The influence of the contact angle on the kinetics of vapor adsorption and unsaturated flow
by Edward T Kanemasu

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Soils
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The liquid-solid contact angles between water and ethanol soil extract or ethanol soil extract + clay coated on glass slides were measured. The extract + clay produced the largest contact angle. These slides were equilibrated at various relative humidities and small drops of water of known volume were placed on the slide and the width (X) was measured by a measuring microscope. The contact angles (α) were computed from the formulas tan α/2Zh for angles less' than 90 degrees and sin - 90) = x (Formula not captured by OCR) for angles greater than 90 degrees. Values of h/X were obtained from the corresponding calculated values of V/X where h and V represent the height- and the volume of the drop, respectively. As the relative humidity increased, the contact angle tended to decrease. Analysis of variance show variation due to soils and extracts to be highly significant at 65% relative humidity.

Differences between high and low contact angle soils were found in unsaturated flow and vapor adsorption studies. The data indicate that the rate-limiting step in unsaturated flow is due to the vapor phase preceding the wetted front. Calculated data from Millville loam indicate that the activation energies for evaporation and vapor diffusion through air + vapor adsorption are 9.6 and 7.7 kcal. per mole, respectively. It appears that evaporation is the rate-limiting step in water movement through unsaturated soils. However, the activation energies for evaporation and, vapor adsorption are nearly equal.

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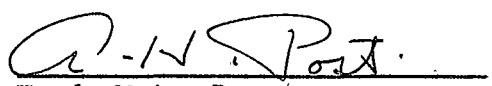

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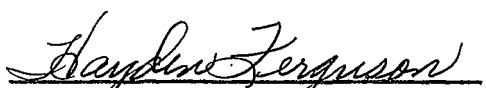

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ABSTRACT

The liquid-solid contact angles between water and ethanol soil extract or ethanol soil extract + clay coated on glass slides were measured. The extract + clay produced the largest contact angle. These slides were equilibrated at various relative humidities and small drops of water of known volume were placed on the slide and the width (X) was measured by a measuring microscope. The contact angles (α) were computed from the formulas $\tan \alpha / 2 = \frac{2h}{X}$ for angles less than 90 degrees and $\sin(\alpha - 90) = \left(\frac{2h}{X} - 1\right)$ for angles greater than 90 degrees. Values of h/X were obtained from the corresponding calculated values of V/X where h and V represent the height and the volume of the drop, respectively. As the relative humidity increased, the contact angle tended to decrease. Analysis of variance show variation due to soils and extracts to be highly significant at 65% relative humidity.

Differences between high and low contact angle soils were found in unsaturated flow and vapor adsorption studies. The data indicate that the rate-limiting step in unsaturated flow is due to the vapor phase preceding the wetted front. Calculated data from Millville loam indicate that the activation energies for evaporation and vapor diffusion through air + vapor adsorption are 9.6 and 7.7 kcal. per mole, respectively. It appears that evaporation is the rate-limiting step in water movement through unsaturated soils. However, the activation energies for evaporation and vapor adsorption are nearly equal.

INTRODUCTION AND LITERATURE REVIEW

In the investigations of liquid penetration into a porous solid or liquid movement over a plane surface, a three phase boundary equilibrium is usually observed. Mathematically, one can describe the pressure difference across a meniscus in a capillary by Young and Laplace's equation,

$$P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad [1]$$

where γ is the surface tension of the liquid and R_1 and R_2 are the two radii of curvature. For a hemispherical meniscus, R_1 and R_2 are equal and equation [1] becomes $\Delta P = \frac{2\gamma}{R}$. A more general form of equation [1] which accounts for the wetting properties of the capillary is

$$\Delta P = \frac{2\gamma \cos\alpha}{r} \qquad [2]$$

where r is now the radius of the capillary and α is the contact angle between the capillary wall and the liquid.

One can also treat mathematically, by Young and Dupres equation

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL}, \qquad [3]$$

the phenomena of a liquid drop on a plane surface, where W is the work of adhesion, γ_{SA} and γ_{SL} are the surface tensions of the solid against air and liquid, respectively, and γ_{LA} is the surface tension of the liquid. Since most liquids rest on solids at a definite angle α, one can write

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA}\cos\alpha . \qquad [4]$$

Combining equation [3] and [4],

$$W_{SL} = \gamma_{LA}(1 + \cos\alpha). \qquad [5]$$

Then according to equation [5], a contact angle of zero would indicate that the liquid attracts the solid as much as it attracts itself. Likewise an angle of 90 degrees indicates the attraction for the solid is half of its self attraction and 180 degrees angle would indicate no adhesion of the liquid for the solid. However, Adam (1938) states that angles of 180 degrees are unrealizable. He also emphasizes the distinction between zero contact angle surface and wetting surface. A wetting surface can exhibit a zero or finite contact angle. This suggests the use of the contact angle as an index of the hydrophobic properties of a surface or a porous material.

However, Adam (1938) states that equation [5] has little meaning because of the indefiniteness of α. It is not unusual to observe that advancing and receding contact angles may be very different. The contact angle assumes a maximum when advancing over a dry area and minimum when receding over a previously wetted surface. The exact cause of this hysteresis effect on contact angles is still obscure, however, many explanations have been proposed. Adam (1938) states that the hysteresis effect appears to be related to a frictional resistance to motion of the liquid edge over the solid. Another explanation offered is that the work of adhesion between the solid and the liquid is actually different for a dry surface than for one that has been previously wetted. Surface roughness has also been cogently suggested as an explanation, Shuttleworth and Bailey (1948) and Adam (1938). Adam (1938) states that surface roughness will increase the apparent contact angle if the true angle is greater than 90 degrees and decrease the apparent angle if the true contact angle is less than 90

degrees. However, Bikerman (1950) concludes the surface roughness does not influence the contact angle due to the cancellation effect of grooves and ridges.

Significance

It is possible that if a soil exhibits a resistance to wetting or forms a finite contact angle with water, these hydrophobic properties would modify evaporation, erosion, water adsorption and water movement. Baver (1940) states that the contact angle between the liquid and a soil particle is generally assumed to be zero; however, many studies indicate that this assumption is incorrect. Early work by Linford (1930) shows that the contact angle may be zero for minerals but becomes quite different from zero if an organic constituent is added. Jamison (1945) studied the hydrophobic nature of sandy soil found beneath citrus trees in Florida and attributed this phenomenon to the organic colloids in the soil. His data show that extracting the soil with ethyl and methyl alcohol, diethyl ether and water-free petroleum ether decreased the wetting time. He suggests that the effect of the extractants was due in part to the removal of small quantities of oils, waxes or other organic materials which were not wetted by water. Swartzendruber et al. (1954) state that quantity or quality of organic matter, either or both, may affect the wetting angle. This agrees with the data obtained by Cawlfield (1962)[1/] in which an organic forest soil exhibited a smaller contact angle with water than soils

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[1]Cawlfield, George E. The contact angle between water and soil materials. Unpublished master's thesis. Montana State College Library. 1962.

with lower organic matter content. Emerson and Bond (1963) measured the height of rise of water in natural and ignited sand columns. It was assumed that the ignited sand, which was subjected to 500° C. temperature, exhibited zero contact angle and, consequently, the height of rise was greater than in the natural sand column. It is evident that the organic matter would be oxidized at this temperature.

Recent investigations into the hydrophobic effect on soil-water relationships has been conducted by Letey et al. (1962), Pelishek et al. (1962) and Cawlfield (1962). Letey et al. (1962) packed a visibly hydrophobic soil into a glass column, placed a head of water on the soil column and noted rate of water penetration. After 7 minutes, the water had failed to penetrate the soil. Ethyl alcohol which assumed a zero contact angle with the hydrophobic soil (Letey et al. 1962) readily entered the soil, thus indicating that water entry was not prohibited by lack of pores. Cawlfield (1962) found, in a short-time experiment, that soils with larger contact angles lost more water due to evaporation than did soil of lower contact angles. Letey et al. (1962) also studied the effect of contact angle on evaporation and found that the hydrophobic sand lost water at a greater rate at the beginning but the evaporation rate from the treated sand decreased and 400 hours after evaporation started, 60% of the water in the untreated sand had been lost and 45% of the water in the treated sand was lost. This phenomena was explained by the formation of a dry mulch surface layer on the high contact angle sand because of failure of capillary forces in moving water into the high contact angle sand.

Pelishek et al. (1962) studied the effect of wetting agents on infiltration into these same hydrophobic soils. Their data indicate that a wetting agent increases infiltration rates into hydrophobic soils and the wetting agents studied produced a beneficial residual effect. The modified Poiseuille's equation derived by Letey et al. (1962) appears applicable in the studies of liquid infiltration and is given by

$$Q = \frac{Cr^2 \rho gh}{8L\eta} + \frac{2Cr\gamma \cos\alpha}{8L\eta} \qquad [6]$$

where Q is the quantity of liquid entering the soil per unit area with time, C is the volume fraction of the wet soil, r is the effective pore radius, ρ is the density of the liquid, g is the gravitational constant, h is length of the liquid column, L is the wet soil column, η is the liquid viscosity, γ is the surface tension and α is the contact angle. It is obvious from this equation that an ideal wetting agent would be one that maintained a high surface tension and decreased the contact angle. They state that their wetting agents did not appreciably affect the density and viscosity of water. It is also conceivable that a wetting agent could decrease the infiltration rate by decreasing the surface tension and decreasing the contact angle of an already hydrophilic soil. This indicates that the magnitude of the contact angle could be of significant importance in the application of wetting agents.

Another important moisture exchange effect of hydrophobic soils is erosion potential of these soils, Osborn et al. (1963).[2/] It would appear

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[2]Osborn, J. F., Pelishek, R. E., Krammes, J. S. and Letey, J. Annual Report for California Agricultural Experiment Station, University of California, Los Angeles and Riverside. 1963.

that since soil wettability influences soil-water interactions, erosive action of water on a soil would depend upon the soil wettability. An experiment was performed on a watershed which was left barren by fire and was observed to exhibit hydrophobic properties. One-half of the plots were treated with a wetting agent and the other half untreated. Treatment reduced erosion about fifteen-fold, decreased run-off approximately 32% and resulted in the establishment of better vegetative cover.

Another very important aspect of hydrophobic and hydrophilic soils was studied by Dexter and Miyamoto (1959). They found that by coating the surface of sugar beet seeds with hydrophilic colloids increased water uptake from sand and accelerated the emergence of seedlings.

Besides these cogent investigations, it has been suggested that the capillary theory may be modified by determining the wetting angle of a soil, Swartzendruber (1956).

Methods of Measurement

Several methods have been suggested for determining the magnitude of the liquid-solid contact angle. The capillary rise method has been successfully applied by Letey et al. (1962) and Emerson and Bond (1963). The basic equation employed is

$$h = \frac{2\ \gamma\ \cos\alpha}{\rho\ gr} \qquad [7]$$

where h is the height of rise, γ is the surface tension of the liquid, α is the contact angle, ρ is the density of the liquid, g is the gravitational constant and r is the effective pore radius. Letey et al. (1962) coated sand with a water extract of chaparral litter, NH_4OH extract of

chaparral litter and NH_4OH-starch solution to produce various contact angles. They placed these sands into a column and observed height of water rise from free water. There was almost a five-fold difference in height of rise between the untreated and the most hydrophobic sand. In equation [7] r and α are unknown for a given liquid, however, if ethanol is assumed to wet all solids with an apparent angle of zero, r can be determined. The calculated value of r is then used to solve for α when other liquids are used for capillary rise in columns which have been identically packed.

Previous investigation by Cawlfield (1962) has indicated that ethanol extracts coated on glass microscope slides produced contact angles greater than 90 degrees with water. However, since a separation of hot and cold alcohol soluble extract can be made, it seems reasonable that cold ethanol drops on hot alcohol soluble extracts could be used as a measure of ethanol's ability to wet all solids completely. It should be noted that in so doing one assumes that no hot alcohol soluble material will also be soluble in cold ethanol. Moreover, distilled water has a surface tension of approximately 72 dynes per cm. while ethanol has a surface tension of only 20 dynes per cm.

It is conceivable, due to the various amounts and quality of organic matter present in the A horizon, that ethanol may not always exhibit a zero contact angle. Letey et al. (1962) suggest that since ethanol gives the same infiltration rate in all cases, the only conceivable constant angle would be zero.

