

The rate at which the soils reached equilibrium was not the same for all soils and a diffusion phenomena appears to control the rate at which a soil attains its maximum CIPC adsorption.

CIPC adsorption on the soils increased as a function of the organic matter content. Nyssa sil (1% organic matter) and Hembre 1 (29% organic matter) adsorbed $192 \frac{\mu\text{g CIPC}}{\text{g soil}}$ and $636 \frac{\mu\text{g CIPC}}{\text{g soil}}$ respectively. The internal pore space of a soil component such as pumice may also contribute to CIPC sorption as illustrated by the Deschutes sl which contains 0.9% organic matter but adsorbed $334 \frac{\mu\text{g CIPC}}{\text{g soil}}$. In general more CIPC was adsorbed at 0°C and 25°C than at 50°C.

Negative ΔH values over a temperature range of 0°C to 25°C suggest an exothermic process of adsorption while positive ΔH values over a temperature range of 25°C to 50°C suggest a more endothermic process of adsorption. The low ΔH values (+2.5 kcal to -7.0 kcal) indicate a weak physical adsorption due to coulombic forces, Van der Waal forces, and hydrogen bonding. Adsorption of CIPC on soil was described by the Freundlich equation, but not by the Langmuir equation.

Higher than normal rates of CIPC application must be practiced in soils with a high organic matter content as much of the applied CIPC will be adsorbed onto the organic matter complex and thus less effective in weed control. The low ΔH values observed for CIPC

adsorption onto the soil indicates that CIPC from a purely chemical standpoint is weakly adsorbed, however, relative to certain other herbicides, CIPC is strongly retained in a soil system.

Kinetics and Thermodynamics of CIPC
Adsorption on Several Oregon Soils

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KINETICS AND THERMODYNAMICS OF CIPC ADSORPTION ON SEVERAL OREGON SOILS

INTRODUCTION

Demographic projections place the world population at seven billion people by the year 2,000. As the population of the world increases more food of better quality must be grown on less acreage of available land. Intensified use of agricultural chemicals for food production greatly increased following W. W. II and today well over 200 chemicals are used to control weeds, insects, and disease. The use of chemicals has been a great boon to agricultural production. It is estimated that 30% of the protein supply of the United States would be lost if the use of pesticides were to be discontinued; and some 80% of our high vitamin crops could not be grown. Thus the need for use of chemicals in our environment is well documented, but this use has not been without misgivings.

Chemicals introduced into our environment are not stationary. The chemicals are cycled through the soil, water, plant, and gaseous phases of our environment. In each phase, the accumulation, persistence, mode of action, and interaction between different chemicals must be studied. Short and long term effects on the living as well as non-living components of each phase must be understood with the consequences of the effects projected toward man and the quality of

his environment. It is in part with this philosophy that the study of CIPC adsorption on the soil phase of the environment was initiated.

OBJECTIVES

The objectives of this study were to determine the effects of the soil parameters of pH, organic matter, sesquioxides, and clay content on the rate of CIPC adsorption and on the total quantity of CIPC adsorbed at equilibrium conditions. Enthalpy values which reflect the bonding strength of CIPC adsorption onto a soil were to be related to chemical or physical bonding mechanisms.

LITERATURE REVIEW

Isopropyl-N-(3-chlorophenyl) Carbamate, CIPCDevelopment

Carbamic acid and the effect of its esters on plant growth were first studied by Frissen in 1929 (Klingman, 1961). Further work was largely neglected until Templeman (1945) investigated the activity of many arylcarbamic esters and thiocarbamates as plant growth substances. Using oats as a test plant, Templeman retarded plant growth quite effectively with Isopropyl Phenyl-Carbamate (IPC). Further studies by Ennis (1947) on oats and barley demonstrated that soil applied IPC provided the most effective means of growth reduction. Because of the short residual life of IPC, a new derivative of IPC, called Isopropyl-N-(3-chlorophenyl) Carbamate, (CIPC), was developed (Witman and Newton, 1951). Using barley as a test plant, DeRose (1951) found CIPC persisted in the soil about twice as long as IPC.

Use and Mode of Action

CIPC acts as a highly selective pre-emergence and early post-emergence herbicide. Effective control of chickweed, purslane, smartweed, barnyard grass, crabgrass, and dodder is obtained in

such crops as ryegrass, bentgrass, fine fescues, alfalfa, blackberries, blueberries, carrots, and cotton (Pittsburgh Plate Glass Company, 1964a). Plant growth control is obtained principally as the CIPC enters the plant through the root system and acts as a mitotic poison to inhibit new cell growth in susceptible weed species (Klingman, 1961).

CIPC may be applied to the soil either in a water emulsion spray or as dry granules with a rate of application from two to eight pounds per acre (Pittsburgh Plate Glass Company, 1964a). Factors which affect the application rate include: the weed species present, the crop, the soil texture, and the soil temperature (Herbicide Handbook of the Weed Society of America, 1961). Application of CIPC during cooler temperature periods which are followed by low intensity rainfalls increases the effectiveness of CIPC, since the volatility and microbial degradation is reduced (Klingman, 1961). Low intensity rainfall after CIPC applications helps carry the chemical into the soil and also assists the germination of weed and grass seeds to the stage of growth when CIPC is most effective (Pittsburgh Plate Glass Company, 1964b).

Residual Life

The residual life of CIPC depends primarily upon the factors of temperature, moisture, and organic matter content of the soil

(Klingman, 1961). The average persistence of CIPC in a sandy soil is from three to five weeks and less in soils high in organic matter (Herbicide Handbook of the Weed Society of America, 1967). Warm temperatures (75°F) coupled with moist conditions increases the microbial activity and results in rapid CIPC degradation. Using soil enrichment techniques, the degradation of CIPC to 3-chloroaniline, carbon dioxide, and isopropyl alcohol, by Pseudomonas striata, Flavobacterium Sp., Agrobacterium Sp., and Achromobacter Sp. has been demonstrated by Kaufman and Kearney (1965). Recent investigations have shown that CIPC applications with Naphthyl N-methyl Carbamate, (Sevin), acting as a microbial inhibitor has doubled the residual life of CIPC (Appleby, 1968). Application of four pounds per acre of CIPC on a Fincastle silt loam resulted in negligible CIPC vapor losses at 35°C but vaporization of CIPC increased to a 12% loss at 45°C (Parochetti and Warren 1966).

Adsorption

Chemical and Physical Forces

Adsorption systems consist of a liquid, gas, and solid phase, and the accompanying interphases. When the concentration of a substance becomes higher in the interphase than in the solid or liquid phase, the substance is adsorbed. Such a definition based upon

concentration carries no implication of adsorption mechanism (Cassidy, 1951).

Colloidal particles with a diameter of 0.001 to 1 micron possess a large surface area that may offer many sites for adsorption and hence adsorption is often considered to be a colloidal phenomenon (Dean, 1948). Specific types of adsorption that occur on solid surfaces can be related to the various forces that extend from the solid phase (Osipow, 1962).

The potential energy of both the adsorbing surface (adsorbent) and the molecule to be adsorbed (adsorbate) decreases as the molecule approaches the bonding site. The kinetic energy of the molecule increases as it approaches the adsorbing surface. Thus, unless adsorption occurs the molecule may escape the surface. Two general types of adsorption known as chemical and physical adsorption prevent the escape of the molecule from the surface (Daniels and Alberty, 1967).

In chemical adsorption, a chemical bond, generally a result of coulombic forces (Kunze, 1966), forms between the first layer of molecules and the adsorbent surface (Daniels and Alberty, 1967).

The coulombic energy of attraction measured relative to the energy at infinite separation is mathematically represented by $\frac{-e^2}{r}$ where r is the distance between the charge centers (e). Coulombic forces, polarization forces, and London dispersion forces were

termed long range forces by Frissel and Bolt (1962) whereas hydrogen bonds and high order Van der Waal forces were termed short range as they demonstrated a very steep dependency upon distance. Adsorption of O-phenyldiamine, P-phenyleneammonium, benzidine, and other organic cations on the surface of montmorillonite clay include not only coulombic forces due to the ionic nature of the compound, but also Van der Waal forces between surrounding surfaces and the molecule (Hendricks, 1941). Additional adsorption of many molecular layers beyond the first layer of chemically adsorbed molecules may occur through physical adsorption (Bailey and White, 1964).

Physical adsorption may be attributed in part to weak Van der Waal forces (Kunze, 1966). The potential energy of attraction of permanent dipoles is inversely proportional to the distance to the sixth power and inversely proportional to the temperature (Daniels and Alberty, 1967). In physical adsorption, bond formation does not occur between the adsorbate and adsorbent and many layers of adsorbate may associate with the adsorbing surface (Bailey and White, 1964).

Utilizing soil columns of Hagerstown sil saturated with various ions and leaching with organic solvents, Brady (1965) concluded that physical adsorption best described the retention of CIPC in a soil system. Studying the adsorption of CIPC on activated carbon at temperatures of 20°C and 37°C, Schwartz (1967) calculated a heat of

reaction value of -7.0 kcal per mole from the van't Hoff equation. A heat of reaction value in this magnitude may be considered a weak physical bond between the CIPC and the activated carbon.

Influence of Soil Separates and the Soil Environment

The soil consists of various individual fractions each of which contributes to the total adsorptive capacity. Constituents such as organic matter, clay minerals, crystalline and amorphous oxides, pH, and moisture influence pesticide adsorption.

Organic Matter. Organic matter contains functional entities of carboxyl, amino, phenolic, hydroxyl, and alcoholic hydroxyl groups (Bailey and White, 1964). These groupings are dependent upon soil pH and may carry a negative or positive charge. Lambert, Porter, and Schieferstein (1965) have contributed much of the adsorptive ability of a soil to the organic matter fraction. Calculation of sorption coefficients for uncharged organic molecules upon soils of various texture yielded similar sorption coefficient values. The calculation of sorption coefficients is based upon the assumption that sorption of the chemical occurs in the organic matter fraction. These authors further explain that quite different results might be expected when chemicals are used that exhibit ion exchange, pH sensitivity, and other phenomena.

ED₅₀ values obtained from phytotoxicity studies of CIPC on oat seedlings with 32 different soils were found to correlate most closely with percent organic matter (Harris and Sheets, 1965). An ED₅₀ value is the concentration in ppm by soil weight required to reduce the fresh weight of a plant by 50%.

The influence of soil organic matter on CIPC effectiveness was also observed by Blauch and Fults (1953). CIPC application rates of three pounds per acre on Valentine sand and six pounds per acre on Terry clay resulted in non-selective phytotoxicity whereas selective phytotoxicity was observed on Fort Collins loam with application rates of nine pounds per acre. The Fort Collins loam in contrast to the other two soils contained a high percentage of nitrate, phosphate, and organic matter. The investigators felt that the organic colloids played an important role in the adsorption of the CIPC.

Clay and amorphous colloids. Clay minerals carry a net negative charge as a result of broken edges and isomorphous substitution in the crystal lattice, thus sites for cation exchange and electrostatic attraction of molecules from the bulk soil solution are available. A positive charge at low pH values may also occur because of the presence of alumina groups (Frissel and Bolt, 1962). Such groups could serve as adsorptive sites for negatively charged molecules. In addition to electrostatic attraction, physical adsorption of

organic molecules between the silicate sheets of montmorillonite clay in the form of a two dimensional liquid has also been reported (MacEwan, 1948). Crystalline and amorphous oxides and hydroxides of iron and aluminum may also contribute to the adsorptive capacity of a soil (Bailey and White, 1964). CIPC adsorption mechanisms were studied by Brady (1965) by saturating soil with various cations such as sodium, potassium, and calcium and leaching the soil with a 40 ppm solution of CIPC. Examination of the leachate lead Brady to conclude that neither cation nor anion exchange contributed materially to the retention of CIPC by a soil system.

Adsorption studies of CIPC on 32 different soils demonstrated a low correlation value of 0.16 between percent adsorption and clay content; however, a good correlation of 0.62 was observed between ED_{50} values and cation exchange capacity (Harris and Sheets, 1965).

The chemical properties of the soil as well as the nature of the adsorbent affect the adsorption of herbicides. The hydrogen ion concentration of a soil system determines the extent of dissociation of a compound and the adsorbent. At a pH value of 4.8 appreciable quantities of the protonated CIPC molecule could be expected (Schwartz, 1967). A protonated species could be expected to enter into hydrogen bonding with such atoms as oxygen or other electronegative atoms.

Utilizing bentonite at pH 8.4 and pH 2.1, Harris and Warren (1964) observed essentially no change in the CIPC adsorption at a CIPC concentration of 1.0×10^{-4} M. At a CIPC concentration of 1.5×10^{-4} M, the more acid bentonite system adsorbed slightly more CIPC.

The moisture content of the soil also is suspected to influence the CIPC adsorption that occurs. It may actually compete with the herbicide molecule for adsorptive sites. Tubes constructed of paraffin coated cheese wrap were filled with soil and the CIPC penetration was observed after leaching with 1/2 or 1 inch of water. CIPC penetrated three to four inches in a moist clay soil at 60 cm tension and only penetrated one to two inches in a dry clay soil. In a moist clay soil continuous water columns would be expected to aid in the downward movement of the CIPC (Hurtt, Mead, and Santelmann, 1958).

CIPC applied to Gloucester fine sandy loam at a rate of eight pounds per acre resulted in no change in effectiveness as a function of soil moisture (Havis, Ticknor, and Bobula, 1959).

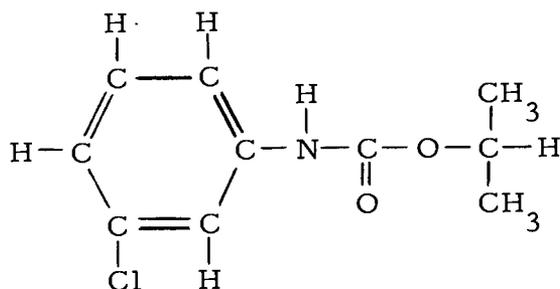
In summary, many factors affect the quantity and strength of adsorption of soil applied herbicides. Many problems face the investigator who tries to discern the contribution of each individual soil fraction to the total amount of herbicide adsorbed. As Harris and Warren (1964) stated:

Herbicide research is at a stage where broad generalizations about adsorption are not very useful. One needs to define specifically such factors as soil type, pH, moisture content, mineralogical character, organic matter content, and temperature of the soils.

MATERIALS AND METHODS

Chemical and Physical Properties of CIPC

Isopropyl-N-(3-chlorophenyl) Carbamate (CIPC) was used in adsorption studies on several Oregon soils. The structural formula with various physical and chemical properties of CIPC are given below.



Isopropyl-N-(3-chlorophenyl) Carbamate

Formula	$C_{10}H_{12}ClNO_2$
Molecular weight	213.7
Melting point	$38^{\circ}C-40^{\circ}C$
Boiling point	Decomposes
Decomposition temperature	$150^{\circ}C$

The CIPC was supplied in crystalline form by the Department of Agricultural Chemistry at Oregon State University.

Selection of Soils

Seventeen Oregon soils were characterized for chemical and

physical properties. After chemical and physical analysis, six soils which provided a broad range of physical and chemical properties were selected for the pesticide adsorption studies. The selected soil types included Hembre loam, La Grande silt loam, Woodburn silt loam, Deschutes sandy loam, Nyssa silt loam, and Kenutchen clay. These soils belonged to a group of Oregon soils known as benchmark soils. The benchmark soils are representative of a great part of the varying soil characteristics within the state of Oregon.

Chemical Characterization of Soils

Seventeen benchmark soils were analyzed for iron oxide, cation exchange capacity, exchangeable aluminum, and extractable aluminum. Information on soil pH, percent clay, and percent organic matter was available from soil survey laboratory reports.

Iron Oxide Content. The free iron oxide content was determined subsequent to the removal of calcium carbonate and organic matter. The carbonate was removed by addition of 50 ml of 1 N pH 5 NaOAc buffer to five g of air dry soil. The sample was placed in a near boiling water bath for 30 minutes and stirred intermittently. The sample was centrifuged and the clear supernatant decanted and saved. Each sample was washed with the NaOAc once if the soil was non calcareous and twice if the soil was calcareous. Following the

removal of the carbonate, the sample was treated with increments of 30% H_2O_2 and heated on a hot plate until the organic matter was oxidized. The sample was then washed twice in pH 7 NaOAc and transferred to a centrifuge tube.

The iron oxide was extracted with a composite solution of 0.12 M sodium bicarbonate (NaHCO_3) and 0.3 M sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$). Forty ml of the composite buffer-citrate solution and one g of $\text{Na}_2\text{S}_2\text{O}_4$ was added to each sample. After heating the samples at 75°C - 80°C for five minutes a second one g portion of $\text{Na}_2\text{S}_2\text{O}_4$ was added and the sample heated for another five minutes. The sample was centrifuged and the decantate collected in a 250 ml volumetric flask. The extraction with the composite buffer-citrate solution was repeated with the decantate from the second extraction added to the 250 volumetric flask.

The iron content of the extractant was determined colorimetrically on a Bausch and Lomb Spectronic 20 spectrophotometer at 500 $\text{m}\mu$ (Snell and Snell, 1949). Iron analysis was also determined on the same extracts by atomic absorption using a Perkin Elmer 303 atomic absorption unit at 248.3 $\text{m}\mu$ wavelength.

