuir equation (see Table IV, p. 28). The major benefit of the Rearranged Langmuir equation is its ability to separate the linear sorption regions which may be indicative of adsorption sites. The sorption isotherms were used to predict b (sorption maxima) and k

(slope) values.

3. Correlation coefficients (r) were used to measure the relationship of various soil characteristics to sorption parameter (b). Significant correlation was found for Fe_2O_3 , OM, and Clay content when both Conventional and Rearranged Langmuir equations were used. The study-identified linear segment (third P sorption region) of the Summit soil is believed to be due to its high Fe_2O_3 and OM content.

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