An alternate method of measuring the hydrophobic properties is to measure the relative wetting time, Jamison (1945) and Sonders et al. (1950). Jamison (1945) recorded the relative time of wetting as the time required for 20 cc. of water to penetrate the surface and be adsorbed by the soil. No specifications were given as to the bulk density and depth of penetration. Sonders et al. (1950) suspended Wyoming bentonite, spraying thin layers on tile and dried at 110° C. for 24 hours. The time was observed for a drop of distilled water to spread on the thin layers. Results from the capillary rise method were found to be comparable with the time of wetting method.

McMillen (1929) and Davis and Curtis (1922) use the "Bartell cell" for measuring the contact angle of a porous solid. This method of studying the wetting process involves the measuring of the pressure exerted when a fluid displaces a liquid from a compressed powdered solid. Disadvantage of this method lies with the tedious equilibration point.

Variations of the drop on plate method for measuring the contact angle have been used by Mack (1936), Adam (1938), Mankowich (1953), Bigelow and Brockway (1956), and Cawlfield (1962). A variation, mentioned by Mack (1936), is a determination of acute contact angles from known volumes of droplets. The volume method appears to be advantageous over the method described by Cawlfield (1962). The volume method requires that only the base of the drop be measured; hence, a more rapid procedure would reduce errors due to evaporation of the drop. Moreover, smaller drops can be applied and their use is favorable especially on irregular surfaces. Mack (1936) states that small drops assume the advancing angle of contact

while large drops exhibit a fluctuating angle of contact between advancing and receding angles. The size of the drop influences the ease with which a drop will spread over a surface. The hydrostatic pressure due to the weight of large drops tend to enhance further spreading. The capillary pressure within the drop opposes any further increase in surface area. This pressure is inversely proportional to the radius of curvature and, hence, greater for small drops. Consequently, with increasing drop size, both hydrostatic and capillary forces favor the probability of irregular extension of the drop. It is conceivable that with large drops the volume may exert a greater influence on the contact angle than the properties of the surface.

Soil-Water Interaction and the Darcy Equation

The Darcy equation has been used to describe unsaturated (larger pores are filled with air) flow through a porous material. However, in many cases deviations from the Darcy equation have been attributed to the soil-water interaction and the changing contact angle as water enters a dry soil. According to Baver (1940, page 251) the Darcy equation for horizontal unsaturated flow can be expressed as

$$Q = -K \nabla \varphi \qquad [8]$$

where Q is the mass of water which passes in one second through 1 square centimeter of an imaginary plane perpendicular to the direction of flow, K is the capillary conductivity and grad φ is the capillary-potential gradient, that is, the amount by which φ increases negatively per centimeter in the direction of flow. The negative sign results from the moisture content of the soil decreasing in that direction.

Because of the heterogeneous properties of soil, the geometry of the water-air interfaces must undergo continual change. Nielsen et al. (1962) tested the validity of the assumption that a unique relationship exists between pressure and moisture content in unsaturated flow studies where the Darcy equation is assumed valid. They found a linear relationship between distance and the square root of time only at -2 millibar pressure and at other pressures the lines were curvilinear. They suggest that the changing contact angles could be responsible for this lack of uniqueness between the water content and pressure. They also suggest that the non-Darcy flow which often occurs immediately after time zero is due to the changing contact angle. Another explanation could be the exothermic reaction of water and water vapor on soils where the Darcy equation assumes isothermal conditions. Non-Darcy behavior has also been explained by a clay-water interaction in which the adsorbed water takes on a modified structure, Low (1961). Henniker (1949) concludes that the adsorbed water assumes a quasi-crystalline ice structure. Low (1961) states four requirements for water flow in the vicinity of a quasi-crystalline structure at a clay surface. First, it should exhibit a yield value at the threshhold hydraulic gradient below which flow will not occur. Second, after flow commences, there should be a range of hydraulic gradients over which non-Newtonian flow occurs, i.e., the viscosity should be dependent on the shearing force. Third, the viscosity should increase with proximity to the clay surface. Fourth, the viscosity of the water near the surface of the clay should be greater than the viscosity of free water. Low (1961)

concluded that there is sufficient evidence to fulfill all the requirements of a quasi-crystalline structure near the surface of the clay particle.

However, Martin (1960) found that the water molecules in the sorbed phase on kaolinite have greater randomness than water molecules in bulk liquid water for at least the first two molecular layers. Moreover, he states that no definite conclusion can be reached about the nature of sorbed water on montmorillonite because of the profound influence of the exchangeable ions. He concludes that the structure of sorbed water is not an "ice-like" structure but all previous data obtained are consistent with either the two-dimensional liquid or the fixed adsorption site model. However, it may be concluded that a clay-water interaction does exist but the exact nature is still obscure.

The mathematical theory of diffusion is given by

$$F = -D \frac{\partial \theta}{\partial x} \qquad [9]$$

where F represents the flux, θ is the volume of water per unit volume of soil and x is the independent variable of position. The diffusion coefficient, D, varies with water content. Assuming that the capillary-potential, φ, is a single valued function of the water content, θ, and combining with the equation of continuity, equation [8] and [9] can be written

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \theta}{\partial x} \right). \qquad [10]$$

The equation of continuity, which expresses the concept of conservation, may be expressed as

$$\frac{\partial \theta}{\partial t} = \frac{\partial V}{\partial x} \qquad [11]$$

where t is time, V is the velocity of flow and θ is the moisture content on a volume basis. Equation [10] has been derived from equation [8] by Klute (1952) and from equation [9] by Ferguson and Gardner (1963).

If we consider a semi-infinite medium with the boundary conditions

$$\theta = \theta_s, \; x = 0, \; t > 0$$

$$\theta = \theta_o, \; x > 0, \; t = 0$$

and that D in equation [9] is a function of only θ, then the Boltzmann transformation,

$$y = \tfrac{1}{2} x t^{-\frac{1}{2}} \qquad [12]$$

can reduce equation [9] to

$$-2y \frac{d\theta}{dy} = \frac{d}{dy}\left(D \frac{d\theta}{dy}\right) \qquad [13]$$

and the boundary conditions become

$$\theta = \theta_s, \; y = 0$$

$$\theta \to \theta_o, \; y \to \infty$$

then θ is a function of y only and, hence, for any given θ, x is proportional to $t^{\frac{1}{2}}$. This treatment of water movement has been studied by Ferguson and Gardner (1963) and Gardner and Mayhugh (1958).

Kirkham and Feng (1949), Biggar and Taylor (1960) and Miller and Gardner (1962) use a similar equation to study infiltration. The general form is given by

$$Q = At^B \qquad [14]$$

where Q is the cumulative infiltration after time, t from the start of infiltration and A and B are parameters. It is obvious that a linear

relationship would exist in a plot of quantity versus t^B. Ferguson and Gardner (1963) and Swartzendruber (1956) found slight deviations near the origin and many of the curves do not pass through the origin. The explanation of deviations has been explained by the diffusivity, D, not being a function of θ alone over the whole range of distance or time and also that the properties of water entering a dry soil are modified by clay-water interactions.

Besides the pressure, which has been found in some cases to produce non-Darcy behavior (Nielsen et al. 1962), bulk density, initial moisture content, and temperature influences on unsaturated flow deserve discussion. Nielsen et al. (1962) show that soil columns packed at 1.289, 1.297, and 1.302 g. per $cm.^3$ average bulk densities show no differences in distance versus the square root of time plots. Box and Taylor (1962) studied the effect of soil matric potential on the bulk density of the soil. Their data show that there is not significant differences in the matric potential between 1.1 - 1.6 g. per $cm.^3$ at all the initial moisture contents studied. The matric potential increased with increasing moisture content. In plotting distance versus time on log-log paper, and moisture content as the parameter, Ferguson and Gardner (1963) obtained slopes of 0.46 - 0.49. They found slopes near 0.50 at high moisture contents and also the relation between diffusivity and water content was linear at high values of θ. This may be explained by the fact that water traveling through previous established channels would tend to flow further out from the clay particle and away from the surface forces of the particle. Because of their effect on the contact angle, adhesive forces exhibit an influence on the initial

wetting process; but after the soil has been wet, these forces no longer are effective in producing liquid movement and serve only to anchor the thin adjacent film.

One would expect that temperature would influence infiltration. This influence would be expected from the capillary theory as a result of viscosity and surface tension of water with temperature. Jackson (1963) studied water infiltration at 5.0, 13.5, 24.0, 33.0 and 42.5° C. and found 2- and 3-fold differences in distance-time relationships but no differences in water distribution curves. He concluded that surface tension and viscosity were the only contributing factors influencing the temperature dependence of water infiltration. He also states that the contact angle is not appreciably influenced with temperature in his studies.

Another source of heat would arise from the heat liberated by the adsorption of the water vapor preceding the liquid front followed by an abrupt temperature drop caused by the cooler liquid front. A temperature fluctuation of 30 and 12° C. for a clay and a sandy loam soil, respectively, with an initial moisture content near zero were observed by Anderson et al. (1963). The magnitude of these fluctuations decreased exponentially with the increasing initial water contents and became essentially zero at water contents up to about 60% of the 15-bar moisture content. They concluded that when the soil is dry, the vapor pressure of the water adsorbed on the soil is very low, the heat of adsorption is at a maximum and the specific heat capacity is at a minimum. In this environment, the unobstructed pores permit rapid vapor movement and, hence, the temperature fluctuation will be greatest. When the soil is wet, the circumstances are

reversed. The most important influence on the magnitude of a temperature fluctuation is the textural classification. It appears that vapor adsorption may play an important part in unsaturated flow when water initially moves into an air-dry soil and at the wetted front where liquifaction may occur. Anderson et al. (1963) concludes that the rate-limiting step in unsaturated flow is the evaporation at the wetted front.

Activation Energy

Before one can establish a rate-limiting step in a reaction, the activation energy must be calculated for each specific reaction and the largest activation energy would correspond to the rate-limiting step. Hence, the activation energy is the energy barrier that a particular reaction encounters and the highest energy barrier encountered in a process is the rate-limiting step. Low (1960) found apparent activation energies for Wyoming bentonite plugs ranging from 3.8 to 4.4 kcal. per mole. Biggar and Taylor (1960) found energies ranging from 1 to 3 kcal. per mole of water. They concluded that the barrier or barriers opposing water infiltration into dry soil are located at the air-water interface associated with the advancing water front. They suggest that a large contact angle could cause an energy barrier which could account for the steep wetting front. Moreover, Anderson et al. (1963) suggest that the activation energy for simple viscous flow is 3.8 kcal. per mole and that higher values result from interfacial interactions. These interfacial interactions can be interpreted as air-water and clay-water interactions.