Exchangeable Aluminum. Exchangeable aluminum was extracted from five g of air dry soil four times with 20 ml portions of 1N KCl. After each addition of KCl, the sample was thoroughly

mixed, centrifuged, and the clear supernatant saved. Upon final extraction the collected supernatant was diluted to 100 ml with 1N KCl. The extractant was analyzed for aluminum colorimetrically according to the method developed by Hsu (1963) with thioglycollic acid added to eliminate iron interference. The aluminum in the extract was measured colorimetrically with a Bausch and Lomb Spectronic 20 spectrophotometer at a wavelength of 525 m μ . The extractant was also analyzed on a Perkin Elmer 303 atomic absorption unit at a wavelength of 309.6 m μ wavelength utilizing a nitrous oxide flame.

Extractable Aluminum. The procedure followed for determination of extractable aluminum was identical with the method for exchangeable aluminum except that 1N pH 4.8 NH₄OAc was used as the extraction reagent.

Cation Exchange Capacity. A five g air dry soil sample was weighed into a centrifuge tube and washed twice with 50 ml portions of 1N pH 5 NaOAc to remove carbonates if their presence was suggested by soil pH. The soil was saturated with calcium ion by four separate washings with 25 ml portions of 1N CaCl₂. Each time the sample was thoroughly shaken, centrifuged, and the clear supernatant discarded. Excess CaCl₂ was removed by washing the sample twice with 25 ml portions of H₂O and twice with 25 ml portions of 99%

methanol, each time discarding the clear supernatant. The supernatant after each wash was checked for the presence of chloride with 0.2 M AgNO_3 . The sample was considered free of excess Ca ion upon a negative chloride test. The adsorbed calcium was displaced by five extractions with 15 ml portions of 1N MgCl_2 . Each time the sample was shaken for five minutes, centrifuged, and the clear supernatant added to a 100 ml volumetric flask. The MgCl_2 extract was diluted to 100 ml with 1N MgCl_2 after the final extraction. The calcium in the extract was determined with a Perkin Elmer 303 atomic absorption unit at 422.7 m μ .

Adsorption of CIPC

Kinetics of CIPC Adsorption

Preparation of CIPC adsorption isotherms requires equilibrium between the CIPC in solution and that adsorbed onto the soil surface. The following procedure was used to determine the time required to achieve equilibrium in the CIPC adsorption system.

Four hundred ml of 50 ppm CIPC in aqueous solution was added to 16 g of air dry soil. The soil-CIPC system was placed in a constant temperature water bath at 25^oC and mixed continuously with a magnetic stirrer. Solution samples were removed through a fritted glass filter (4-5.5 μ pore size) by application of a vacuum. Soil

solution samples were collected in graduated centrifuge tubes and the volume measured. Samples were removed after ten minutes, one-half hour, one hour, three hours, five hours, and seven hours equilibration time. The CIPC in the soil solution was extracted with slightly less than 25 ml (in three eight ml portions) reagent grade CS_2 in 125 ml separatory funnels. The extractant from each separation was collected in a 25 ml volumetric flask and diluted to volume with CS_2 after the final addition of extractant.

Effects of Temperature and Concentration on CIPC Adsorption

Calculation of heat of adsorption values requires adsorption isotherms at several temperatures. The following procedure was used for adsorption studies as a function of temperature and CIPC concentration.

Four hundred ml of the CIPC aqueous solution (20, 25, 30, 40, 50, or 60 ppm) was added to a 600 ml beaker which contained 16 g of air dry soil. The soil-CIPC system was placed in a water bath which was controlled at a temperature of either 0°C , 25°C , or 50°C . Each soil-CIPC system was stirred continuously with an immersible magnetic stirrer or with a stirring rod powered by an electric motor. After three hours of equilibration time, samples of the soil-CIPC system were removed through a fritted glass filter by application of a vacuum. The volume of solution removed was measured in

graduated centrifuge tubes. The solutions were extracted for CIPC with CS₂ in the same manner as described for the equilibrium time CIPC adsorption studies. Solutions of CIPC were treated similarly to determine the adsorption of CIPC on the apparatus as a function of time, temperature, and CIPC concentration.

Quantitative Analysis of CIPC

The CIPC concentration in the CS₂ extracts of the CIPC-soil system solutions was determined with an Aerograph Hy-Fi model 600 gas chromatograph. A 10 μl syringe was first filled with CS₂ and drained until it contained exactly one μl. Five or six μl of the CS₂ extract solution was introduced into the syringe followed by a discharge of solution until the syringe contained four μl of solution (three μl of CS₂ extract and one μl of pure CS₂ solvent). The four μl were then injected into the gas chromatograph. Duplicate injections were accomplished on each sample. A third injection was introduced if the peak heights from the two initial injections did not agree within 10% limits. Operating conditions of the gas chromatograph were as follows:

Oven temperature - 200°C

Column - Five feet, 10% SE 30 on 60/80 gas chrom Q

Detector - Flame ionization

H₂ flow rate - 95.5 ml/min

N₂ flow rate - 85.5 ml/min

Air flow rate - 600 ml/min

Detector time - Four min/sample

Recorder type - Microcord 44

A standard curve from 20 ppm to 60 ppm CIPC was prepared by plotting peak height versus CIPC concentration.

Calculation of CIPC Adsorbed

The quantity of CIPC adsorbed per 16 g of air dry soil was calculated from the following equation:

$$\frac{X}{m} = A - [(BC) + (DC)] \frac{400 \text{ ml}}{C}$$

$$\frac{X}{m} = A - [B + D] 400$$

where: $\frac{X}{m}$ = μg CIPC adsorbed per 16 g of air dry soil.

A = total initial μg CIPC in the soil-CIPC system.

B = adjusted ppm, i. e., ppm CIPC in the CS₂ extract multiplied by 25 over the volume of sample obtained from the soil-CIPC system by vacuum sampling.

C = volume of the sample obtained from the soil-CIPC system by vacuum sampling.

D = CIPC adsorption in ppm on the glass sampling system, i. e., ppm CIPC in initial solution minus the CIPC concentration in ppm of the CIPC solution after a given time of equilibration.

RESULTS AND DISCUSSION

Kinetics and Magnitude of CIPC Adsorption

Attainment of Equilibrium

Equilibrium between the CIPC in solution and that adsorbed was considered complete upon no further increase in CIPC adsorption by the soil with an increase in equilibration time. Nyssa sil, Deschutes sil, Woodburn sil, and La Grande sil achieved equilibrium after three hours (Table 1). Equilibration between the CIPC in the aqueous and the adsorbed phase on the Hembre 1 was not achieved until after nine hours.

Magnitude. Oregon soils equilibrated for seven hours with 50 ppm CIPC exhibit striking differences in the adsorption of CIPC. After seven hours equilibration in a 50 ppm CIPC solution, Hembre 1 had adsorbed 636 μg of CIPC per g of soil or 51% of the total available CIPC (Tables 1 and 2), more than twice the CIPC adsorption capacity of the other soils. The high CIPC adsorption capacity by the Hembre 1 is postulated to relate to the 29% organic matter content (Table 3). Organic matter possesses a large surface area with many functional organic groups that could act as bonding sites for the CIPC molecule. In addition to a high organic matter content, Hembre 1 contained 16.8 milliequivalents Al per 100 g of soil and a free iron oxide content of 3.5%.

Table 1. CIPC adsorbed on five Oregon soils as a function of time

Soil Series	Time, hours									
	.5	.75	1	1.5	3	5	7	8	9	10
	CIPC adsorbed, $\frac{\mu\text{g}}{\text{g}}$									
Hembre l	364	408	452	500	560	606	636	647	655	659
La Grande sil	212	232	252	280	300	302	306	--	--	--
Woodburn sil	232	243	248	252	262	268	268	--	--	--
Deschutes sl	220	244	256	296	308	332	334	--	--	--
Nyssa sil	96	110	132	148	176	192	192	--	--	--

-- not determined

Table 2. CIPC adsorbed on five Oregon soils expressed as a percent of the total CIPC added

Soil Series	Time, hours									
	0.5	.75	1	1.5	3	5	7	8	9	10
	CIPC adsorbed, %									
Hembre l	29	33	36	40	45	48	51	52	52	53
La Grande sil	17	18	20	22	24	24	24	--	--	--
Woodburn sil	18	19	20	20	21	21	21	--	--	--
Deschutes sl	18	19	20	24	25	26	27	--	--	--
Nyssa sil	8	9	10	12	14	15	15	--	--	--

-- not determined

Table 3. Chemical and physical properties of six Oregon soils

Soil Type	CEC	Exch. Al meq/100g	Extract. Al	pH (1:1H ₂ O)	Fe ₂ O ₃	O. M %	Clay
Hembre l	57.0	3.3	16.8	5.0	3.5	29.0	12.0
La Grande sil	36.4	0	0.3	8.4	0.4	4.1	25.1
Woodburn sil	10.5	0	2.1	6.6	2.1	3.3	16.2
Deschutes sl	10.9	0	0.7	6.7	0.9	0.9	7.2
Nyssa sil	18.8	0	0.6	7.5	0.7	1.1	17.0
Kenutchen c	45.2	0	1.9	6.9	1.0	4.7	63.7

Nyssa sil, as a striking comparison to Hembre 1, adsorbed only 15% of the total available CIPC (192 μg of CIPC per g of soil) during the seven hour equilibration period (Tables 1 and 2). Assumably the fewer adsorption sites of the Nyssa sil and the resultant low adsorption capacity could result from the low extractable aluminum content, the low percentage of Fe_2O_3 and organic matter, and the high pH value (Table 3). The Woodburn sil soil which adsorbed 268 μg of CIPC per g of soil or 21% of the total available CIPC has properties similar to Nyssa sil but contains more organic matter, Fe_2O_3 , and extractable aluminum.

Deschutes sl (334 μg of CIPC per g of soil) displayed a CIPC adsorption capacity similar to Woodburn sil. The two soils, however, are quite different in their adsorption mechanism. Deschutes sl contains 7.2% clay, 0.9% organic matter, and has a cation exchange capacity of 10.9 milliequivalents per 100 g of soil (Table 3). This soil contains volcanic ash materials such as pumice which possesses a high internal pore space and hence a high internal surface area. Two possibilities thus exist for CIPC removal from the free solution: 1. entrapment of CIPC in the internal liquids contained in the pores, and 2. adsorption of CIPC on the internal and external surfaces. La Grande sil, although displaying the highest pH, adsorbed considerable CIPC probably because of its cation exchange capacity of 36.4 milliequivalents per 100 g of soil and 4%

organic matter content. The La Grande sil and Deschutes sl adsorbed approximately 25% of the initial CIPC present in solution.

The adsorption of CIPC on soils examined in this study exceeded the CIPC adsorption on the clay and soil systems reported by Freed, Verneetti, and Montgomery (1962). These workers utilized systems containing four g of clay and 100 ml of six ppm CIPC solution which resulted in CIPC adsorption values of 10.3 μg of CIPC per g for a sandy soil, 30.1 μg of CIPC per g for kaolin clay, 77.0 μg CIPC per g for bentonite clay, and 77.5 μg of CIPC per g for illite clay. The lower adsorption values reported by Freed are probably related to the lower initial CIPC concentrate introduced to the clay and soil systems.

Using carbon-14 labeled CIPC, Schwartz (1967) reported only 4% of the initial CIPC added was sorbed on clay minerals such as montmorillonite, illite, and kaolinite, after 21 hours of equilibration. The concentration of clay in suspension was 800 mg per liter with an initial CIPC concentration of 0.40 mg per liter. In the same study, illite and kaolinite showed a slight decrease in CIPC adsorption when the pH of the system was increased from 4.8 to 9.3. On the other hand montmorillonite demonstrated a slight increase in adsorption with the same pH change.

The adsorption rate of CIPC was calculated for each soil and plotted as a percentage of the maximum CIPC adsorption versus time (Figure 1). The maximum CIPC adsorption capacity for all soils was

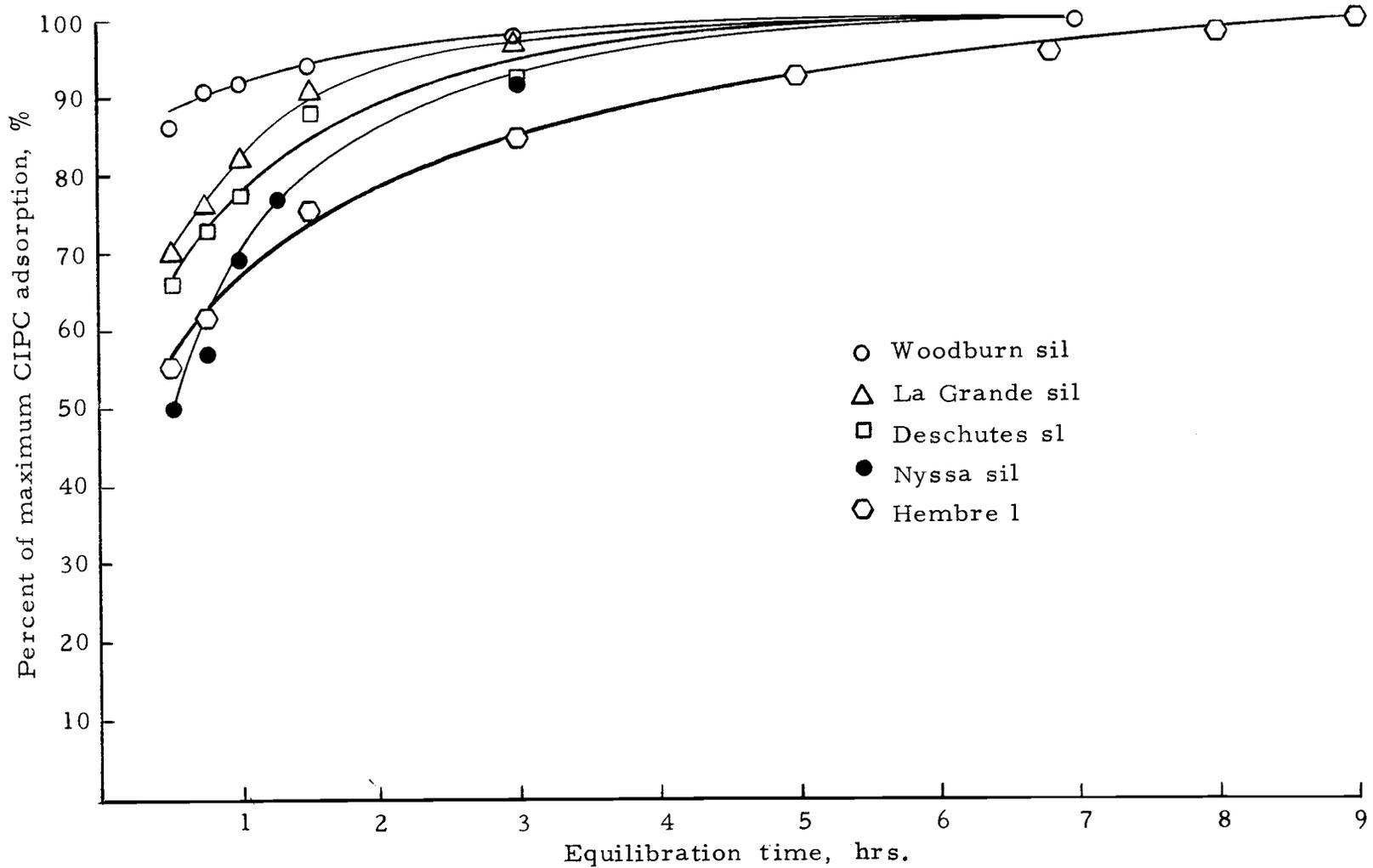


Figure 1. Percent of maximum CIPC adsorption on five Oregon soils as a function of time

taken as the amount adsorbed after seven hours equilibration with the exception of the Hembre 1 where the nine hour equilibration value was utilized.

After one half hour of equilibration time, the soils exhibited quite varied adsorption rates as follows: Woodburn sil > La Grande sil > Deschutes sl > Hembre 1 > Nyssa sil (Figure 1). Hembre 1 had adsorbed only 55 percent of its total adsorption capacity while Woodburn sil had adsorbed 86 percent of its maximum CIPC adsorption capacity (Figure 1). After three hours of equilibration time, the relative rates of maximum CIPC adsorption between the soils showed no change with the exception of Nyssa sil which adsorbed more of its maximum than the Hembre 1.

The slow rate at which Hembre 1 adsorbed its maximum quantity of CIPC may be related to 1) a required configuration or position of the CIPC molecule in relation to the complex structure of the organic matter surface or 2) a time factor involving diffusion of the CIPC molecules along a tortuous path to the adsorption site.

Consideration of a diffusion controlled adsorption process leads one to note the linear relationship between both the amount of CIPC adsorbed per g of soil and the percent of maximum CIPC adsorption with the square root of time (Figures 2 and 3). This relationship was consistent for all soils during the first one and one half hours of equilibration time. Deschutes sl and La Grande sil show nearly the

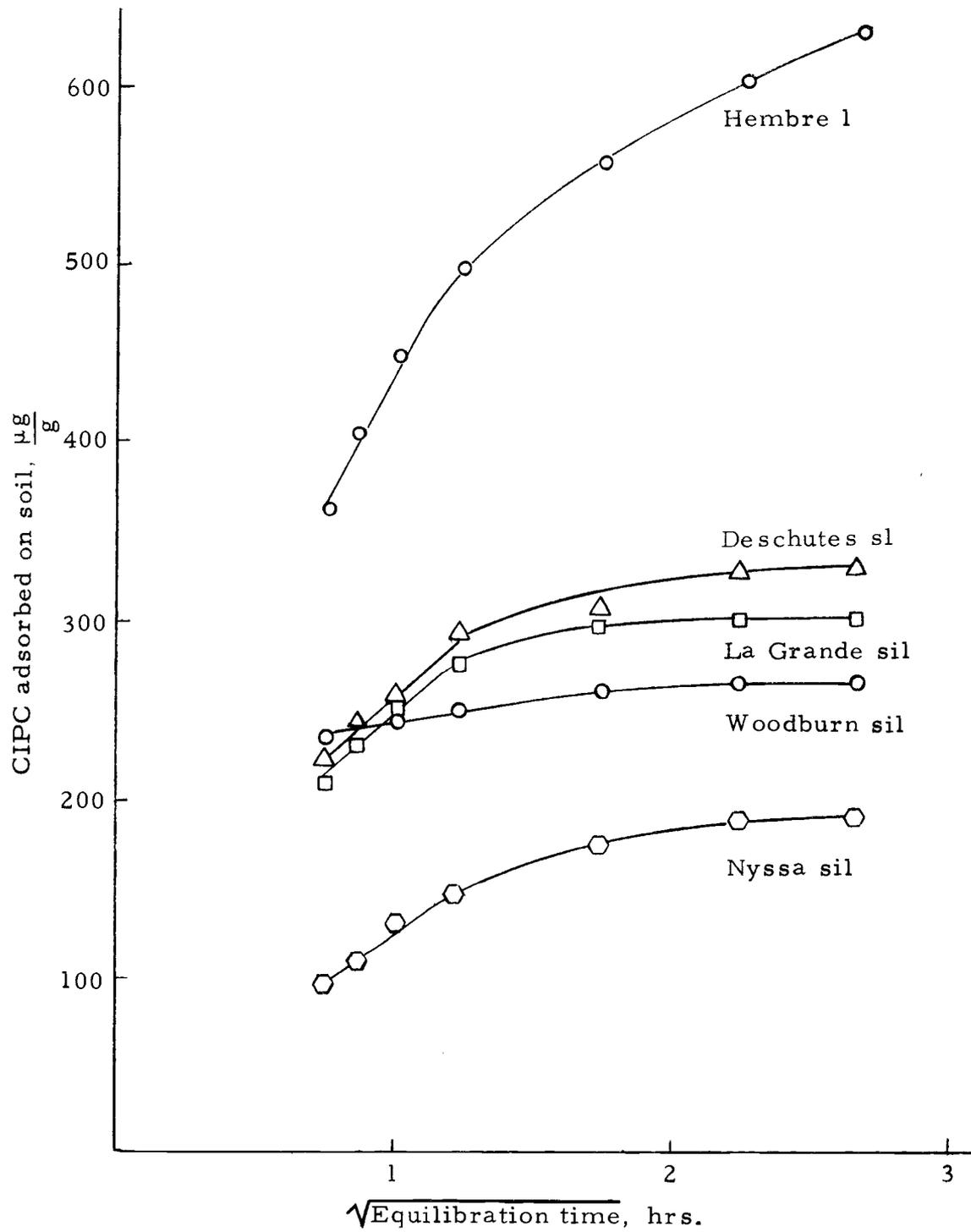


Figure 2. Adsorption of CIPC on five Oregon soils as a function of $t^{1/2}$

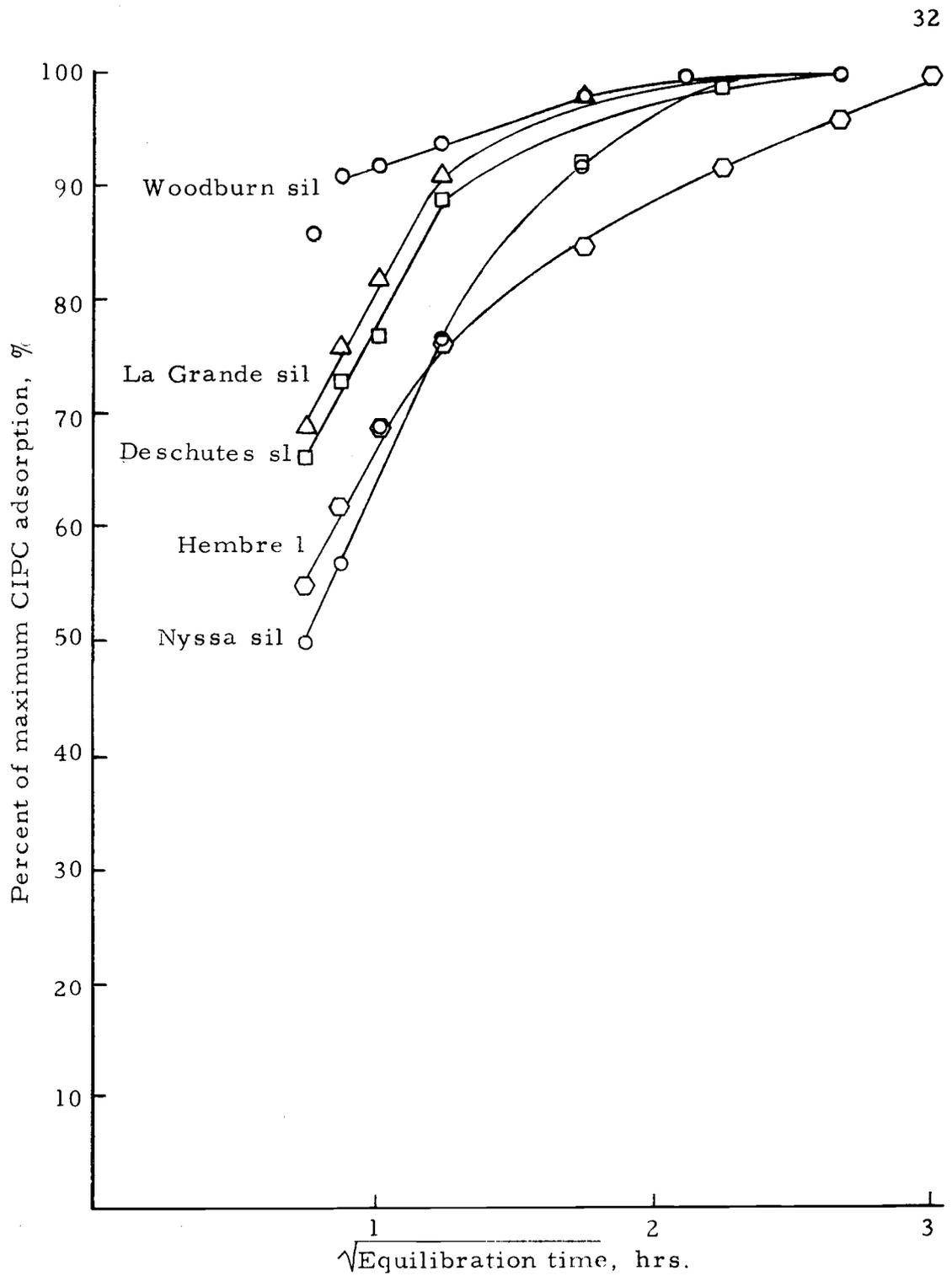


Figure 3. Percent of maximum CIPC adsorption on five Oregon soils as a function of $t^{1/2}$

same relationship suggesting that the geometry governing the diffusion of the CIPC molecules is similar for the two soils.

Adsorption of carbon-14 labeled CIPC on activated carbon has also been shown to follow a diffusion controlled relationship for the initial adsorption period (Schwartz, 1967). The uptake of 3-dodecyl benzenesulfonate by carbon also varied proportionally for initial adsorption periods with the square root of time rather than with time. The relationship was attributed to intraparticle diffusion (Morris and Weber, 1964). In summary it would seem that a diffusion phenomena controls the rate at which a soil attains maximum CIPC adsorption.

CIPC Adsorption Isotherms

The adsorption of a chemical upon a surface may be described by various methods including plots of adsorption ($\frac{X}{m}$) versus initial concentration (C), the Freundlich equation, and the Langmuir equation.

Initial Concentration Adsorption Relationships

The five soils studied show increased CIPC adsorption with an increase in the initial CIPC concentration at 0°C, 25°C, and 50°C (Figures 4, 5, and 6) with Hembre 1 showing the largest CIPC adsorption capacity of the soils studied.