The activation energy for unsaturated water flow is determined from the Arrhenius equation,

$$\frac{d \ln K}{dT} = \frac{E_A}{RT^2} \qquad [15]$$

where K is the rate constant, E_A is the energy of activation, R is the gas constant and T is the absolute temperature (Glasstone 1940, page 1088). The Arrhenius equation is explained on the physical phenomena that only molecules containing energy larger than some minimum value will take part in the reaction; hence, an increase in temperature will induce a larger concentration of such molecules. The Boltzman equation, $\frac{n}{n_o} = \exp. \left(\frac{E-E_o}{RT}\right)$, expresses the probability that a molecule will obtain this energy. By the use of the integrated form of equation [15],

$$\ln K = \frac{-E_A}{RT} + \text{Const} \qquad [16]$$

where ln K is a linear function of 1/T, the activation energy, E_A, can be calculated. Low (1959) uses a somewhat similar approach in determining activation energies for water flow in Na - bentonite plugs. Starting with the Darcy equation for unsaturated flow

$$Q = KAi \qquad [17]$$

where Q is the volume of fluid per unit time, K is the conductivity, A is the cross-sectional area and i is the pressure gradient. It should be pointed out that equation [8] is the same as equation [17] where the total potential gradient is replaced by the pressure gradient. Equation [17] can be written as

$$Q = \frac{k}{\eta} Ai \qquad [18]$$

where k is the permeability, which depends on the geometry of the porous system, and η is the viscosity of the fluid. The effect of temperature

on the viscosity of a liquid can be described as

$$\eta = J \exp. (B/RT) \qquad [19]$$

where J and B are empirical constants for a given liquid (Glasstone 1940, page 499). According to the Maxwell-Boltzman distribution law the number of molecules possessing the necessary energy for flow is given as the Boltzman probability factor $e^{-E_A/RT}$, where E_A is the energy of activation. It is clear that, since the rate of flow is proportional to $e^{-E/RT}$ and viscosity is inversely proportional to fluidity or flow, viscosity will depend upon $e^{E/RT}$ and B in equation [19] is the activation energy. From the theory of absolute reaction rates (Glasstone, Laidler, and Eyring 1941, page 484) one obtains

$$J = \frac{hN}{V} \exp. (-\Delta S\ddagger/R) \qquad [20]$$

where h is Plank's constant, N is Avogadro's number, V is the molar volume, $\Delta S\ddagger$ is the entropy of activation and R is molar gas constant. By substituting equation [19] into equation [18] one can write

$$Q = \frac{kAi}{J} \exp. (-E/RT) \qquad [21]$$

Taking logarithms on both sides, one has

$$\ln Q = \ln \frac{kAi}{J} - \frac{E}{RT} . \qquad [22]$$

Therefore, the energy of activation can be determined by plotting the logarithm of the flow rate against the reciprocal of the absolute temperature and determining the slope of the resulting line. Anderson et al. (1963) used this approach to the activation energies of viscous and vapor flow while Biggar and Taylor (1960) make use of the modified Darcy equation,

$$Q = Kt^{\frac{1}{2}}, \qquad [23]$$

where Q is the flow rate, K is adsorption coefficient and t is the time of infiltration. Anderson et al. (1963) state that the K in the above equation does not correspond to the K in equation [16] since it does not have the dimensions of a rate constant, i.e., reciprocal time. In order to have the correct dimensions, the K should be replaced by K^2 and, hence, the slope of the linear plot of log K^2 against 1/T would enable the calculation of the activation energy.

Data obtained from the activation energy concept indicate that a rate-limiting step does exist and probably is located at the air-water and clay-water interface. Associated data show that the bulk density of Millville silt loam between the range of 1.14 to 1.21 g. per $cm.^3$ does not significantly change the activation energy. However, the activation energies appear to be higher for the finer size fraction of the Millville silt loam. This can be explained by data presented by Kemper (1961). He states that in addition to viscous movement, which includes the movement of the whole semi-crystalline mass of water, diffusion takes place. From time to time each molecule obtains that amount of energy (free energy of activation) to allow it to break the hydrogen bonds tying it to the semi-crystalline lattice and move to a new position. Since the driving force of viscous and diffusion flow is pressure gradient and free energy, respectively, Kemper derives the relationship

$$P = \frac{6.5 \times 10^{-17}}{b^2} \Delta G \qquad [24]$$

where ΔP is the pressure gradient in dynes per $cm.^2$, b is the depth of

the film through which water travels and ΔG is the free energy gradient which may rise from concentration gradients expressed in ergs per mole. From this relationship he states that diffusive movement is predominate when the film is reduced to 20 Å and viscous flow becomes nil at the molecular thickness of 4.3 Å. This indicates that the free energy term becomes large when the pore size or water films becomes small.

Anderson et al. (1963) disregards the clay-water interaction, arguing that a definite cleavage plane exists about each particle and beyond that plane the water is not influenced by the particle. One is then led to believe that the air-water interaction is the rate-limiting step. The air-water interface would be located ahead of the wetted front and associated with the vapor phase. Since their data indicated an activation energy of 9.7 kcal. per mole which correspond to the energy of vaporization, they conclude that evaporation at the wetted front is the rate-limiting step in infiltration. It appears, however, that vapor movement ahead of the wetted zone may play an important role in the rate of infiltration.

Vapor Adsorption

Glasstone et al. (1941) states that many reactions involving gases will occur more rapidly as a heterogeneous process on the surface of a solid than as a homogeneous reaction in the gas phase. This can be attributed to the surface acting as a catalyst. Since adsorption of the gases must play an important part in heterogeneous reactions, this subject will be given some consideration. There are two main types of adsorption of gases by solids. They are separated by the forces involved; physical or van der Waals adsorption involving physical forces and chemisorption forces

concerned with chemical bond formation. Adsorption of the van der Waal type is accompanied by relatively low heat of adsorption, e.g., 5 kcal. per mole compared to chemisorption values of 10 to 100 kcal. per mole.

Most of the investigations on vapor adsorption on soils have been concerned with calculating pore size and surface area. The Kelvin equation or its modifications are usually used in calculating the pore size, (Foster 1951; Cohan 1944; and Emmett and Cines 1947). It may be expressed as

$$r_d = \frac{2\ \gamma\ V \cos}{RT\ \ln\ P/P_o} \qquad [25]$$

where r_d is average radius of the capillary tube (pore size), γ is the surface tension of the adsorbed liquid, V is the molal volume of the liquid, R is the gas constant, T is the absolute temperature, P is the pressure in which the solid and adsorbed film are in equilibrium, P_o is the vapor pressure of free water and α is the angle between the liquid and the wall of the capillary. Cohan (1944) suggested that r_d was the radius after a monolayer had been adsorbed and the proper equation is

$$r_c = \frac{V \cos\alpha}{RT\ \ln\ P/P_o} \qquad [26]$$

The BET equation has been extensively used to calculate the amount adsorbed at the monolayer point. Brunauer et al. (1938) have derived an equation for multilayer adsorption which can be expressed as

$$\frac{X'}{V\ (1-X')} = \frac{1}{C\ V_M} + \frac{(C-1)X'}{C\ V_M} \qquad [27]$$

where X' is the relative pressure, V is the amount adsorbed per gram of solid, V_M is the amount adsorbed per gram at the monolayer point and C is

equal to exp. $[(Q_1^o - Q_L)/RT]$ where Q_1^o is the heat of adsorption of the first layer and Q_L is the heat of liquifaction and RT is the gas constant and absolute temperature, respectively. The terms V_M and C can be obtained from the slope and intercept of the linear plot of $\frac{X'}{V(1-X')}$ versus X'.

This approach was used by Mortland (1955) in which he tested the BET equation for ammonia adsorption on clays. He obtained linear plots in the usual BET range of 0.1 to 0.4 relative pressure. He found Q_1^o for kaolinite and bentonite to be 6.5 and 6.3 kcal. per mole, respectively. Heats of adsorption (ΔH) can also be calculated from the integrated form of the Clausius - Clapeyron equation:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad [28]$$

where P_1 and P_2 are the equilibrium pressures for a given adsorption at temperatures T_1 and T_2, respectively. The heat of adsorption (Q_1^o) calculated from the constant C of the BET equation and the heat of adsorption (ΔH) from the Clausius - Clapeyron equation are not directly comparable. Q_1^o from BET equation is derived from kinetic theory and represents the average heat of adsorption on the least active portion of the surface of the adsorbent and assumes perfect gas behavior. ΔH from the Clausius - Clapeyron equation comes out of thermodynamic theory and, hence, considers the total range of adsorption. Mortland (1955) found a general decrease in heat of adsorption as a gas is adsorbed. From 20 to 50% of a completed monolayer, a heat of adsorption (ΔH) was 22.0 to 24.0 kcal. per mole of ammonia and from 70 to 80% it was 12.0 to 14.0 kcal. per mole. These high heats of adsorption are typical of a strongly polar molecule indicating a

strong bond between ammonia and clay surface. Heats of adsorption (ΔH) showed the surface adsorption sites of Wyoming bentonite to be heterogeneous, since the energy of adsorption varied according to the amount of surface covered while Q_1^o from the BET equation varied little with the nature of the adsorbent. Goates and Hatch (1953) state that Q_1^o represents a quantitative measure of the affinity of a surface for an adsorbate. It is an intensive factor and, hence, is independent of surface area and is determined only by properties of the adsorbate and the nature of the soil colloids. They found linear BET plots for four soils and calculated the parameter C and Q_1^o. Results show C values range from 9.31 to 28.33 and Q_1^o values ranging from 3.37 to 4.03 kcal. per mole. Goates and Hatch (1954) found heat of adsorption (ΔH) of water vapor on silica ranging from 14.08 kcal. per mole at 74% monolayer coverage to 11.52 kcal. per mole at 26% more coverage than at a monolayer. The weight of water necessary to produce a monolayer on one gram of the adsorbent was 0.0073 gram. It appears that while ΔH may be influenced by the surface being covered, Q_1^o will represent the properties of both the adsorbate and adsorbent.

The surface area may also be calculated from the BET equation since

$$V_M = Vo \frac{\Sigma}{N\sigma} \qquad [29]$$

where V_M is again the amount adsorbed at the monolayer, Vo is molar volume of adsorbate, N is Avogadro's number, σ is the area per molecule of adsorbate and Σ is the surface area. This approach to calculating surface area of clays has been used by Mooney et al. (1952) and Orchiston (1953).

Orchiston (1953) found differences in the amount of water vapor adsorbed by montmorillonite, illite, and kaolinite. These differences can be explained by particle size and the relative strength of the bonds between the lattices. As one would expect, the exchangeable ions on the clays affect water sorption. This can be attributed to the hydration of the ions, direct effect of the space utilized by the hydrated ions and the effect on the packing area of the water layer. Keenan et al. (1951) found surface area decreasing with various ions on kaolinite in the following order: Ca, H, Sr, Na, Ba, K, Rb, Cs, Li. It was found that lithium was not hydrated in kaolinite because the lithium ions were sterically hindered by the outer oxygen atoms of the lattice. Mooney et al. (1952) found that in the case of expanding-lattice clays, the BET theory gives not the monolayer capacity on each surface of the expanded platelets but the adsorption when only one layer of molecules occurs between each pair of platelets. The nitrogen molecule is too large to fit between lattices and, therefore, gives only the external surface. Thus, the total surface area is obtained by subtracting the nitrogen area from twice the water monolayer area. Repeated adsorption-desorption measurements of water on montmorillonite showed that the desorption isotherms were reproducible while the adsorption isotherms were dependent upon the initial water content. Orchiston (1953) noted this same hysteresis with the expanding clays but kaolinite did not exhibit hysteresis.

Physical adsorption would be expected to occur rapidly. Mooney et al. (1952) states that montmorillonite at a relative pressure of 0.65 had adsorbed about 90% of the total water sorbed in the first few minutes and

the increase in total adsorption from the end of 24 hours to 10 days was only 0.31%. Physical adsorption is an exothermic reaction and, hence, an increase in temperature would decrease the amount adsorbed. Data from Goates and Hatch (1954) show that isotherms at 50 and 75° C. would roughly parallel one another with the adsorption at 50° C. being always larger than the adsorption at 75° C.

It appears that since the contact angle can be used as an index of the hydrophobic properties of a soil, it may be used as a measurable parameter to quantitatively describe the wettability of a particular soil. The wettability of soil may have significant application in erosion and evaporation control, water movement upward from a water table and irrigation practices.

Moreover, in addition to direct practical application, information on the magnitude and interaction at the soil-water or air-water interface may produce valuable knowledge on the kinetics of water movement in unsaturated soil. Hence, a study of the liquid-solid contact angle was undertaken.

METHODS AND MATERIALS

A forest silt loam soil from the Coram Experimental Forest near Glacier National Park was chosen because of the visible hydrophobic properties that these soils exhibited. One sample, designated as CII, was taken from an elevation of 4,000 feet and a location of SE¼, NW¼, Sec. 1, T30N, R19W. The parent material is glacial till and the main vegetation is Western larch, Douglas fir, Rosa and Berberia. Another sample, designated as CIII, was taken at an elevation of 4,850 feet at a legal description of NW¼, SE¼, Sec. 6, T30N, R18W. Douglas fir and spruce predominate the tree species and thimbleberry and huckleberry dominate the low vegetation. Both samples were taken in the upper 2 feet of the soil profile.