The 0°C adsorption isotherms show that Nyssa sil, Woodburn

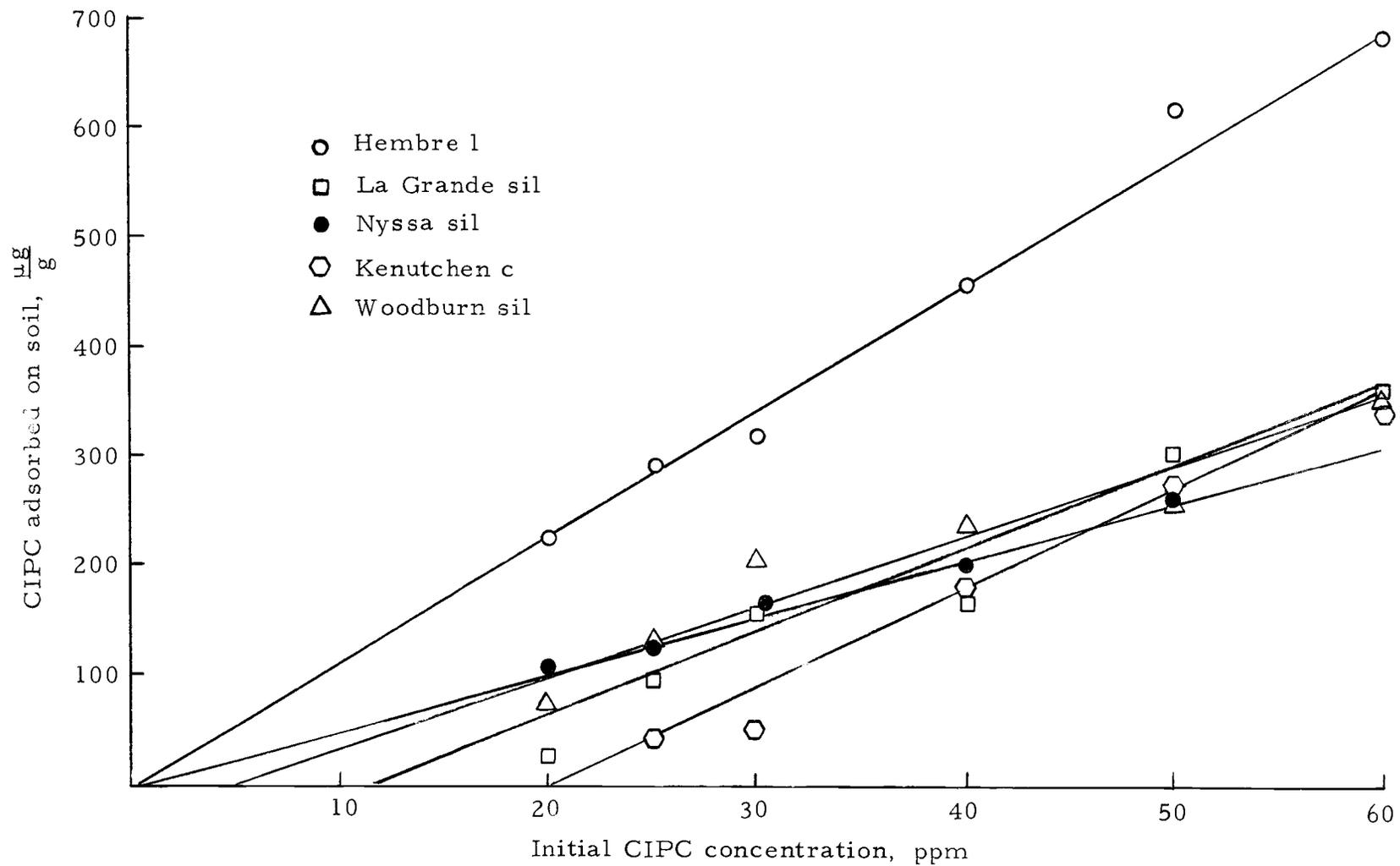


Figure 4. Adsorption of CIPC on five Oregon soils at 0°C

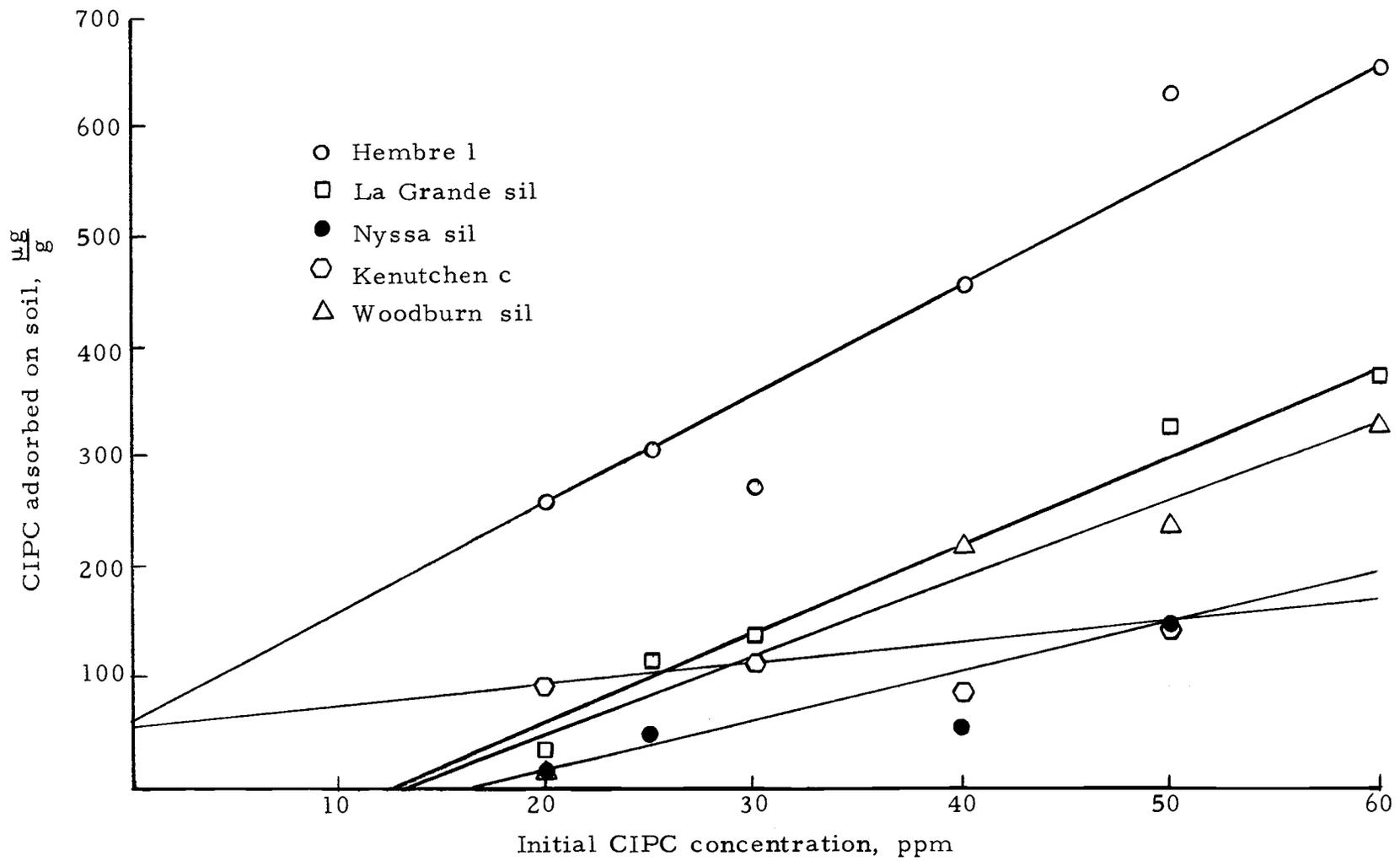


Figure 5. Adsorption of CIPC of five Oregon soils at 25°C

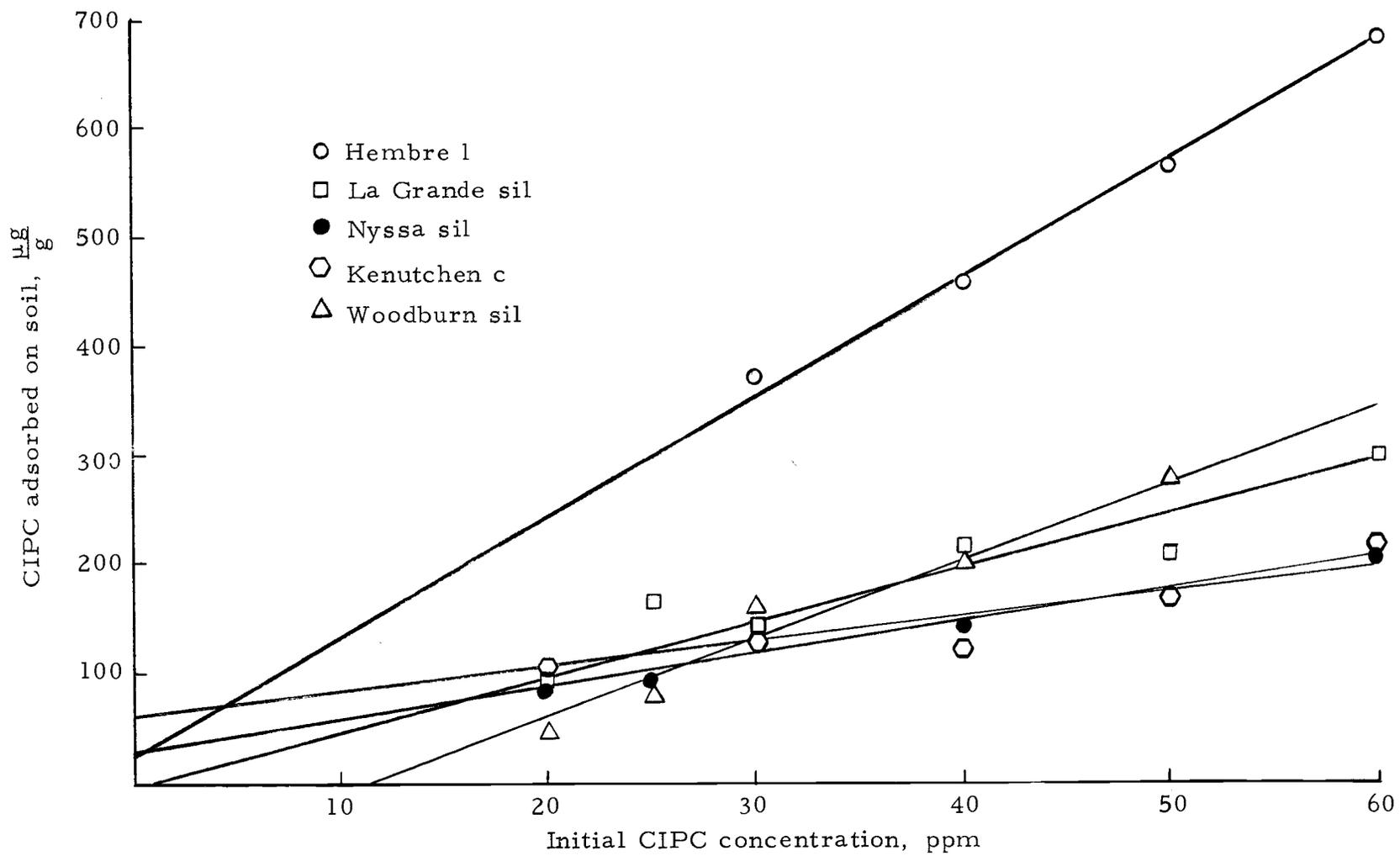


Figure 6. Adsorption of CIPC on five Oregon soils at 50°C

sil, and Kenutchen c displayed approximately an equal CIPC adsorption capacity (Figure 4) while the isotherms of Nyssa sil and Hembre l were most ideal in that they passed through the origin. Because of experimental difficulties no equilibrations were conducted below 20 ppm. If one were to extrapolate from the adsorption curve obtained, one would find that no appreciable adsorption occurred on Woodburn sil, La Grande sil, or Kenutchen c below an initial CIPC concentration of 20 ppm. Adsorption studies of sulfate ion on Oregon soils have also indicated no appreciable adsorption until the equilibrium concentration reached five ppm of sulfate ion (Fang, et al., 1962).

The 25^oC adsorption isotherms revealed only minor differences between the La Grande sil, Woodburn sil, Nyssa sil, and Kenutchen c (Figure 5).

At 50^oC adsorption was again very similar among the soils (Figure 6); however, close observation revealed three adsorption classes of soils. Nyssa sil and Kenutchen c demonstrate similar adsorption isotherms; Woodburn sil and La Grande sil are similar, with the Hembre l in a third class.

Table 4 shows the percent of the initial CIPC adsorbed. The same percent adsorption at all the initial concentrations was observed for Nyssa sil at 0^oC and 50^oC, Hembre l at all three temperatures, La Grande sil at 50^oC and Woodburn sil at 0^oC. Increased percent adsorption with increasing initial CIPC concentration was

Table 4. Percentage of CIPC adsorption as a function of initial CIPC concentration

Soil Series	Temperature	Concentration, ppm					
		20	25	30	40	50	60
Nyssa sil	0°C	21	21	21	21	21	21
	25°C	4	8	11	13	15	17
	50°C	18	17	16	15	14	14
Hembre l	0°C	45	46	45	45	46	45
	25°C	52	49	48	46	45	44
	50°C	48	48	46	46	46	24
Kenutchen c	0°C	2	7	12	18	22	28
	25°C	17	16	14	13	12	11
	50°C	21	19	17	15	14	13
La Grande sil	0°C	11	15	17	21	23	24
	25°C	12	16	19	22	24	23
	50°C	18	19	16	20	20	20
Woodburn sil	0°C	20	21	22	23	23	24
	25°C	10	14	16	19	21	23
	50°C	12	15	17	20	22	23

observed for Nyssa sil at 25°C, Kenutchen c at 0°C, La Grande sil at 0°C and 25°C, and Woodburn sil at 25°C and 50°C. Kenutchen c at 25°C and 50°C demonstrated a decrease in percent adsorption with increasing initial CIPC concentration.

The adsorption isotherms of Hembre l indicate similar adsorption of CIPC at the three temperatures studied (Figure 7). The deviation of the isotherms at 25°C and 50°C from the origin is attributed to experimental error.

Isotherms of Woodburn sil show CIPC adsorption to be very

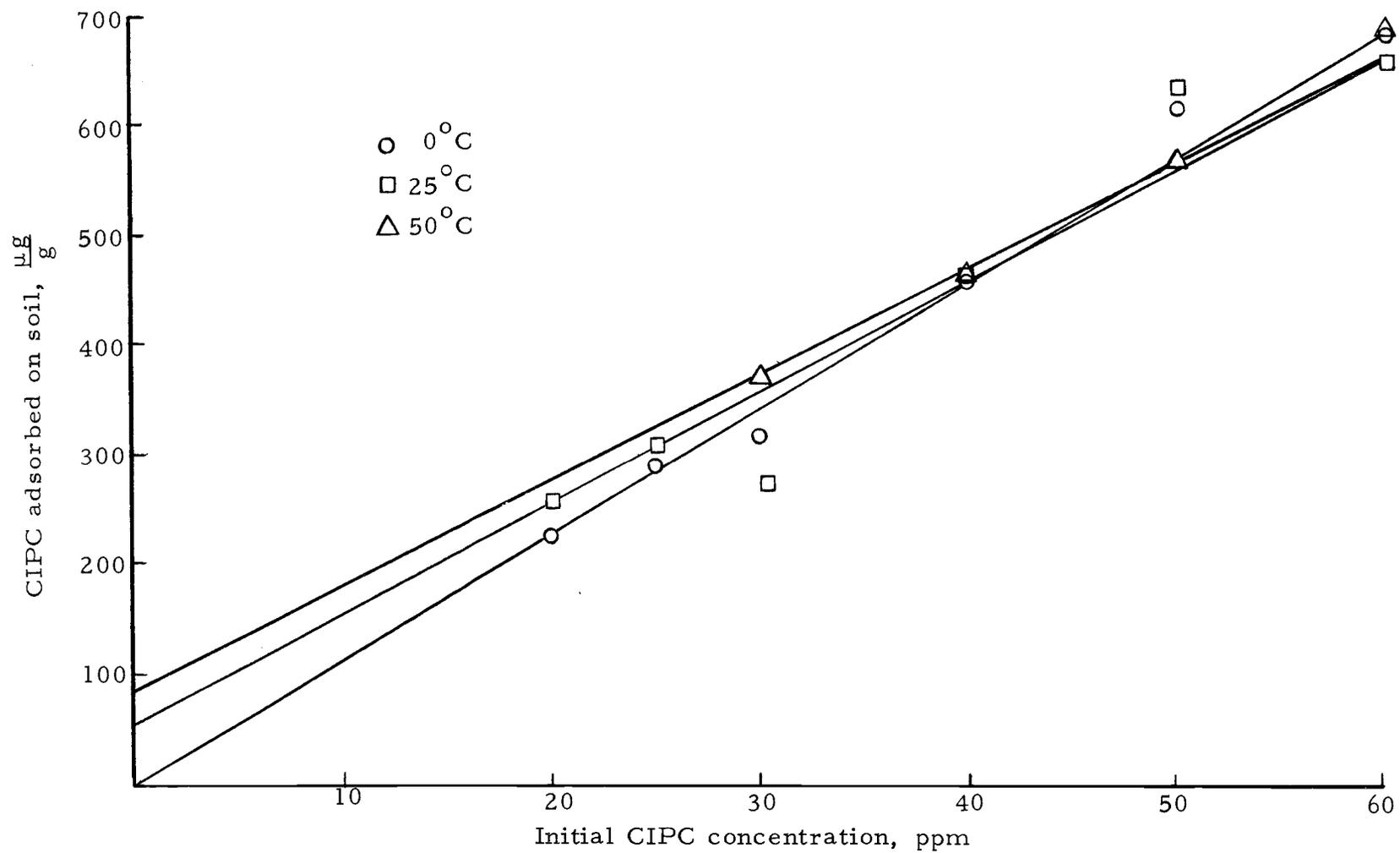


Figure 7. Adsorption of CIPC on Hembre 1 at three temperatures

similar at 25°C and 50°C (Figure 8) with slightly higher CIPC adsorption observed at 0°C explained by temperature related decrease in solubility and molecular activity.

The adsorption isotherms of La Grande sil show adsorption to be essentially equal at 25°C and 0°C with the 50°C isotherm intersecting at an initial CIPC concentration of approximately 30 ppm CIPC (Figure 9). Initial CIPC concentrations less than 32 ppm thus show more adsorption at 50°C than at 0°C and 25°C. Appreciable adsorption did not occur at 25°C and 0°C until the initial CIPC concentration reached 12 ppm.

More CIPC was adsorbed by Nyssa sil at 0°C than at 50°C and 25°C (Figure 10). The isotherms show more adsorption of CIPC at 50°C than at 25°C.

The adsorption isotherms of Kenutchen c demonstrate a large difference in slope of the three isotherms (Figure 11). The slope of the 0°C isotherm is much steeper than the slopes of the 25°C and 50°C isotherms. Adsorption by Kenutchen c was essentially the same at 25°C and 50°C with more adsorption at 0°C with initial CIPC concentrations greater than 38 ppm.

Freundlich Isotherms

The Freundlich equation may be written as $\frac{X}{m} = KC^n$ where:

$$\frac{X}{m} = \mu\text{g of CIPC adsorbed per 16 g of soil}$$

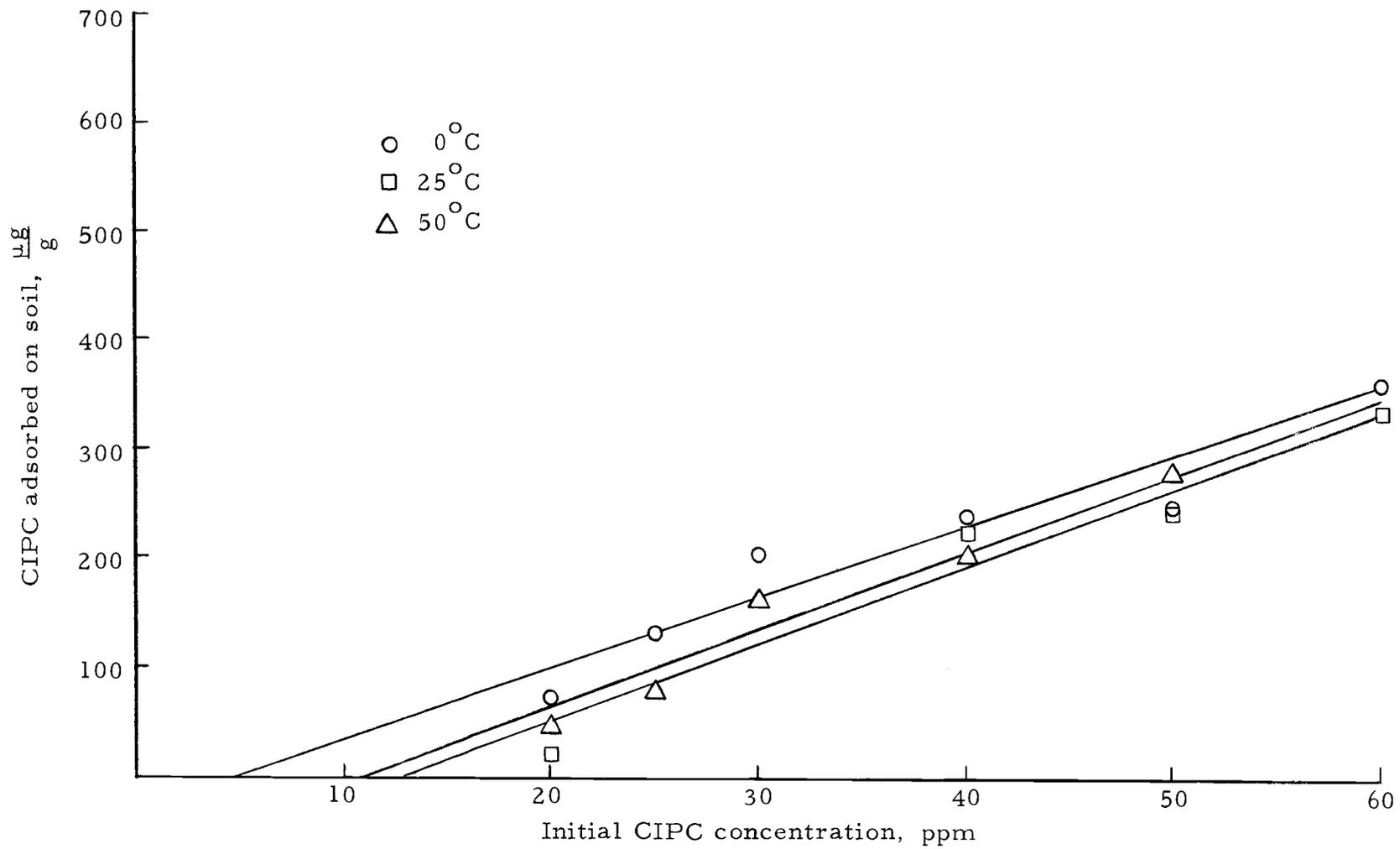


Figure 8. Adsorption of CIPC on Woodburn sil at three temperatures

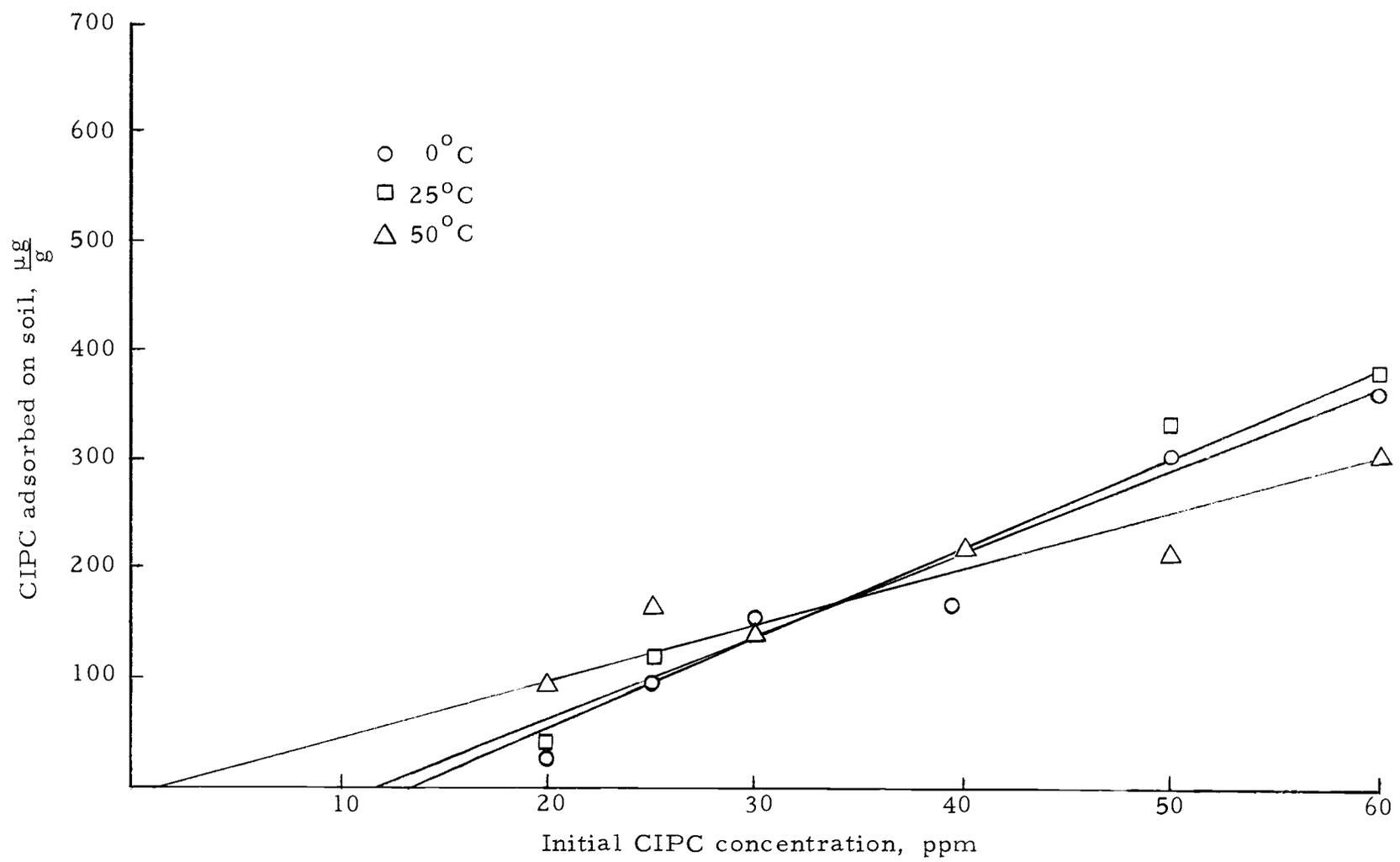


Figure 9. Adsorption of CIPC on La Grande sil at three temperatures

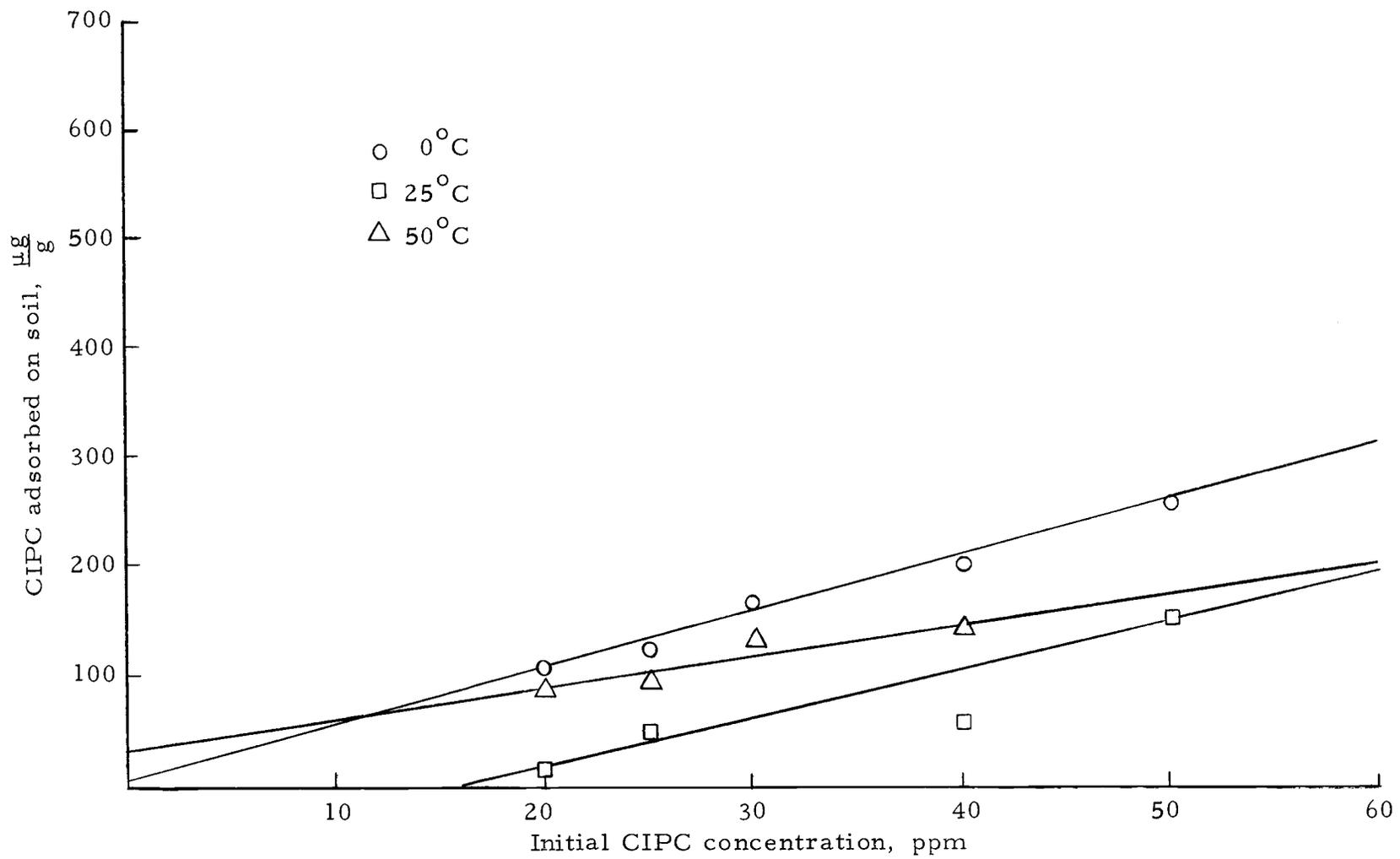


Figure 10. Adsorption of CIPC on Nyssa sil at three temperatures

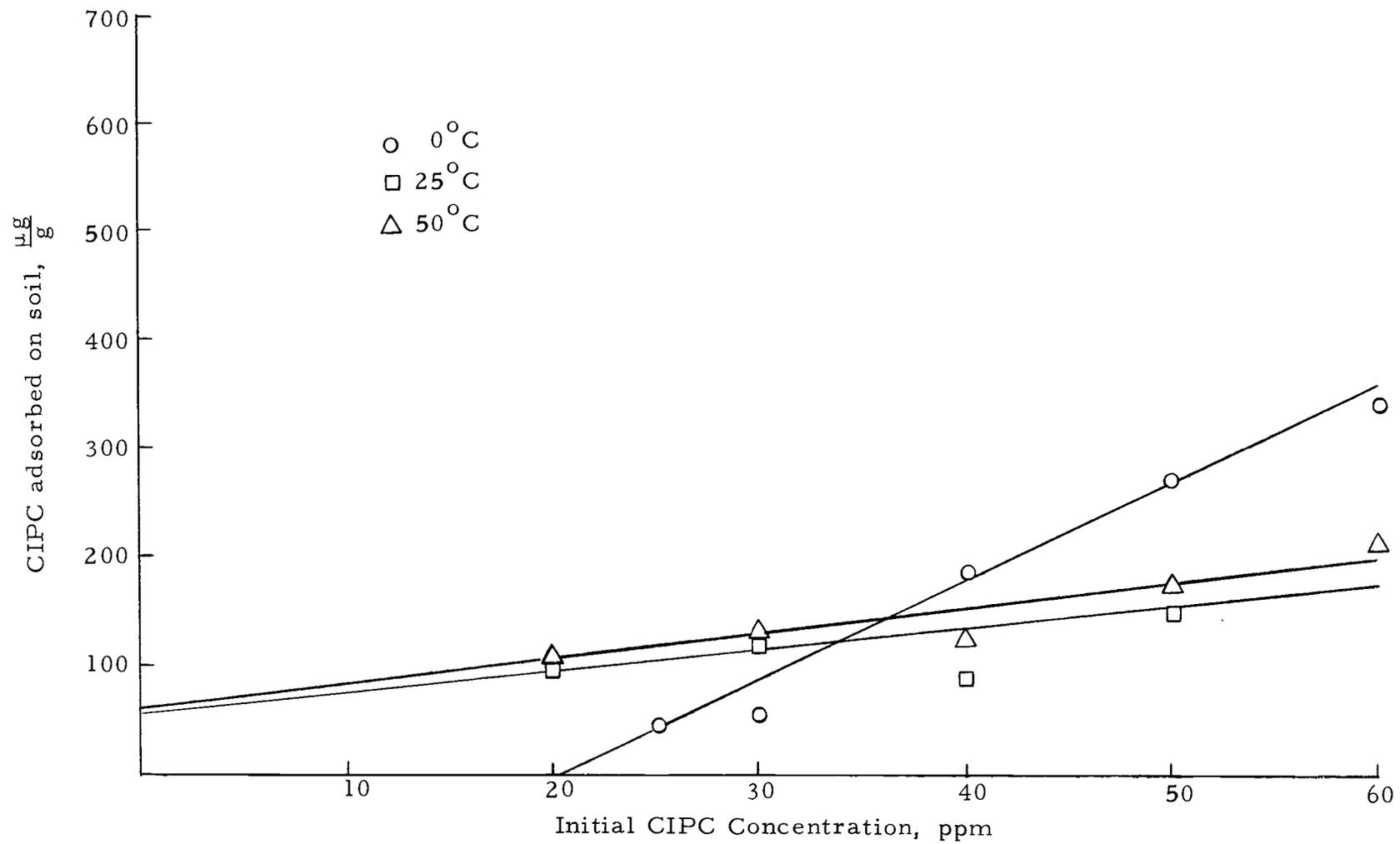


Figure 11. Adsorption of CIPC on Kenutchen c at three temperatures

K = constant

C = equilibrium CIPC concentration expressed
as μg of CIPC per 400 ml of solution

n = constant

The equation may be rewritten as $\log \frac{X}{m} = \log K + n \log C$ and plotted such that n becomes the slope and K becomes the antilogarithm of the intercept.

The Freundlich equation considers adsorption upon a heterogeneous surface and is often used to describe the adsorption of an adsorbate on a soil surface. It should be noted, however, a Freundlich isotherm does not indicate an adsorption mechanism. Application of the Freundlich isotherm to the adsorption of monuron and diuron on several Hawaiian soils resulted in a linear relationship (Yuen and Hilton, 1962). Studies of 2,4-D adsorption on illite, montmorillonite, silica gel, sand, humic acid, and alumina followed the Freundlich plot with the values of n very close to unity and the slopes decreasing with a decrease in temperature (Haque and Sexton, 1967).

The Freundlich plots for each soil at 0°C, 25°C, and 50°C are indicated in Figures 12, 13, 14, 15, and 16. The adsorption of CIPC on each soil followed the Freundlich equation. Table 5 lists the n and log K value for each soil at the temperatures studied. In general the slope of the Freundlich isotherms at 50°C are less than the n