These soils were air dried and sieved through a 2 mm. screen. Approximately 100 to 125 grams were placed in Buchner funnels and leached with cold distilled water until the effluent appeared clear. The soil was then leached with hot 0.05 N $CaCl_2$ until tensiometer readings corresponded with the inffluent. After cold and hot water treatments, the soil was assumed free from water-soluble constituents. A small volume of alcohol was used to displace the water left in the soil. The soils were then subjected to 95% ethanol extractions in the soxhlet apparatus. To concentrate the alcohol extract, the soil in the thimble was changed from 3 to 5 times and the evaporating flask maintained at a safe level. The extraction temperature for ethyl alcohol was approximately 70° C. Ethanol was chosen as a solvent rather than an inorganic solvent because of lack

of residue on drying. Cawlfield (1962) has stated that materials which exhibit high and intermediate contact angles can be obtained in an ethanol extract of soil. It was observed that a precipitate formed in the ethanol extract in the CIII extract upon cooling. The cold and hot alcohol soluble fractions were separated and designated as CA-III and HA-III, respectively, and refrigerated in sealed containers until used. Materials used in the study; Superbrite glass beads,[3] a kaolin-type clay (dickite),[4] a silt, and glass microscope slides were coated with the extracts and stored until used.

The method of cleaning the 3 by 1 inch glass microscope slides was similar to the method used by Bigelow and Brockway (1956) and Cawlfield (1962). The slides were washed in hot detergent, rinsed and placed in cleaning solution for 15 minutes, rinsed again in hot water, distilled water and placed in a special dust-free oven to dry. The glass slides were then coated with the various extracts and evaporated, coated and evaporated again. This cycle was repeated from 2 to 3 times until a uniform heavy coating was obtained.

The contact angles of the extracts on glass slides were measured at various vapor pressures by enclosing them in a plexiglass chamber with an optical flat on one side and measured by the drop on plate method with a Gaertner measuring microscope with a filar micrometer eyepiece.

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[3] 3M. Company.

[4] The sample was taken by Dr. H. Ferguson from a mine at Lewistown, Montana, and established to be a pure dickite clay.

The apparatus has a total magnification of 32 diameters which is sufficiently accurate for readings to within 0.001 mm. Small droplets were admitted with a microliter syringe through a small opening on the side of the chamber. All measurements were conducted in a constant temperature room at 20 $\pm$ 1° C. Slides were allowed to equilibrate in the pressure chamber for at least 3 hours previous to contact angle determinations. This method was also applied to glass slides coated with a uniform layer of coated dickite and silt.

The equation used in calculating the contact angle from the drop on plate method is similar to the equation given by Mack (1936), Mankowich (1953), and Cawlfield (1962). The equation

$$\alpha = 2 \tan^{-1} (h/X), \qquad [30]$$

where α is the contact angle in degrees, h is the maximum height of the droplet and X is the radius of the base, can be applied to acute angles. This equation can be easily converted to a volume-radius equation

$$h^3 + 3hX^2 = 6 (V/\pi) \qquad [31]$$

where V is the volume of the droplet. Mack (1936) gives the values of h/X corresponding to values of V/X^3 from 0 to 2.0944, this being the range where the angle remains acute. These values of h/X can be used to calculate acute angles by the use of equation [30] and the formula $\sin (\alpha - 90) = (2h/X) - 1$ is used for obtuse angles. The formula for acute and obtuse angles are derived by Cawlfield (1962).

While the contact angle may vary from one extract to another when coated on glass slides, it is conceivable that the organic molecules or groups of molecules may re-orientate when coated on silt and on clay par-

ticles. Several 0.5 gram samples of dickite or silt were thoroughly shaken for two hours with 50 ml. of extract and coated on the clear glass slides with an eye-dropper and allowed to evaporate. Repeated evaporations were carried out until a uniform coating was observed. Slides were kept in a clean container until contact angle measurements could be made under various vapor pressures. Henniker (1949) cites data from a study by Lenker and MacHaffie (1925) in which flat surfaces were exposed to various water and benzene vapor pressures. They obtained films of definite thickness which were interpreted as an equilibrium approached from both sides. The water films ranged from 45 Å on silica to 5300 Å on glass. Henniker (1949) stated that clays and glass have a peculiar power on orienting water. Bangham (1946) found that these abnormal films, which are several angstroms thick, condense only on solids whose surface exhibit finite contact angles and the abnormality persists only out to a definite distance from the solid surface. The criterion of dissimilarity between adsorbed film and the bulk liquid was that a drop of the liquid would form a wetting angle with the solid surface until the adsorbed film reached a critical thickness when the drop adsorbed onto the film and would take the form of the bulk liquid. It appears then that a wetting surface would not show critical thickness films and, hence, zero contact angle would be observed at any vapor pressure while a non-wetting surface would exhibit Bangham's "critical films".

The silt was obtained from a Huffine silt loam. The silt loam was air dried and screened through 2 mm. sieve. The soil was then subjected to a particle size separation based on Stokes' law to produce particles

of 0.01 mm. diameter. In order to disperse the silt loam, Calgon and NaOH were used; and after the separation, the silt was leached with $CaCl_2$ solution and then with distilled water.

Glass beads were placed in stainless steel photographic pans and mixed with the various extracts. The coating was accomplished by evaporating the mixture at room temperature, and stirring frequently until air-dry, and placed in an 85° C. oven for 8 to 10 hours. This cycle was repeated two to three times to form a heavy coating. This procedure of coating was also used on the dickite and silt. All coated materials except the glass beads were placed in Buchner funnels and leached with a weak solution of $CaCl_2$ until the surface tension, as measured by a du Noüy tensiometer, of the effluent and inffluent became comparable. It was observed that some of the extracts were leached from the coated materials. The glass beads were leached with distilled water and surface tension measurements were made. The influence of the extracts on these materials were then compared by desorption curves, vapor adsorption and unsaturated flow properties.

The desorption curves were drawn from the data obtained from the pressure membrane apparatus, the porous plate and hanging water column. The hanging water column consisted of a fritted glass plate which attached to a pre-boiled distilled water reservoir coated with a thin film of oil to prevent re-adsorption of air. The tension applied could be adjusted by raising and lowering the fritted glass plate and the centimeters of water tension corresponded to the distance from the glass plate to the

top of the water reservoir. The maximum tension that could be applied was approximately 180 cm. of water.

A dynamic method was used in determining the adsorption isotherms of the dickite samples. Water vapor of a given vapor pressure was forced to flow past the sample until equilibrium between the dickite and atmosphere was established. The vapor pressure was controlled by bubbling air through a heated 2000 ml. flask of distilled water in which the temperature was controlled by a "Glas-cool" heating mantle adjusted by a variac. The saturated vapor was then led through about 10 feet of copper tubing in which the surrounding air was held at 20 $\pm$ 1° C. and through a glass slide chamber in which vapor pressure measurements could be made. Finally, the air was fed through a plexiglass tube in which the dickite was suspended from a quartz spring balance. The suction was adjusted by a pinch clamp to maintain a tension of 85 cm. of water. The amount of vapor adsorbed could be measured by a traveling cathetometer with an accuracy of 0.003 g. This procedure is similar to the apparatus used by Goates and Hatch (1954). Rao (1941), Foster (1951) and Dacey and Thomas (1954) employed the quartz spring balance in similar vapor studies. Equilibration time in most cases was approximately 10 hours. The samples were stored in a $CaCl_2$ dessicator until used. The average time lapse between filling the bucket until measurement was approximately 2 to 3 minutes. It is quite conceivable that some water would be adsorbed prior to measuring. The study was conducted in a constant temperature room held at 20 $\pm$ 1° C. and relative humidity of 60 to 65%.

The vapor pressure during adsorption was measured by the use of two thermocouples, one wrapped in muslin and the other bare. Temperatures were taken after water saturation of the muslin with a potentiometer. The assumption was made that the relative velocity of the air past the thermocouples were at least 3 meters per second. A check with a sling psychrometer against the thermocouples was found to be favorable.

In order to obtain vapor pressures of less than 0.65, an alternate method was employed. Approximately 10 gram samples of dickite, which were coated with ethanol and HA-III and designated as DPA and DHA-III, were placed over concentrated H_2SO_4 until weighing showed equilibrium was reached. It was found that almost all the samples reach equilibrium within 24 hours. Samples were then equilibrated at 27, 35, 47, 67, and 78% relative humidity by adjusting the concentration of H_2SO_4 at 20° C. The relative humidities were found by titrating the H_2SO_4 solutions with NaOH using phenol red as an indicator. The values for vapor pressures were obtained from the International Critical Tables (Volume III). A similar method of vapor adsorption was used by Orchiston (1953).

An experimental investigation into the influence of the contact angle on unsaturated flow was undertaken. Experimental apparatus and procedure were similar to Nielsen et al. (1962). Soil columns were prepared from air-dried SPA and SHA-III. Due to the poor reproducibility of structure with dickite, only the silt was used to observe differences between high and zero contact angle on unsaturated flow. The silt was packed into a 3.0 cm. diameter lucite cylinder composed of thirty-two

1-cm sections with an average bulk density of 1.35 g. per $cm.^3$ Infiltration of water into the horizontal column was controlled at -2 mb. pressure by means of a fritted glass bead plate connected to a constant head graduated burette. Measurement of time began the instant the glass plate was placed in contact with the soil. All observations of quantity and distance with respect to time were carried out at a temperature of 20° C. Packing the soil column was accomplished with a mechanical adjustable vibrating block to which the soil column was attached. The filling of the column was accomplished with an automatic withdrawal funnel. A precision of $\pm$ 0.06 g. per $cm.^3$ could be obtained.

A method similar to the one used by Biggar and Taylor (1960) was used to determine activation energies. A glass cylinder of 3.0 cm. diameter and overall length of 17.2 cm. was packed with the zero and high contact angle silt and unsaturated flow studies at 4.5, 20.0, 30,0, and 40.0° C. in a constant temperature bath were undertaken. The constant temperature bath was sensitive to less than 0.1° C. Packing was performed to the same bulk density of 1.3 g. per $cm.^3$ with a hand vibrator. Bulk density was obtained by filling the cylinder with a known amount of silt and vibrated to the same level in the cylinder. All the vibrating times were approximately equal. The soil column was packed and the apparatus was immersed in the constant temperature bath and equilibrated for at least 3 hours prior to infiltration. Anderson et al. (1963) found with sensitive themocouples that in 2 to 3 hours their columns had equilibrated. One end of the soil column was held with a wire screen and a rubber stopper with a length tubing connected to permit an air

outlet during the study. This end was coated with paraffin wax. The source end of the column consisted of a porous glass plate connected to a length of copper tubing and to an outside burette. A constant tension of 10 cm. was obtained with an attached bubbler on the burette. Converse to Nielsen et al. (1962), Biggar and Taylor (1960) found straight line relationship between quantity of water entering and square root of time with different tensions. However, Biggar and Taylor (1960) present only data after an initial time interval. This becomes necessary because of the deviations from the Darcy law due to clay-water interaction and non-one-dimensional flow. At time zero the porous glass plate was put in contact with the silt when the column was in an upright position and immediately turned to a horizontal position. By observing the quantity of water entering and the time, one can compute the absorption coefficient and, hence, the activation energies can be found from the Arrenhius equation by the plot of log K^2 versus 1/T. This was done for zero and high contact angle silts by assuming that viscosity and temperature of water can be linearly related within our temperature range and that the contact angle is independent of temperature. Low (1959) plots - log N against 1/T between the temperature range from 25 to 36° C. and found a linear relationship. Jackson (1963) concluded that the contact angle remain constant between the temperature range of 5 to 45° C. from experimental data of the modified intrinsic factors. This can best be explained by the effect of polarization on wettability. Sonders et al. (1950) state that wettability is a function of the polarizability of the surface ions. It would seem that nonpolar molecules would

exhibit hydrophobic properties with polar molecules, e.g., water. The dependence of polarization on temperature may be written as

$$p = a + \frac{b}{T} \qquad [32]$$

where p is the polarizability and a and b are parameters. This effect of decreasing polarization with increasing temperature would be masked by the same relationship of viscosity and temperature in equation [19], Glasstone (1940, page 546).

RESULTS AND DISCUSSION

The original forest silt loam soils were characterized by desorption curves obtained from the pressure membrane (Figure 1) and exhibits typical silt loam curves. CII and CIII soils were similar in texture and produced roughly parallel desorption curves. This indicates that differences may be due to the quantity or quality of organic matter contained in these two soils. The modified Walkley-Black method of determining oxidizable organic matter showed that CII and CIII soils contained 1.3 and 4.4% organic matter, respectively. It appears, then, that quantity of organic matter may account for much of the difference in the desorption curves.