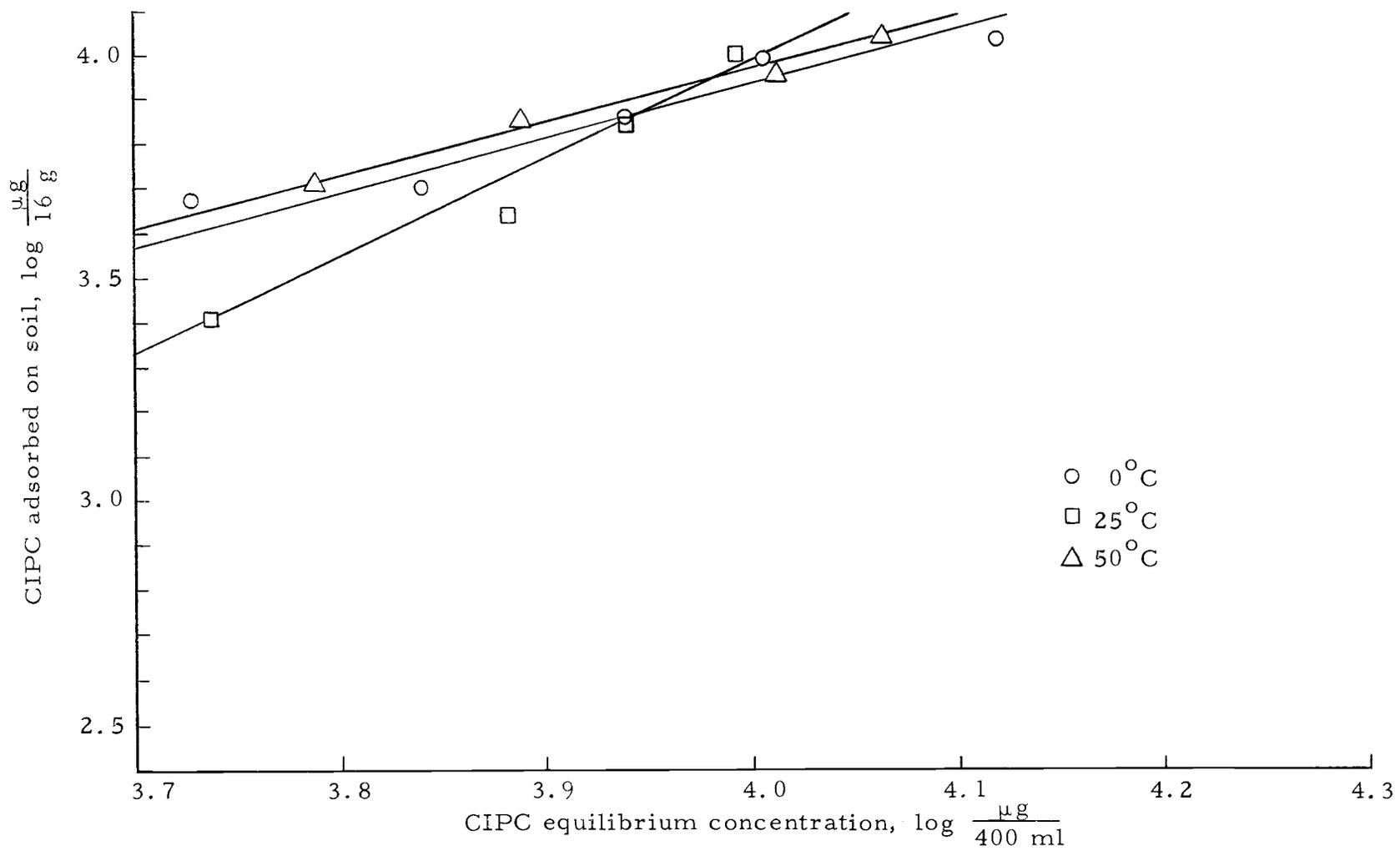


Figure 12. Freundlich isotherms of Hembre 1 at three temperatures

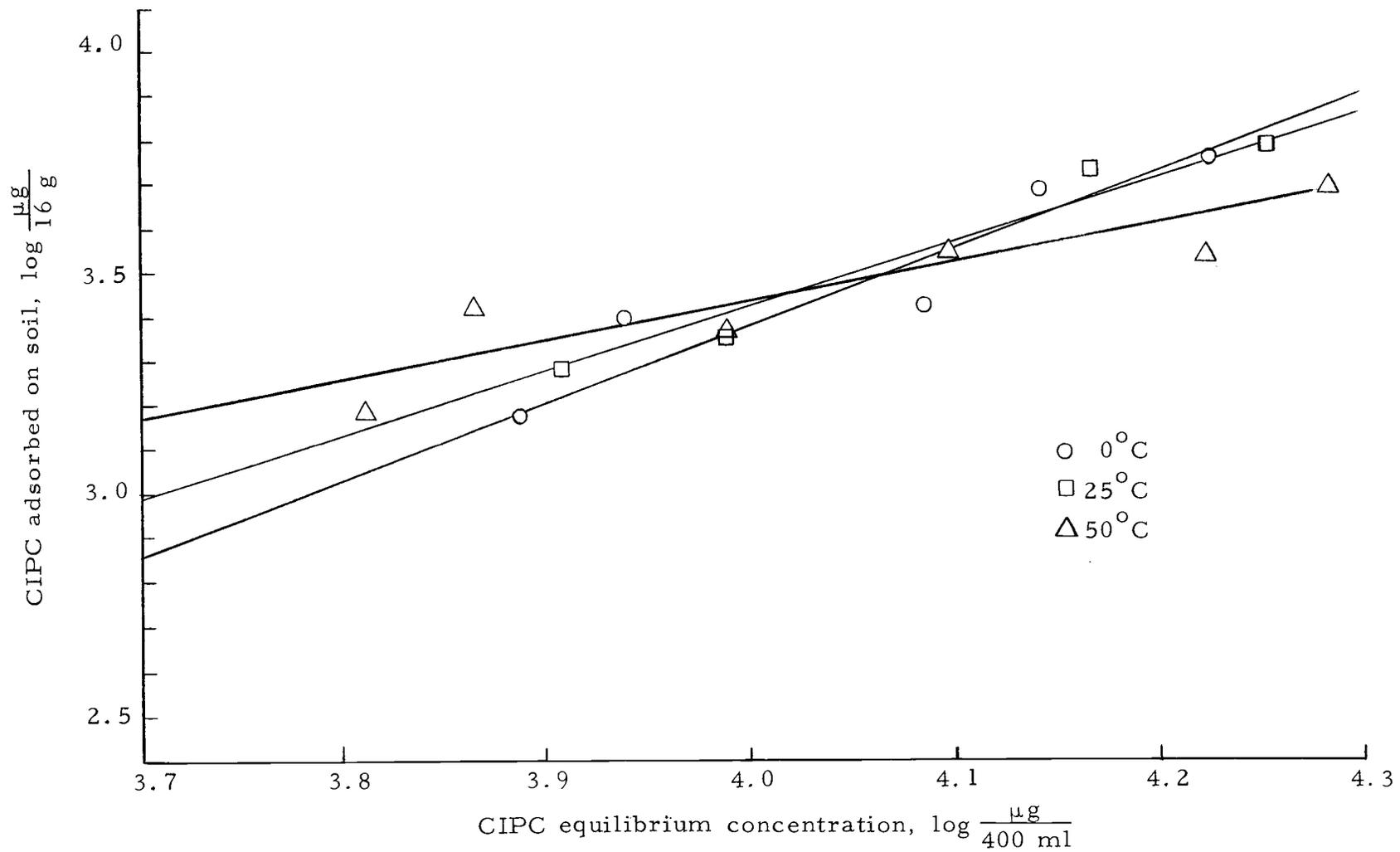


Figure 13. Freundlich isotherms of La Grande sil at three temperatures

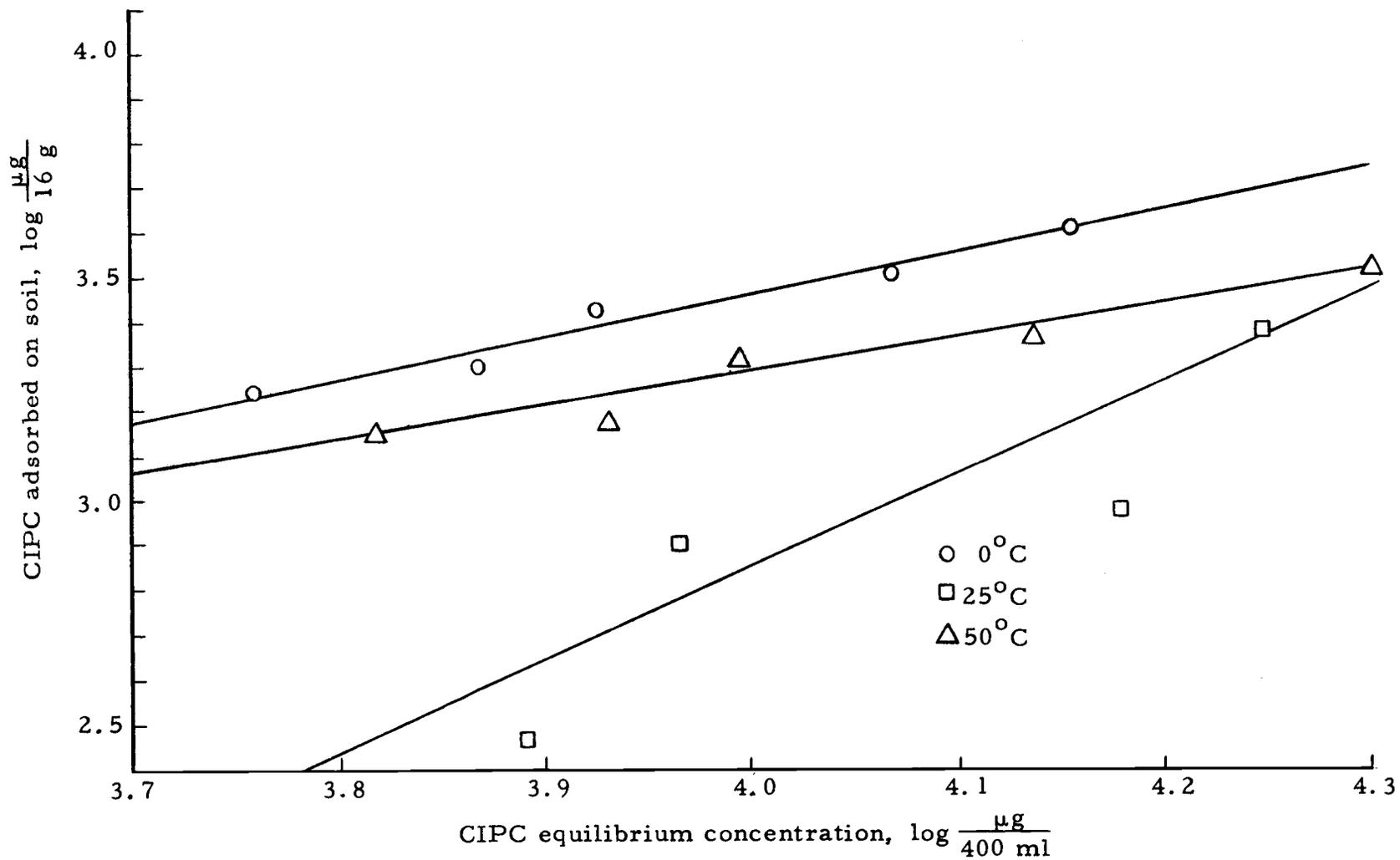


Figure 14. Freundlich isotherms of Nyssa sil at three temperatures

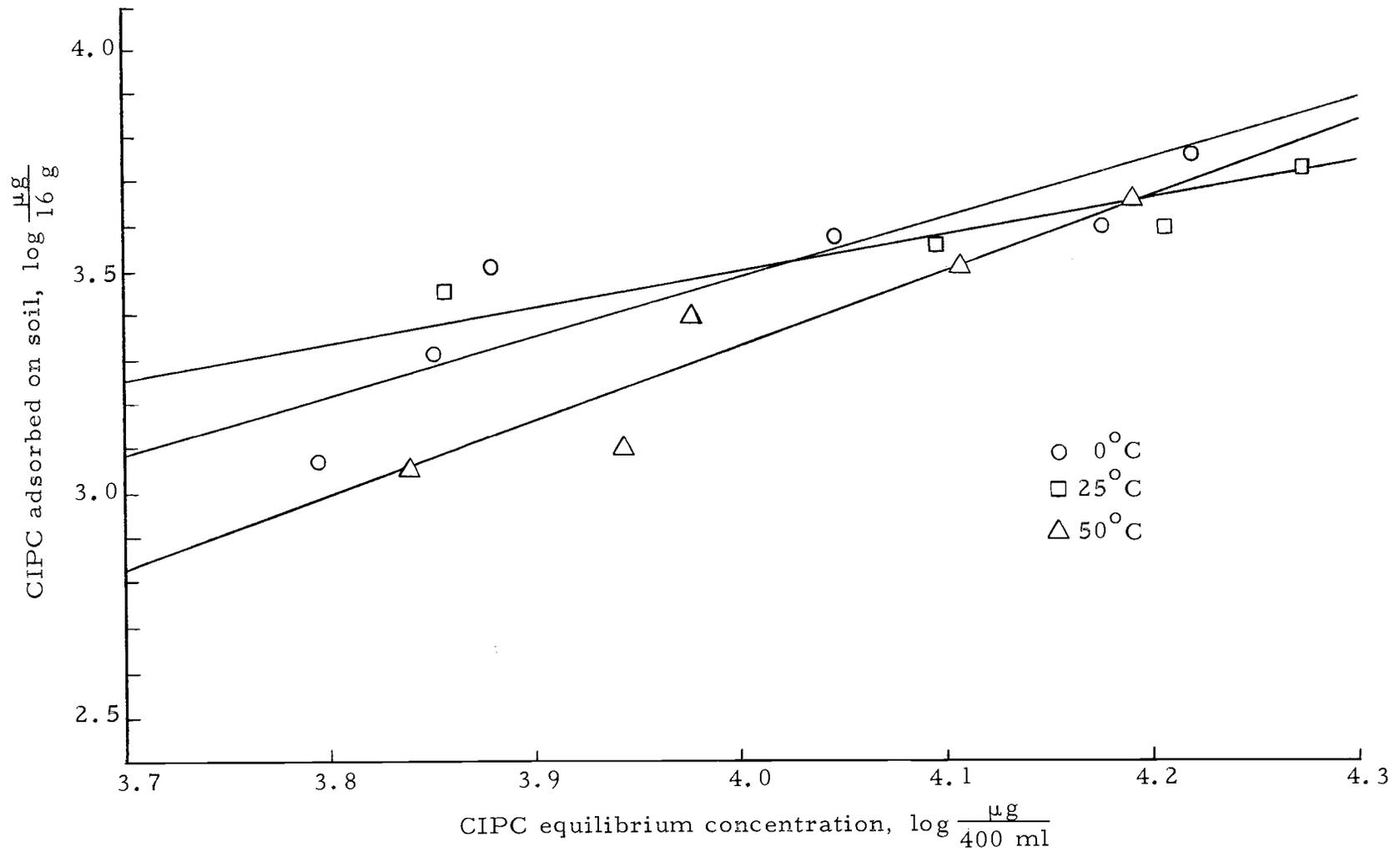


Figure 15. Freundlich isotherms of Woodburn sil at three temperatures

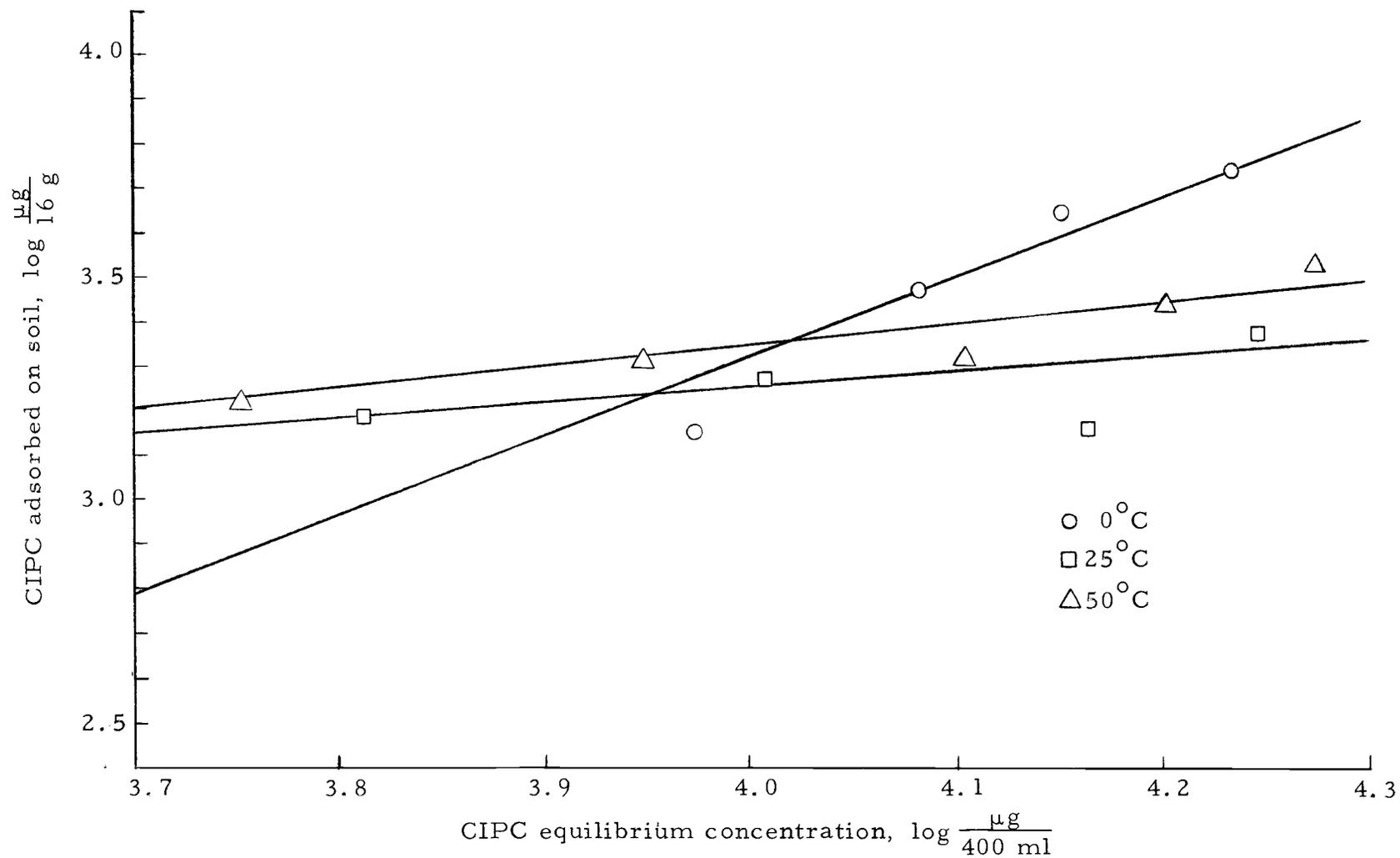


Figure 16. Freundlich isotherms of Kenutchen c at three temperatures

Table 5. Values of Freundlich equation for adsorption of CIPC on five Oregon soils

Soil Series	Temperature	Log k	n
Hembre l	0°C	3.56	1.29
	25°C	3.33	2.19
	50°C	3.60	.96
La Grande sil	0°C	2.85	1.77
	25°C	2.98	1.44
	50°C	3.16	.91
Woodburn sil	0°C	3.09	1.33
	25°C	3.26	.80
	50°C	2.86	1.60
Kenutchen c	0°C	2.76	1.87
	25°C	3.14	.37
	50°C	3.20	.27
Nyssa sil	0°C	3.18	.97
	25°C	2.11	2.34
	50°C	3.06	.77

values of the isotherms at lower temperatures. At 0°C, 25°C, and 50°C, the Freundlich isotherms of the Hembre l soil are isolated from the Freundlich isotherms of the other soils studied (Figures 17, 18, and 19). At 0°C all soils other than Hembre l showed similar Freundlich plots (Figure 17). A grouping of the isotherms was also observed at 50°C (Figure 19). The Freundlich isotherms for each soil at 25°C show wide differences in $\log \frac{X}{m}$ values relative to the $\log C$ values (Figure 18).

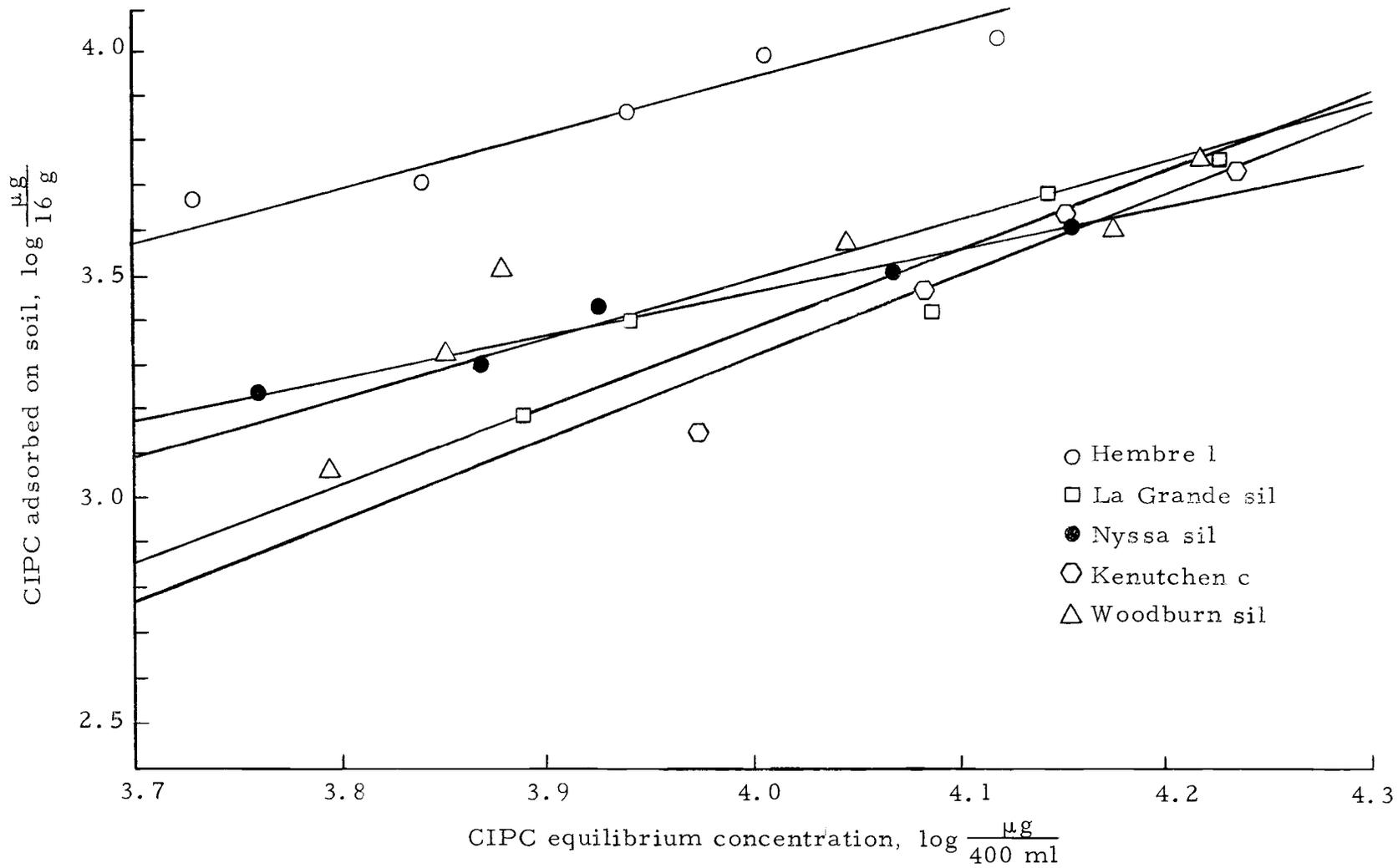


Figure 17. Freundlich isotherms for five Oregon soils at 0°C

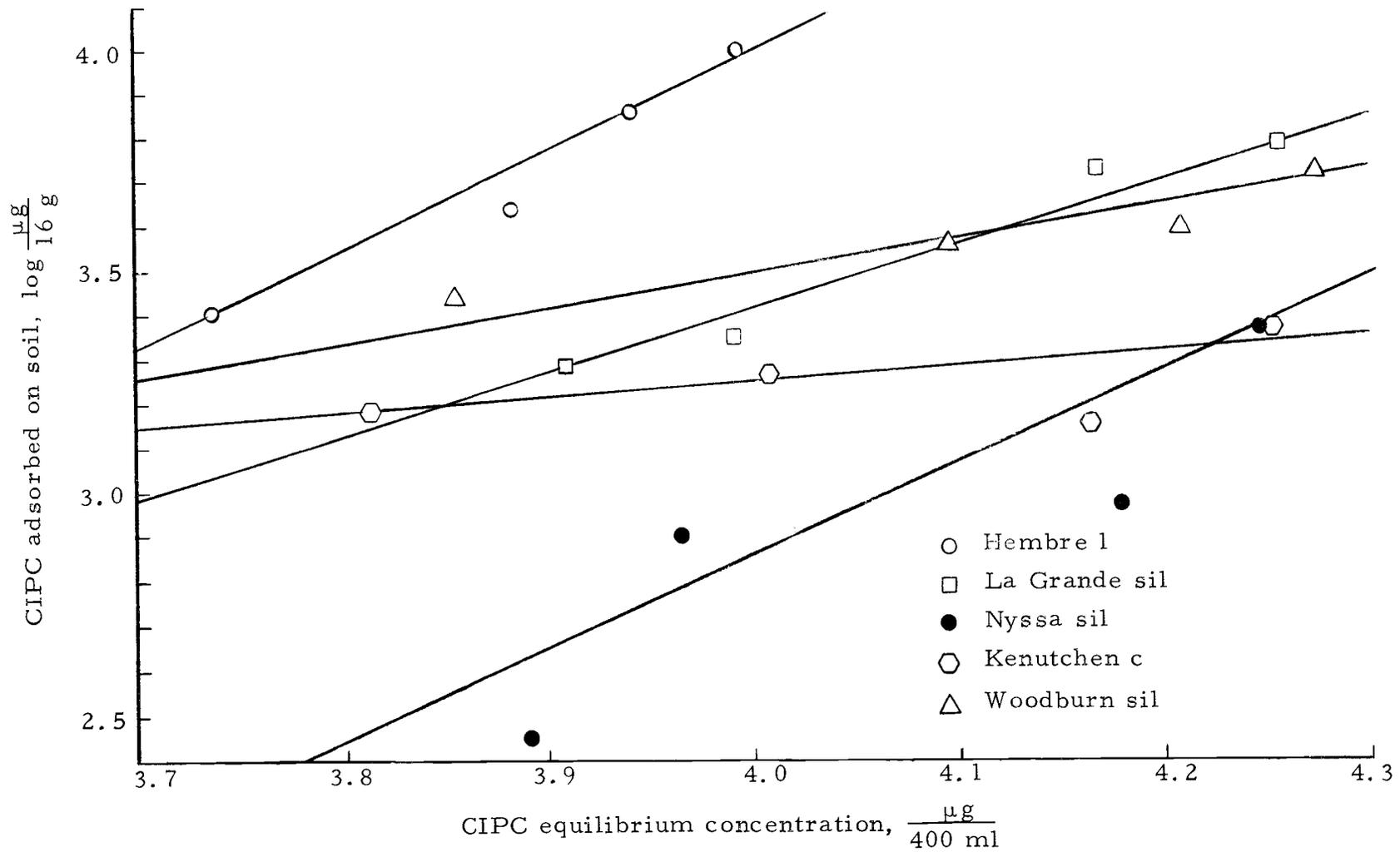


Figure 18. Freundlich isotherms for five Oregon soils at 25°C

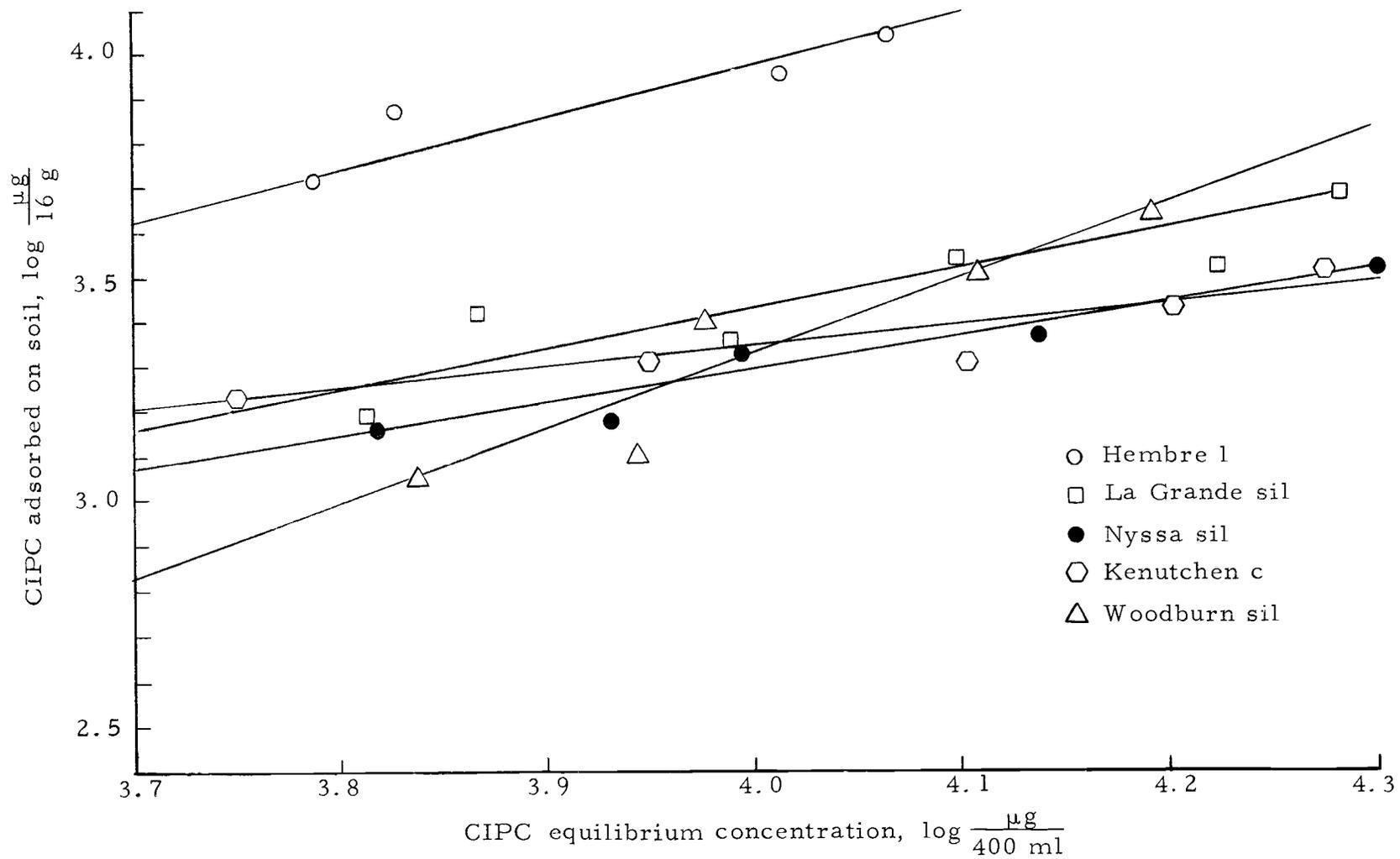


Figure 19. Freundlich isotherms for five Oregon soils at 50°C

Langmuir Isotherm

The Langmuir equation describes the adsorption of a monomolecular layer upon a homogeneous surface. The equation may be

written as $\frac{C}{\frac{X}{m}} = \frac{C}{b} + \frac{1}{ab}$ where:

C = equilibrium concentration of CIPC

$\frac{X}{m}$ = μ g of CIPC adsorbed per 16 g of soil

a = constant

b = constant

The adsorption data did not yield a linear relationship when plotted according to the Langmuir equation. Such a plot is indicated for the Woodburn sil at 25^oC (Figure 20). Schwartz (1967) used labeled C-14 CIPC to study adsorption upon activated carbon at equilibrium CIPC concentrations ranging from 0 to 24 mg per liter. After plotting the adsorption data according to the Freundlich and Langmuir equations, Schwartz felt the validity of the Langmuir plot at low CIPC concentrations was questionable and that the Freundlich isotherm more closely represented the actual adsorption equilibrium.

Thermodynamics of CIPC Adsorption

Nomenclature

Adsorption in a soil system obeys certain thermodynamic

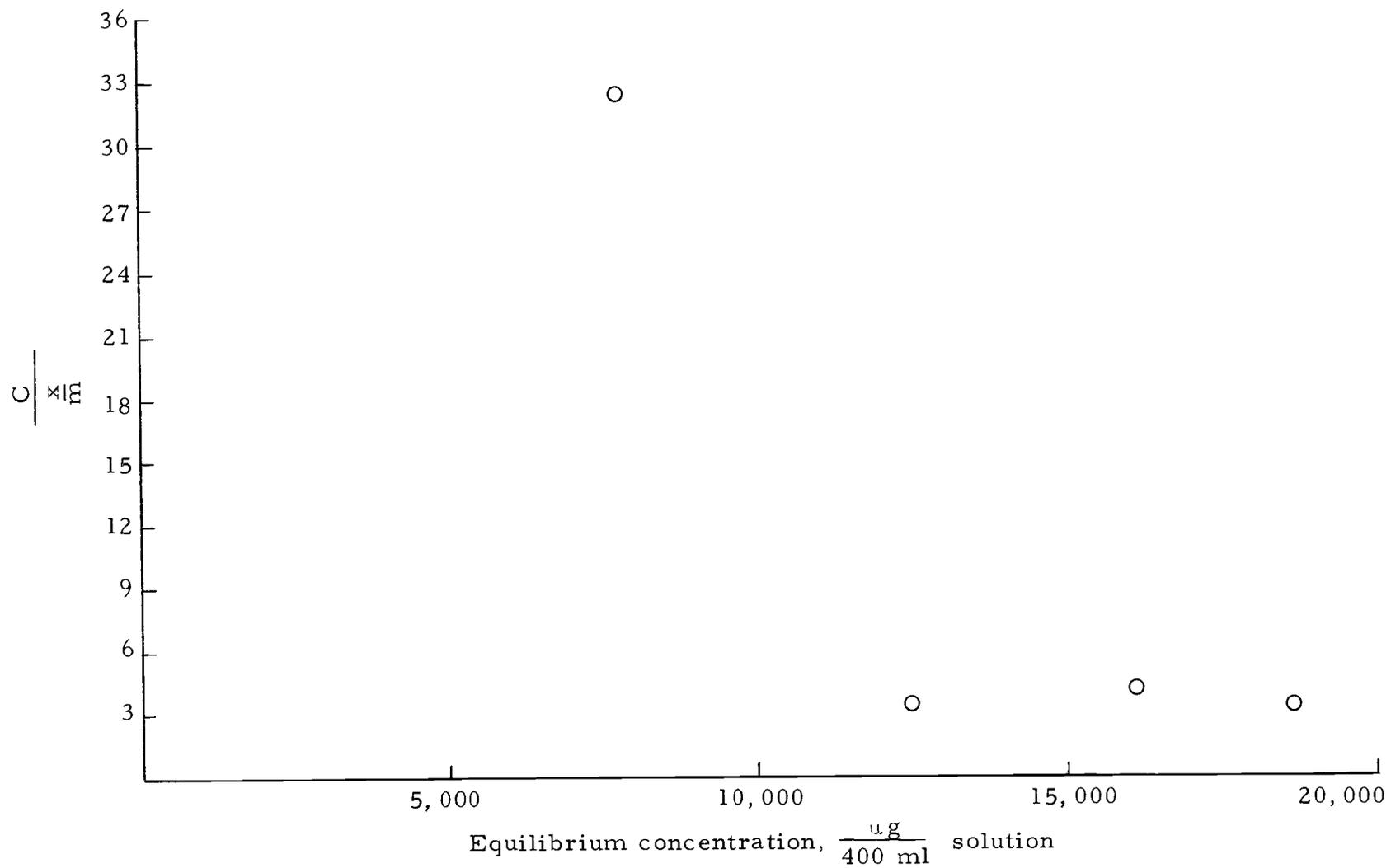


Figure 20. Langmuir plot for Woodburn sil at 25°C

principles and laws. In the analysis of adsorption data, the thermodynamic parameters most often considered include ΔH (enthalpy), ΔG (Gibbs free energy), and ΔS (entropy).

Heat of reaction or enthalpy (ΔH) values reflect the bond energy released or adsorbed as chemical bonds form during an adsorption reaction. Upon the formation of a bond between an adsorbent and adsorbate, energy is usually released, resulting in a negative ΔH value. Gibbs free energy values measure the occurrence spontaneity of a reaction. As ΔG values become more negative, a given reaction becomes more spontaneous. Entropy is a measure of the order attained during bond formation. The stronger the bond between the adsorbent and the adsorbate the higher the degree of order and the lower the entropy value. Gibbs free energy, entropy, and enthalpy are related by the formula, $\Delta G = \Delta H - T\Delta S$.

An increase in the heterogeneity of a surface leads to a decrease in binding energy as the surface coverage increases (Daniels and Alberty, 1967). Haque and Sexton (1967) observed the adsorption of 2,4-D on illite, montmorillonite, and humic acid and calculated ΔH values which changed from negative to positive as the surface coverage increased. Koral, Ullman, and Eirich (1958) have also reported the occurrence of positive ΔH values. The results were explained by postulating the release of solvent molecules from adsorptive sites thus creating a positive change in entropy. By

increasing the entropy of the system the Gibbs free energy remains negative as required for a spontaneous process of adsorption.

Equations for ΔH Calculations

A system to calculate ΔH values for the adsorption of polyvinyl acetate on iron and tin powders and alumina has been described by Koral, et al., (1958). The equation used in the ΔH calculation assumes the chemical potential of the pesticide in the liquid phase (μ_1) to be equal to the chemical potential (μ_s) of the pesticide at the surface (equation 1). Equations 2 through 7 show the mathematical development to relate the enthalpy of a system to concentration and temperature.

$$\mu_1 = \mu_s \quad (1)$$

μ_1 = chemical potential of pesticide in the liquid phase

μ_s = chemical potential of the pesticide at the surface
of the solid phase

$$\mu_s^0 + RT \ln A_s = \mu_1^0 + RT \ln A_1 \quad (2)$$

μ_1^0 = chemical potential at unit activity

μ_s^0 = chemical potential at unit activity

A_s = activity of pesticide at surface of solid phase

A_1 = activity of the pesticide in the liquid phase

$$G_i = \mu_i \quad (3)$$

$$\Delta G_i = \Delta \mu_i$$

G_i = Gibbs free energy of component i at equilibrium

μ_i = chemical potential of component i at equilibrium

$$\Delta \mu_i = \Delta G_i = \mu_1^o - \mu_s^o + RT \ln \frac{A_1}{A_s} \quad (4)$$

$$\frac{\Delta G_i}{T} = 0 + R \ln \frac{A_1}{A_s} \quad (5)$$

$$H_i = \left[\frac{\frac{\partial G_i}{\partial T}}{\frac{\partial}{\partial \frac{1}{T}}} \right]_P \quad (6)$$

P = pressure constant

$$\Delta H_i = \left[\frac{\frac{\partial \frac{\Delta G_i}{T}}{\partial T}}{\frac{\partial}{\partial \frac{1}{T}}} \right]_P \quad (7)$$

By substitution (8)

$$\Delta H_i^o = R \left[\frac{\frac{\partial \ln \frac{A_1}{A_s}}{\partial T}}{\frac{\partial}{\partial \frac{1}{T}}} \right]_P$$

Assume (9)

(a) $A_1 = C_1$ as chemical activity equals concentration
in a dilute solution.

(b) The activity of the pesticide at the surface does not change
if the quantity of chemical adsorbed remains constant.

Equation eight may be rewritten as: (10)

$$\Delta H_i = R \left[\frac{\partial \ln C}{\partial \frac{1}{T}} \right]_{P, C_s}$$

C_s = concentration of chemical at surface constant

Integration yields (11)

$$\Delta H_i = \frac{R [\ln C_2 - \ln C_1]}{\frac{1}{T_2} - \frac{1}{T_1}}$$

Consideration of constants R and T yields equations a and b (12)

Equation a ΔH $0^\circ - 25^\circ C$

$$\Delta H \frac{\text{kcal}}{\text{mole}} = \frac{4.58 [\log C_2 - \log C_1]}{-0.30}$$

Equation b ΔH $25^\circ - 50^\circ C$

$$\Delta H \frac{\text{kcal}}{\text{mole}} = \frac{4.58 [\log C_2 - \log C_1]}{-0.26}$$

Values of C_1 and C_2 , the equilibrium concentrations of CIPC in the liquid phase at the two different temperatures, may be obtained from the Freundlich plots for a given $\frac{X}{m}$ value (i. e., constant surface coverage) at each temperature.