The organic fraction of soils has been the subject of voluminous literature, Broadbent (1953). However, due to its chemical complexity, a complete identification has been unsuccessful.

The organic extract from the soils was subjected to various analytical procedures to obtain a general idea of the types of organic compounds present. A separation of the chloroform soluble fraction from 300 ml. ethanol extract was performed. Approximately 29 µg. per µl. of the chloroform soluble was placed on a thin layer chromatogram plate with lecithin, behenyl alcohol, stearic acid, methyl sterate and triolein. The unknown gave a streak with a concentration near triolein which may correspond to some vegetable oils. Adsorption with iodine showed about 10 to 12 different groups. At least two groups were more nonpolar than triolein. A few choices of compounds that may exist are fatty acids,

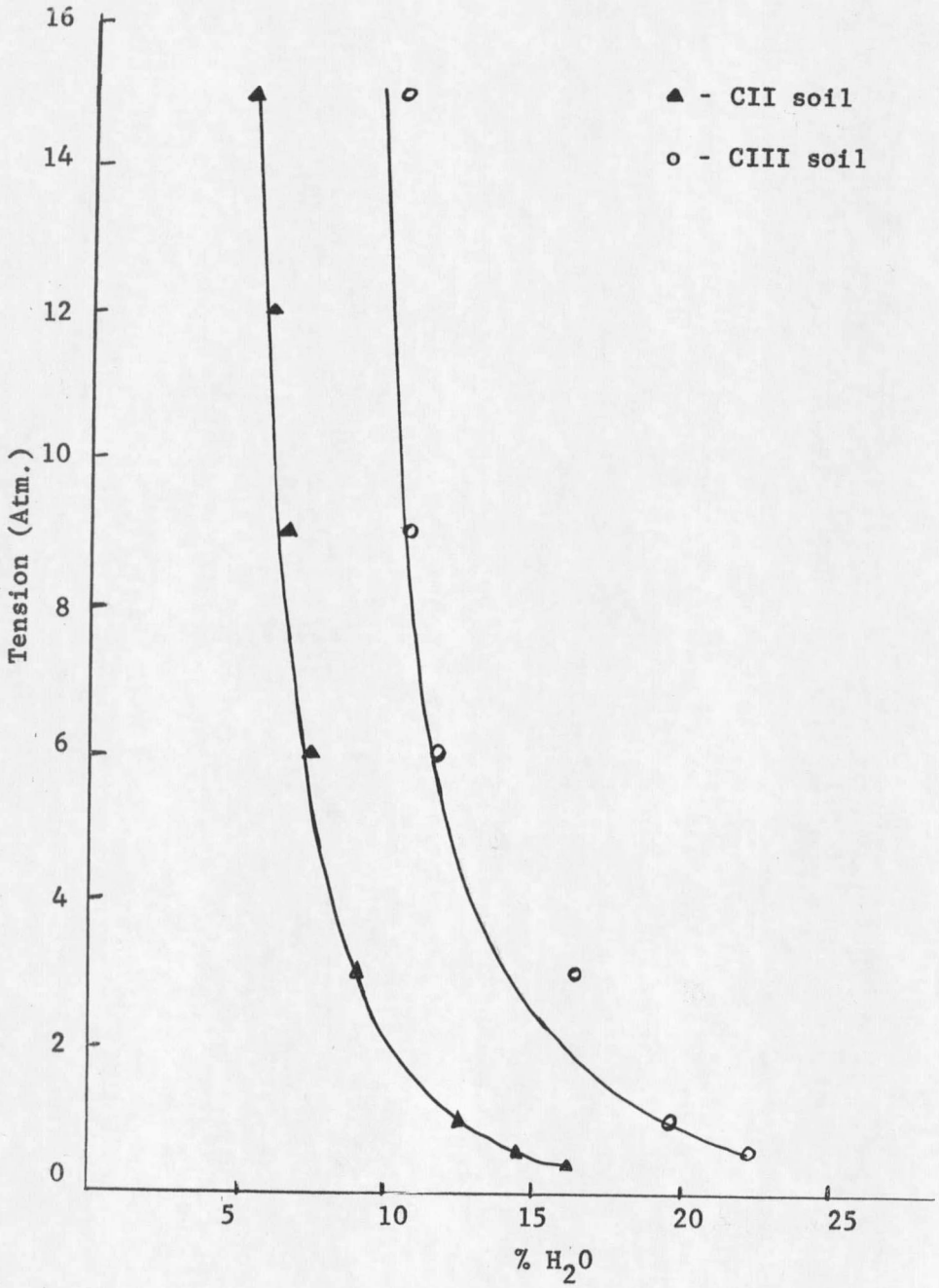

Figure 1. Desorption curves for two forest silt loam soils.

wax esters, aldehydes or a hydrocarbon. An extensive search would be required in order to separate all the groups indicated. However, it should be noted that the extracts did include many nonpolar groups that may be responsible for their hydrophobic properties and this in turn may contribute to differences in the desorption curves in Figure 1.

Table 1 shows the effect of relative humidity on the contact angle of various extracts and extracts mixed with dickite clay and coated on glass slides. The contact angles represent averages from at least 10 drops.

The results of analysis of variance and Duncan's multiple range test for contact angles at 65% relative humidity are presented in Tables II and III, respectively. The highly significant F value at the 1% level is expected in light of Cawlfield's (1962) results. Data from Duncan's multiple range test at the 1% level indicate that a difference between the water-solid contact angle means of 5.3 degrees is required for significant differences, however, a minimum of 4.5 degrees could be interpreted as significance in all cases. If any two means are underscored, they are not significantly different. The slides coated with ethanol and ethanol + dickite produced zero contact angles and, hence, no significant differences would be possible. The slides coated with SCA-III produced an initial finite contact angle but the drop was quickly adsorbed; hence, in the statistical analysis it was given a value of zero degrees contact angle. The HA-III extract produced the highest contact angle in each case; hence, it was chosen to represent the high contact angle material in vapor adsorption and unsaturated flow studies. It

Table I. Values for contact angles at various relative humidities.

R.H.	PA	DPA	C-II	DA-II	CA-III	DCA-III	HA-III	DHA-III	SPA	SC-II	SCA-III	SHA-III
65	0	0	54.0	111.1	77.5	115.3	94.1	122.8	0	53.9	0	87.5
70	0	0	--	107.0	--	97.3	--	119.0	0	--	--	--
75	0	0	--	--	--	--	83.8	--	0	0	0	77.0
78	--	--	--	--	--	78.0	--	112.8	--	--	--	--
80	--	--	--	--	--	--	--	--	--	0	0	56.0
83	0	0	0	78.4	67.6	60.4	53.5	99.4	0	--	--	--

PA - Only ethanol.

DPA - Dickite coated with ethanol.

C-II - Ethanol extract from C-II soil.

DA-II - Dickite coated with C-II extract.

CA-III - Cold ethanol soluble extract from C-III soil.

DCA-III - Dickite coated with CA-III extract.

HA-III - Hot ethanol soluble extract from C-III soil.

DHA-III - Dickite coated with HA-III.

SPA - Silt coated with ethanol

CA-II - Silt coated with C-II extract.

SCA-III - Silt coated with CA-III extract.

SHA-III - Silt coated with HA-III extract.

Table II. Analysis of variance for contact angles of materials coated on glass slides at a relative humidity of 65%.

Source of variation	d.f.	Sum of squares	Mean square	Calculated F value
Among treatments†	9	12,209.22	1356.58	102.3**
Within treatments (Error)	110	14,593.37	13.27	
Total	119	26,802.59		

† A treatment is the extract mix with the silt or dickite and coated on a glass slide.

** Significant at the 1% level.

Table III. Duncan's multiple range test at the 1% level.

	PA	DPA	SPA	SCA-III	SCII	CII	CAIII	SHA-III	HAIII	DA-II	DCA-III	DHA-III
Means	0	0	0	0	53.9	54.0	77.5	87.5	94.1	111.1	115.3	122.8

Treatments underscored indicate the means are not significantly different at the 1% level.

should be noted that there is a definite decrease in the contact angle with increasing relative humidity. This can be attributed to Bangham's "critical films" in which at a certain distance from the surface, the drop would no longer be under the influence of surface forces and will be identical to the adsorbed water. The marked increase in the magnitude of the contact angles on the dickite coated slides may be attributed to what Adam (1938) calls "surface roughness" and/or orientation of the organic groups. It is conceivable that certain organic groups will be orientated with respect to the negatively charged clay particle, leaving the nonpolar groups, which would tend to be hydrophobic, exposed.

An attempt was made to determine the angle between alcohol and the extract. In order that the drop would not dissolve the extract coatings, cold ethanol drops were placed on the hot alcohol soluble extract coated slides. Only the HA-III glass slides exhibited finite angles. Exact measurements were prohibited since ethanol wets the stainless steel needle and in order to obtain a drop, a relatively large volume of ethanol is required and then the range of the microscope is limiting. However, a visual approximation of 30 degrees was made. This would seem to indicate that Letey's et al. (1962) assumption of a zero contact angle with ethanol may not always be correct.

Moisture retention curves were drawn for glass beads coated with CII, CA-III and HA-III and for DPA, DHA-III, SPA, and SHA-III. Figure 2 represents the desorption and adsorption curves for beads coated with CII, CA-III, HA-III and ethanol. These curves are typical of moisture retention curves at high moisture contents. The initial tension applied to

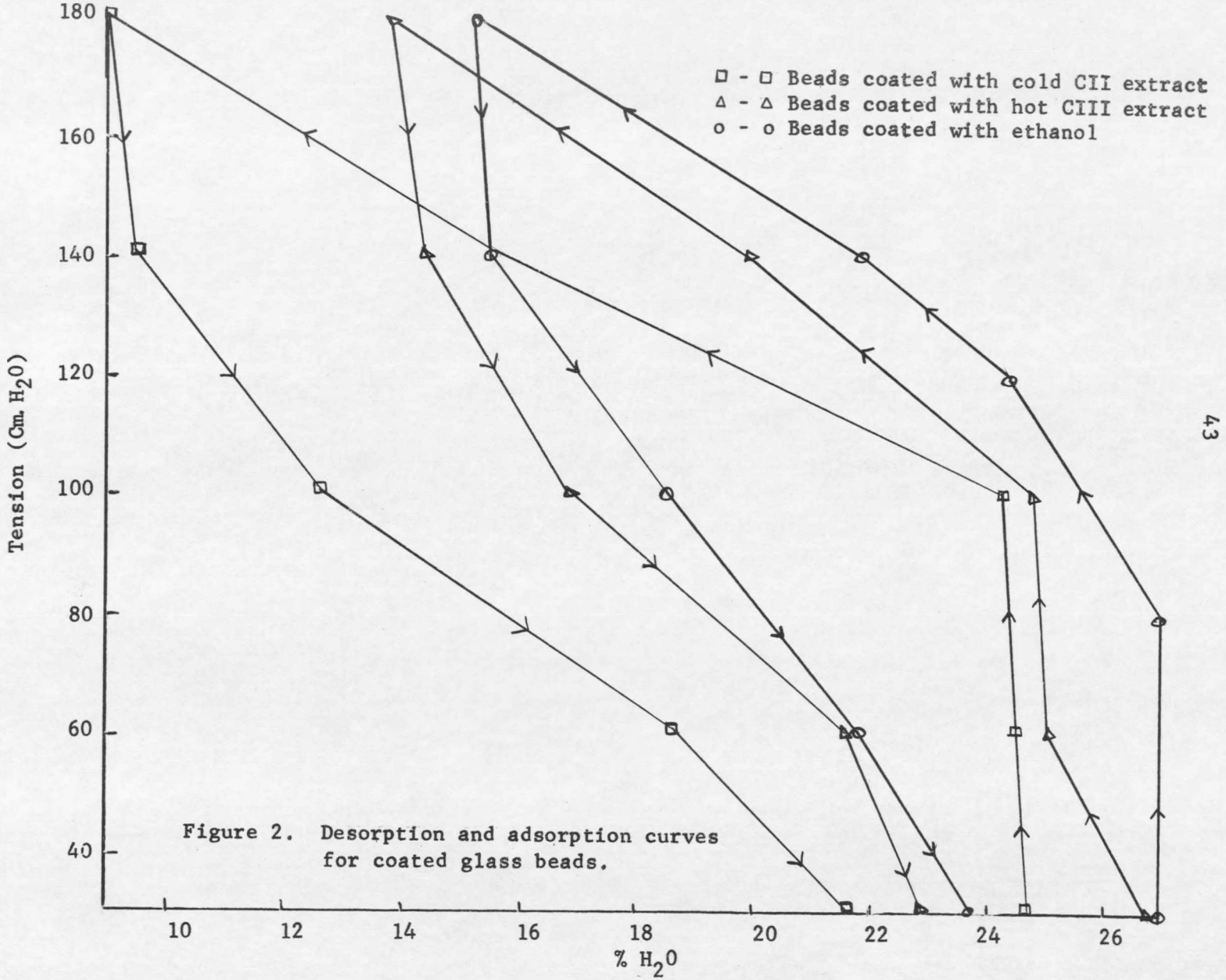

Figure 2. Desorption and adsorption curves for coated glass beads.