The ΔH values for the adsorption of CIPC on the Oregon soils studied ranged from +5.0 kcal to -6.7 kcal (Figures 21 and 22), a magnitude generally associated with a weak physical bond formation. Schwartz (1967) reported a heat of reaction value of about -7.0 kcal for an activated carbon-CIPC system. Freed (1966) calculated ΔH

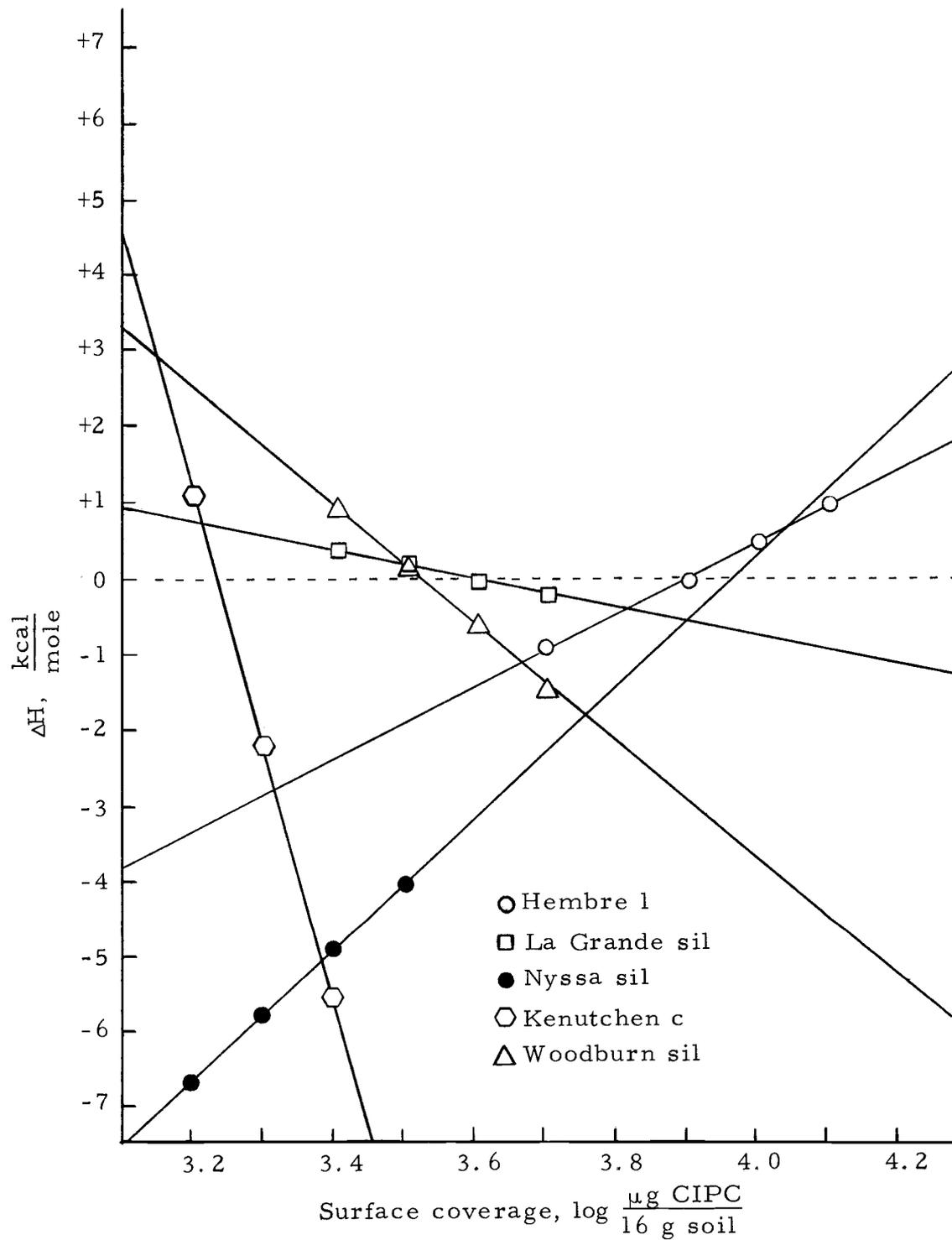


Figure 21. Relationship of ΔH at 0°C to 25°C and surface coverage by CIPC

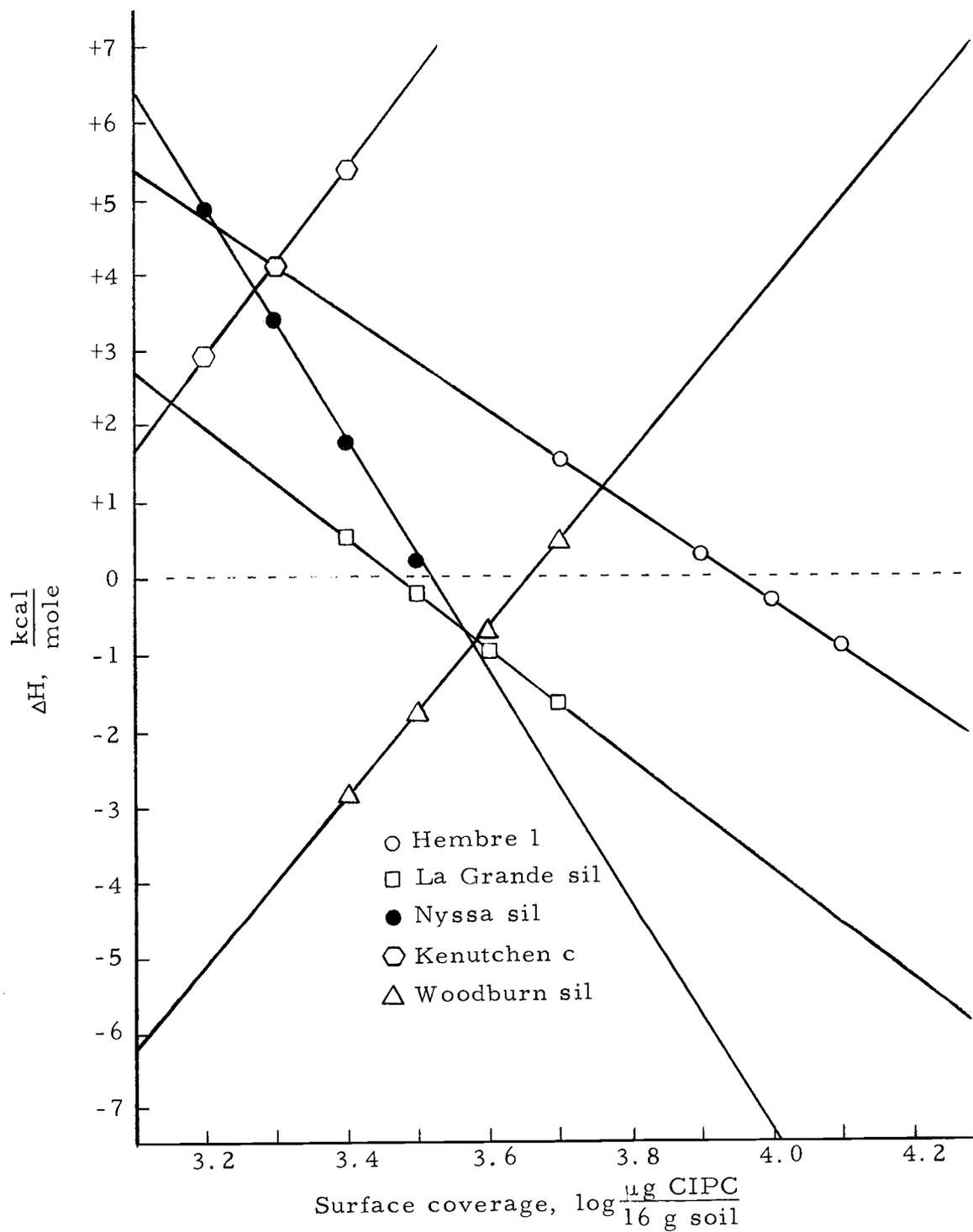


Figure 22. Relationship of ΔH at 25°C to 50°C and surface coverage by CIPC

values ranging from 0.4 to 4.7 kcal for the adsorption of CIPC on clay minerals.

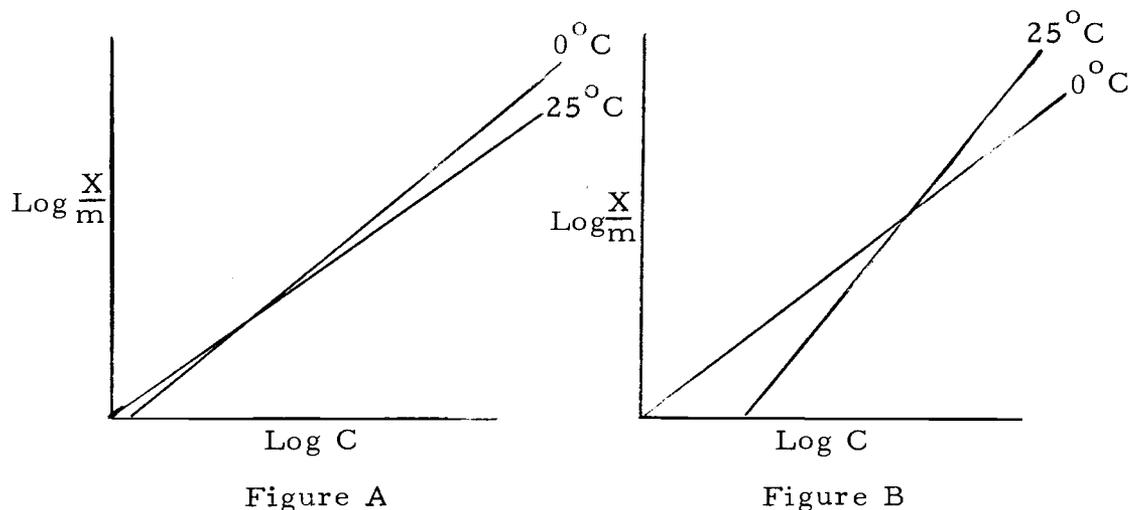
The majority of the ΔH values in Figure 21 are negative for most of the surface coverages of each soil. Over a temperature range of 0°C to 25°C more negative ΔH values should be expected as less thermal energy is imparted to the CIPC molecules relative to a temperature range of 25°C to 50°C and hence the contribution of the $T\Delta S$ term in the equation $\Delta H = \Delta G + T\Delta S$ would be less significant.

Enthalpy changes decreased between the $0 - 25^{\circ}\text{C}$ temperature range for La Grande sil, Woodburn sil, and Kenutchen c while the enthalpy values for Nyssa sil and Hembre l increased from negative to positive as the surface coverage increased. A trend of ΔH values from negative to positive is expected as the heterogeneity of a surface leads to a decrease in bonding energy as the surface coverage increases.

Woodburn sil and Kenutchen c showed a trend of negative to positive ΔH values at 25°C to 50°C as surface coverage increased. Hembre l, La Grande sil, and Nyssa sil showed an opposite trend of positive to negative ΔH values with increasing surface coverage.

The method utilized to calculate ΔH values involves the use of the CIPC equilibrium concentration for each isotherm at a given $\frac{X}{m}$ value. Negative or positive trends of ΔH values for a soil as a function of surface coverage will therefore be dependent on the

position of the two Freundlich isotherms relative to each other.



In illustration; both Figures A and B show more adsorption at 0°C for the majority of the range of equilibrium concentrations. However, ΔH calculations for Figure B would result in ΔH values which increase from negative to positive with increasing surface coverage while Figure A would show a decrease in ΔH values with increasing surface coverage. It is most probable that the specific surface properties of each individual soil determine the slope of the Freundlich isotherms at each temperature and hence the relationship of the isotherms to each other.

The van't Hoff equation may also be used to calculate ΔH values. The equation may be written:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H (T_2 - T_1)}{R T_1 T_2} \quad (13)$$

K_1 = rate constant at T_1

K_2 = rate constant at T_2

T = temperature in degrees kelvin

R = gas constant

ΔH = heat of reaction in $\frac{\text{kcal}}{\text{mole}}$

The van't Hoff equation was used by Schwartz (1967) to calculate ΔH values for the adsorption of CIPC on an activated carbon surface. The model system proposed by Schwartz is as follows:



where:

P = pesticide

C = activated carbon

PC = adsorbed pesticide-carbon complex

K_1 and K_2 = reaction rate constants

The equilibrium constant K is defined as:

$$K = \frac{PC}{(P_o - PC)(C_o - PC)} \quad (15)$$

where;

PC = amount of pesticide adsorbed per unit volume

P_o = initial pesticide concentration

C_o = concentration of activated carbon adsorption sites

To enable the use of the van't Hoff equation, it was assumed that the amount of pesticide adsorbed was very small relative to the

number of active sites available for adsorption. Equation 15 then becomes:

$$K = \frac{PC}{(P_o - PC)(C_o)} \quad (16)$$

Since C_o is a constant value for K_1 and K_2 the term C_o is eliminated when the ratio of $\frac{K_1}{K_2}$ is considered. Thus K_1 can be defined as follows:

$$K_1 = \frac{\mu\text{g CIPC adsorbed per 16 g soil at } T_1}{(\text{Total } \mu\text{g CIPC in system at } T_1 - \mu\text{g CIPC adsorbed per 16 g soil at } T_1)}$$

K_2 is defined in the same manner but conditions at T_2 are utilized.

The ΔH values calculated by the van't Hoff equation over the temperature range of 0°C to 25°C are generally negative (Table 6). The negative sign reflects the energy lost to the system upon the formation of a bond between the CIPC and the soil. ΔH values calculated over the temperature range of 25°C - 50°C are positive. Energy is thus required to form bonds at the higher temperatures. Since adsorption of CIPC was observed at 50°C , one must assume the existence of negative ΔG values. The positive ΔH values at a higher temperature range reflect the fact that in the equation $\Delta H = \Delta G + T\Delta S$ the positive magnitude of the entropy term exceeds the negative magnitude of the free energy term.

Table 6. Heat of enthalpy (ΔH) values for five Oregon soils as calculated by the van't Hoff equation

Soil series	CIPC	$\Delta H(0^\circ\text{C}-25^\circ\text{C})$	$\Delta H(25^\circ\text{C}-50^\circ\text{C})$
	Initial concentration ppm	kcal mole	kcal mole
Hembre l	25	+0.7	+0.9
	60	-0.3	+0.2
Woodburn sil	25	-3.2	+1.2
	60	-0.6	+0.4
Nyssa sil	25	-2.5	+8.3
	60	-3.5	+0.6
La Grande sil	25	0	+2.2
	60	+0.4	-2.3
Kenutchen c	25	+6.5	+1.3
	60	-6.1	+1.5

SUMMARY

Adsorption of CIPC on soil systems was studied as a function of temperature, equilibration time, and CIPC concentration. Equilibrium between CIPC and the soil was achieved in three hours for all soils with the exception of Hembre 1 which required nine hours. The increase in time required for Hembre 1 to achieve equilibrium is perhaps related to 1) a required configuration or position of the CIPC molecule in relation to the complex structure of the organic matter or 2) a time factor involving diffusion of the CIPC molecule along a tortuous path to the adsorption site. Although the soils did require a similar time period to achieve equilibrium, the rate at which the soils reached equilibrium was different. A diffusion phenomena appears to control the rate at which a soil achieved maximum CIPC adsorption.

In general the soils adsorbed more CIPC at the lower temperatures (0°C and 25°C) than at the higher temperature of 50°C .

The high CIPC adsorption (52% of the initial CIPC in the system) of Hembre 1 is postulated to relate to the 29% organic matter content of this soil. Organic matter possesses a large surface area with many functional organic groups that could act as bonding sites for the CIPC molecule. Equal adsorption of CIPC by Hembre 1 at 0°C , 25°C , and 50°C suggests that perhaps a soil with a high organic matter

content would not be as temperature dependent as soils with lower organic matter contents. The adsorption of CIPC on a soil as a function of varying CIPC concentration was best described by the Freundlich equation. The adsorption data was not described by use of the Langmuir equation.

ΔH values calculated over a temperature range of 0°C to 25°C were negative, thus indicating the process of CIPC adsorption onto a soil surface to be exothermic. Calculation of ΔH values over a temperature range of 25°C to 50°C yielded positive ΔH values indicating a more endothermic adsorption process. The low ΔH values for CIPC adsorption (+2.5 kcal to -7.0 kcal) suggest a weak physical adsorption due to coulombic, weak Van der Waal, and hydrogen bonding.

Effective weed control with CIPC in soils high in organic matter would require higher than normal rates of CIPC application as much of the CIPC would be adsorbed onto the organic matter and perhaps unavailable for weed control. Higher than normal rates of CIPC application in soils with pumice like material would be dependent as to whether or not the CIPC trapped in the internal pore spaces would be available for effective weed control. The low ΔH values observed for CIPC adsorption onto soils indicates that CIPC from a purely chemical standpoint is weakly adsorbed, however,

relative to some other herbicides, CIPC is strongly retained in a soil system.

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