the saturated coated beads did not remove any moisture. This may be attributed to the capillary forces of the beads which would be very small at this water content and to the head loss across the porous glass plate. The first movement of water began at approximately 100 cm. of water tension and water was rapidly lost due to the uniformity of the beads and, consequently, the pore size. The zero contact angle sample (ethanol-coated beads) did not lose as much water as compared to the high contact angle sample. One would expect this type of curve on the basis of the contact angle since the water molecules on the high contact angle samples would have a greater attraction for itself than for the surface. Moreover, it would become more pronounced as the tension increased and moisture decreases since the surface forces would have an even greater effect as the liquid films surrounding the particles decrease in depth. The differences in the tension at which drainage occurs, therefore, can be attributed to the surface tension of the liquid or the liquid-solid contact angle. Since tensiometer readings did not indicate a change in surface tension, the difference in tensions must be due to the contact angle. These same samples were examined at greater tensions on the porous plate. However, the precision at these low moisture levels were inconsistent due to the uniformity of the pore size.

Figure 3 shows the desorption curves for DHA-III and DPA. These curves show similar patterns of hydrophobic and hydrophilic clays. Pressures of 3, 6, 9 and 15 atmospheres were applied to these same samples and the moisture contents of all the samples were inconsistent

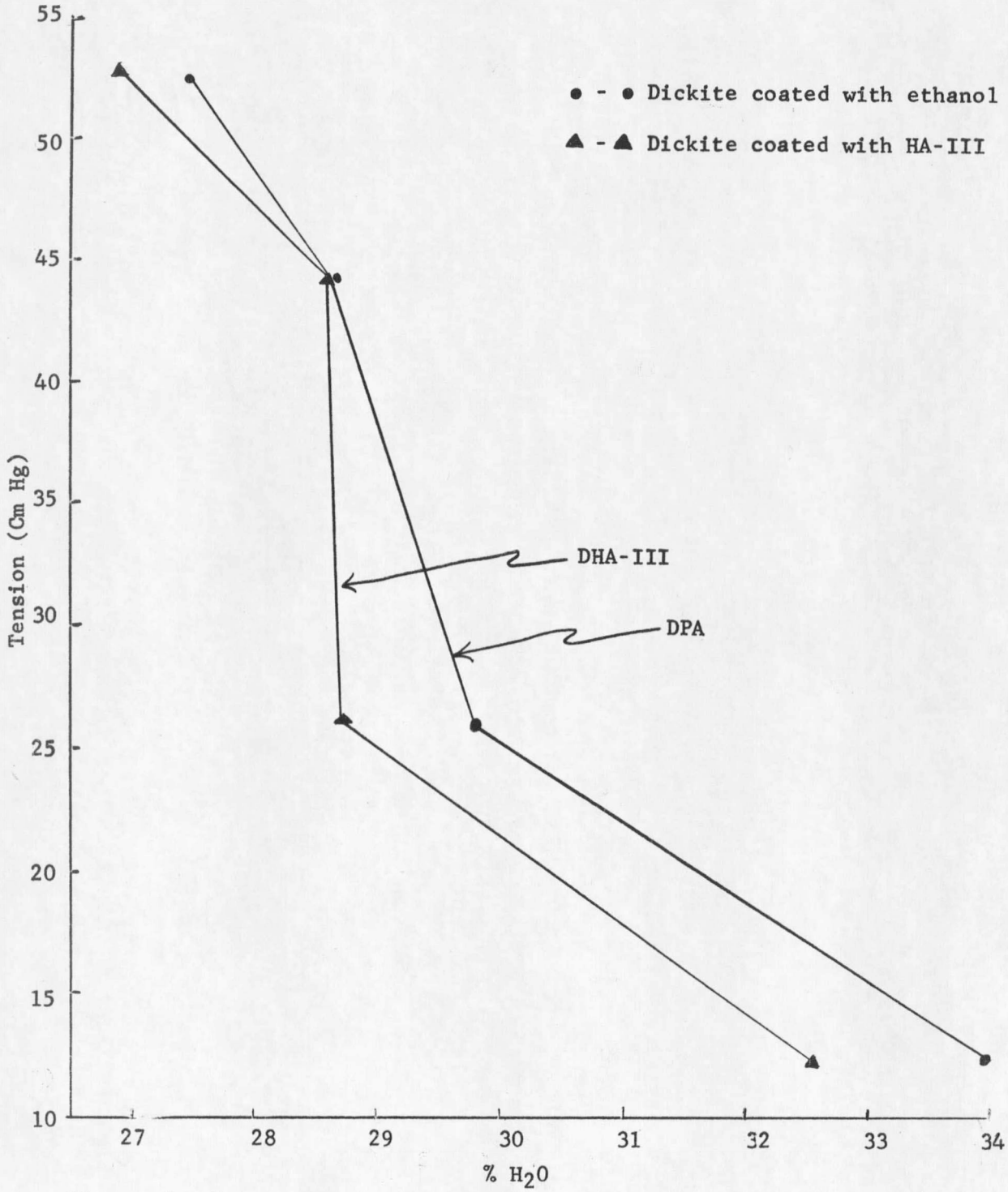

Figure 3. Desorption curves for DHA-III and DPA.

at these relatively low moisture contents and interpretation was impossible. The desorption curves described are similar to the curves described by Letey et al. (1962).

It is clear that a soil with relatively large pores (e.g. sandy loam) and a soil with fine pores (e.g. silt loam) can have different moisture contents and be adjacent to each other without water movement ocurring. This can be seen from their respective desorption curves; the silt loam will contain a higher moisture content at any pressure. Hence, water movement will tend to occur as a result of differences in tension and not moisture. This can also be true with a homogenous soil with a layer of hydrophobic silt at the surface and hydrophilic silt below. The hydrophilic silt could have a higher moisture content and yet no liquid movement upward would occur. This may not be unusual in that generally the high organic content of the A horizon may exhibit temporary or permanent hydrophobic properties. The hydrophobic silt at the surface would have a tendency for rapid evaporation due to the lack of adhesive forces. This may also be important in water availability to plant roots.

Assuming the Darcy equation is valid in unsaturated flow treatment of SPA and SHA-III, a plot of quantity and distance of water movement against the square root of time was determined (Figure 4). An essentially linear relationship was attained; however, deviations from linearity were more pronounced at the beginning of the experiment. These deviations have been attributed to clay-water interaction and the changing contact angle. The desorption curves (Figures 2 and 3) indicate that the organic coatings affect the adhesive forces at the relatively low tension range.

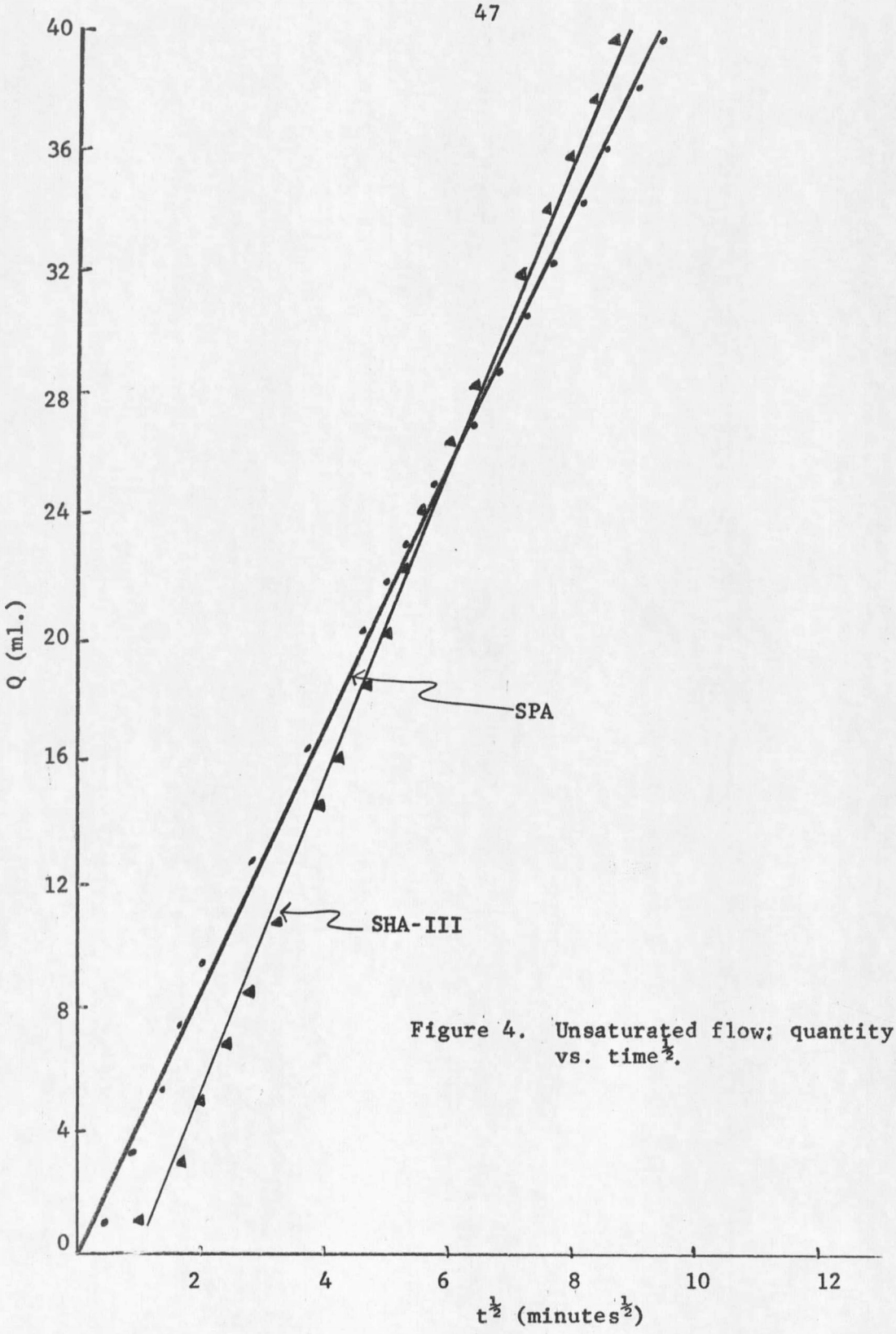

Figure 4. Unsaturated flow; quantity H_2O vs. time$^{\frac{1}{2}}$.

However, it is conceivable that a soil-water interaction may be negligible due to the physical nature of a silt or sandy system.

The depressed initial entry of water into the SHA-III silt system appears to be the result of the high contact angle since the SPA does not exhibit this delay in entry. It is rather interesting to note the intersection of the two lines at approximately 36 minutes. Observing the slopes of the two lines, one concludes that the SHA-III is adsorbing a greater quantity of water which seems contrary to any previous discussion on hydrophobic soils. It is also interesting to observe that the SPA curve intersects the axis at the origin whereas the SHA-III curve does not which favors Swartzendruber's (1956) suggestion of non-Darcy behavior due to the contact angle. Liquid movement occurs only through thin films of adsorbed water; hence, liquid movement will cause the enlargement of the films and changes at the liquid-particle and liquid-air interfaces.

Data from Figure 4 was used to plot the rate versus time curve which is presented in Figure 5. The rate was calculated from the intervals between points plotted on Figure 4. A high initial rate of water entry was observed in the SPA which decreased continually and finally leveling off at 0.2 ml. per minute. The SHA-III showed a somewhat different curve, random peaks or "jumps" of increasing rate of entry were observed. These peaks disappeared after approximately 40 minutes which corresponds to the intersection of the lines in Figure 4. Figure 5 shows that the rate of water entry in the SHA-III is not continually increasing as one might conclude from Figure 4 but after 80 minutes the treated (SHA-III) and untreated (SPA) rates were identical. The erratic peaks may be

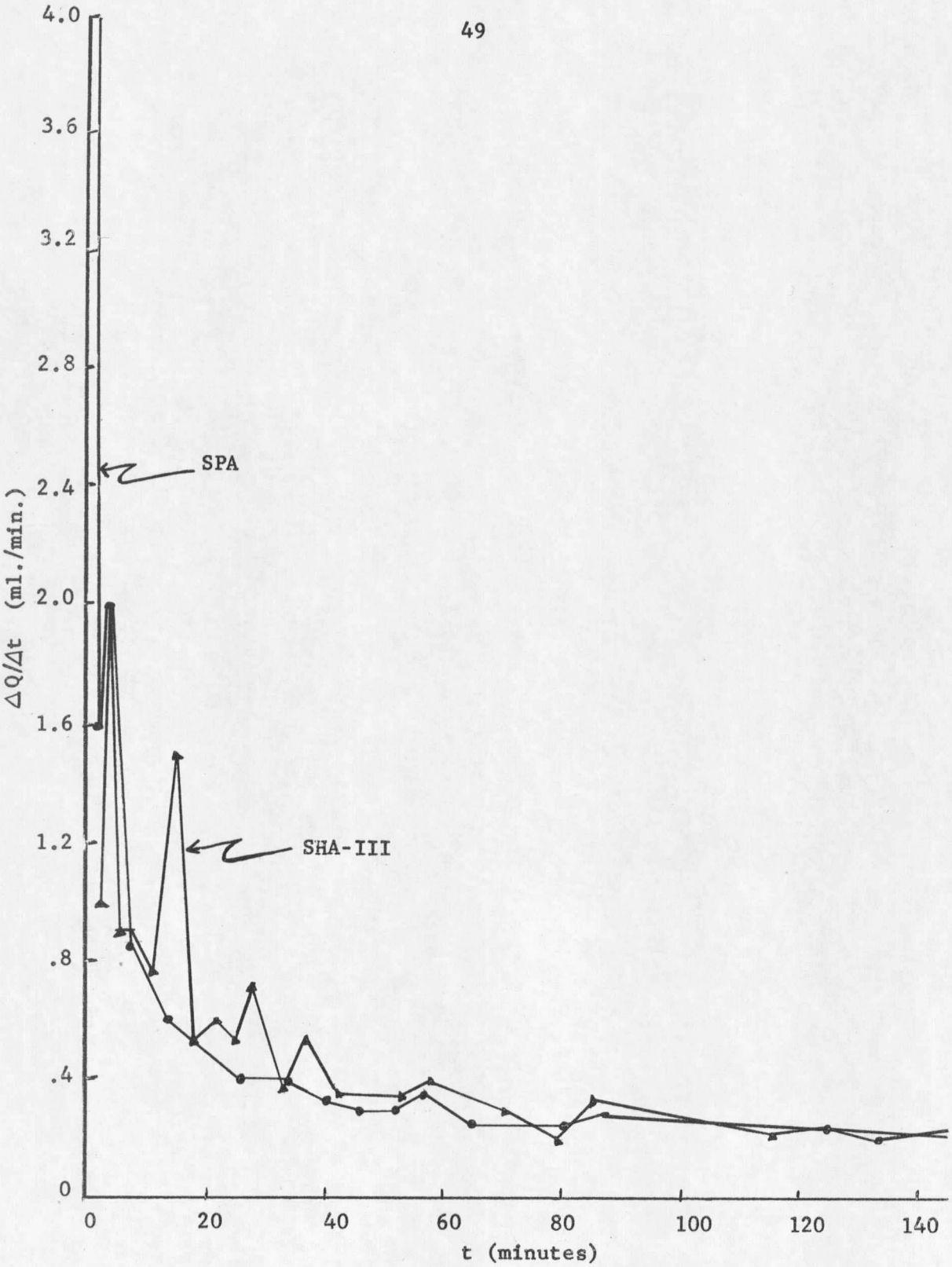

Figure 5. Rate vs. time plotted from Figure 4.

attributed to the soil requiring a minimum moisture content in order for water flow. This minimum moisture can only be transported by vapor movement. It is conceivable that the treated silt would resist vapor adsorption and a certain time interval or vapor buildup need be necessary before liquid movement can occur. Liquid movement would then be observed as sudden "jumps" in the rate versus time curve. The disappearance of these "jumps" can be explained by a smaller moisture gradient at the wetted front as the wetted front advances and to the lapse of time in which vapor adsorption has alrady occurred. That is to say, when water moves from a free source into a dry soil, the moisture content changes continuously at all points within the system. This dynamic system results in the alteration of the thickness of moisture films and changes in the curvature of the air-water interface. Gardner and Hsieh (1956) state that water only moves in unsaturated soil in the liquid state along surfaces and through interstices which contain water. This effective channel would be determined by the moisture content ahead of the mass flow of water. It appears that vapor movement ahead of the wetted zone would influence the rate of flow. This could be a probable explanation to the lack of the "jumps" in the SPA where vapor was rapidly adsorbed on the surface. It appears that these "jumps" may correspond to energy barriers.

Gardner and Hsieh (1956) obtained data using dye tracks as a method of measuring the velocity into blotter paper at short-time intervals. Photographs were taken over these intervals; hence, the velocity could be calculated. The results were erratic and, hence, many measurements had to

be made. They indicated that the velocities were not consistent with uniform flow but erratic and jumpy.

Miller and Miller (1955) discuss the irreversibility of liquid flow through porous media. A given pore will suddenly empty when the tension is just enough to "suck in" the air-water interface through its largest entry port. In order for that pore to refill, the tension must be reduced until the surface tension can pull the interface through the largest pore and, hence, sudden filling will occur. This can be mathematically described by equation [2].

$$P = \frac{2\gamma}{R}$$

and clearly the pore radius will govern water entry. Moreover, this sudden emptying and filling will be macroscopically observed as the hysteresis effect. Miller and Miller (1955) assume that the adsorbed layers of water have a negligible influence on flow in coarse silt to sand range but the complex dependence of the liquid-filled space upon soil moisture tension complicates the capillary flow analysis.

A consequence of the sudden filling and emptying of pores would have its effect on aggregate stability. It would appear that drying would cause shrinkage of the soil mass and, consequently, unequal stress would cause cracks to form. Then, upon wetting, unequal swelling may occur and sudden water movements into the pores might entrap air and tend to explode the clods enclosing the air space. This would indicate that wetting and drying cycles tend to disintegrate the clods but promote smaller aggregates. It is clear that the contact angle would modify this effect since it

affects the rate of wetting and, consequently, the rate of buildup of air pressure within the clods.

Figure 6 and 7 are the linear plots for unsaturated flow at 4.5, 20.0, 30.0 and 40.0° C. for SPA and SHA-III, respectively. The results are averages from duplicate replications. The flow for time less than four minutes was not included since it was found that non-Darcy flow occurred in this interval due to a change in tension applied upon initial water contact with the silt. Table IV relates the slope of the lines at these temperatures. In all cases except at 40.0° C. with SPA, the slope or conductivity (K) was increasing with increasing temperature. Jackson (1963) obtained similar results between the temperatures of 5.0 and 42.5° C. The increase in infiltration can be attributed to the temperature dependence of the viscosity in equation [19]. Since viscosity decreases with increasing temperature (Figure 8), infiltration will increase with increasing temperature. It should be noted that a deviation from linearity exist between 20.0 and 40.0° C. This may explain, in part, the near parallel lines between 30.0 and 40.0° C. with SPA and also the normal increase between the 30.0 and 40.0° C. curves with the SHA-III.

Figure 9 is obtained by squaring the K values in Table IV to give it the proper dimensions of a rate constant and then plotting the log K^2 against 1/T. Hence, from the Arrenhius equation, the slopes from Figure 9 are equal to $E_A/2.3R$. The activation energies (E_A) for SPA and SHA-III are 4.2 and 3.6 kcal. per mole, respectively. These values are in excellent agreement with the activation energies for simple viscous flow obtained by Low (1960) and the re-evaluated energies obtained by Biggar and Taylor

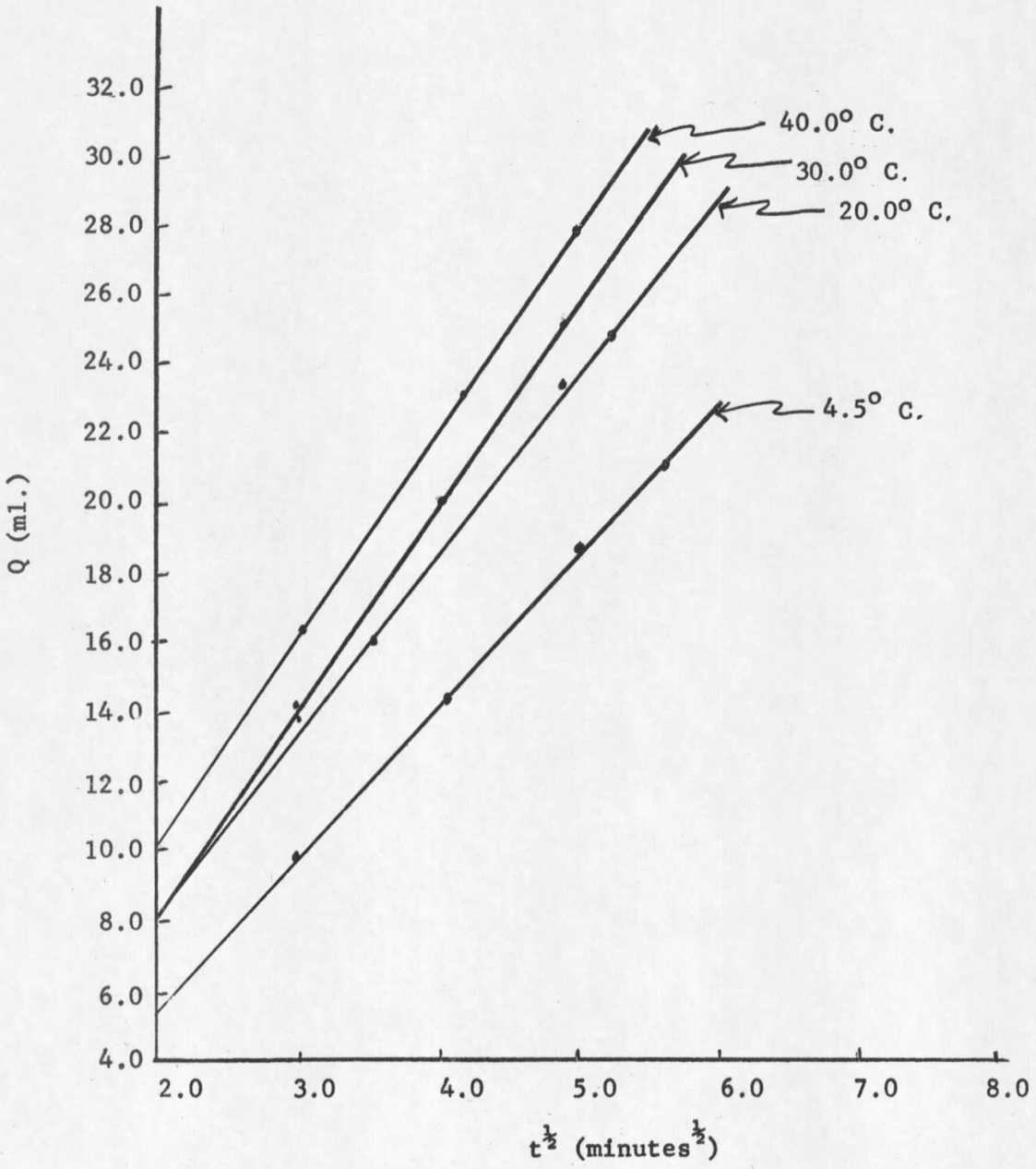

Figure 6. Unsaturated flow at various temperatures in SPA.

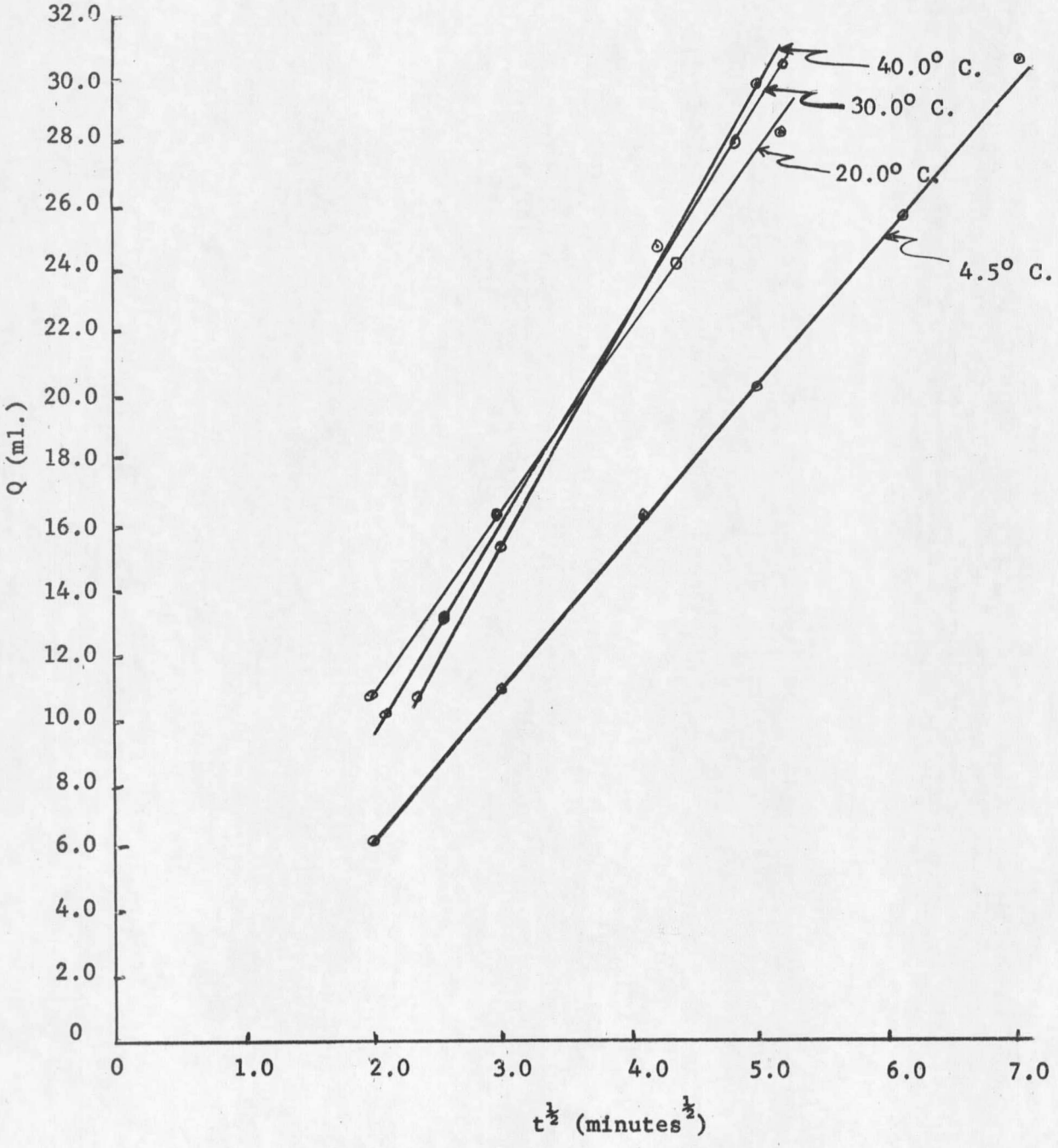

Figure 7. Unsaturated flow at various temperatures in SHA-III.

Table IV. The K values (slope) for Darcy equation in unsaturated flow at various temperatures determined by least squares.

	4.5° C.	20.0° C.	30.0° C.	40.0° C.
SPA	1.27	1.44	1.55	1.55
SHA-III	1.33	1.48	1.57	1.65

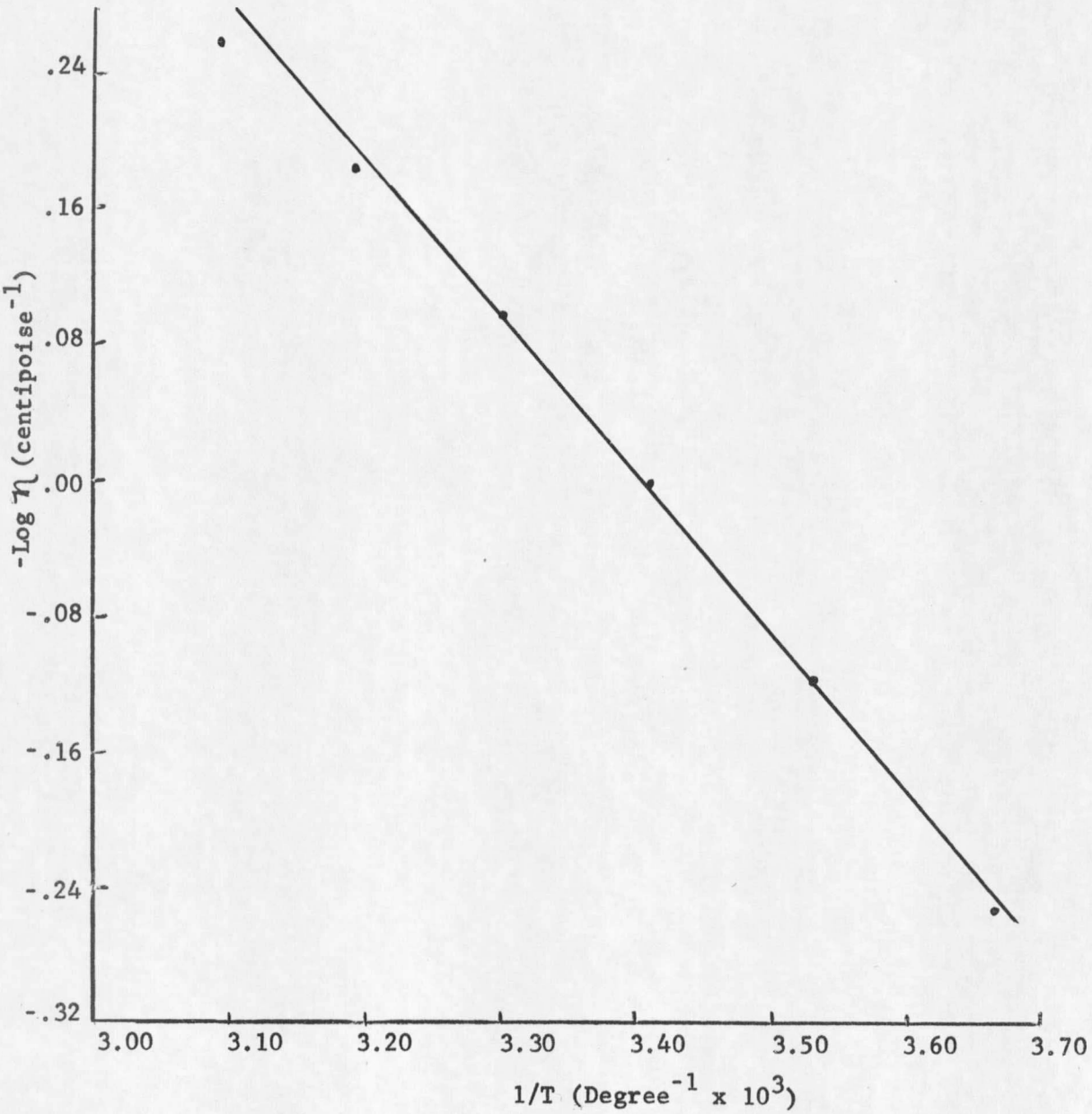

Figure 8. -Log η vs. 1/T for H_2O.

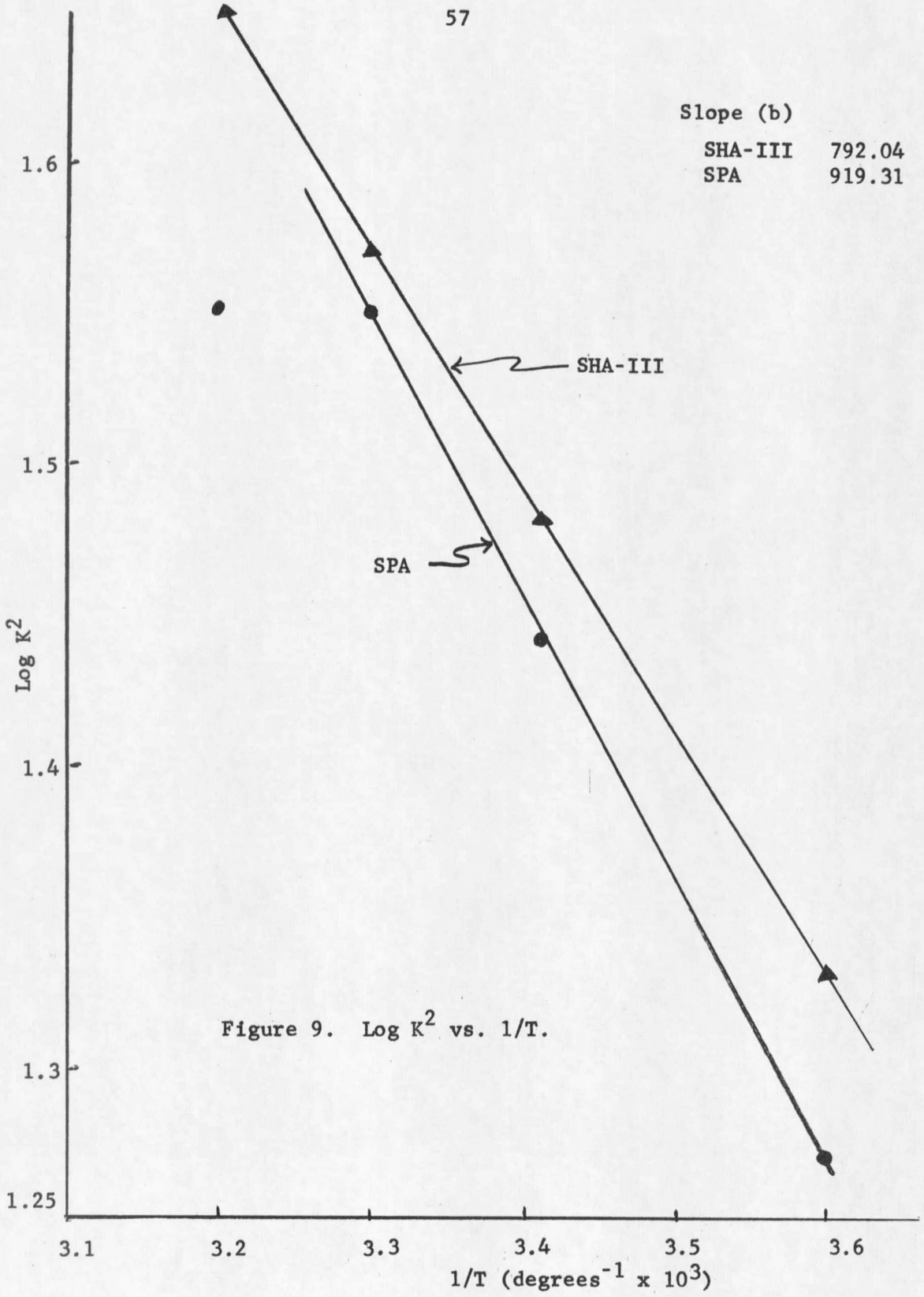

Figure 9. Log K^2 vs. 1/T.

(1960). However, if the contact angle presents an initial energy barrier to water flow, it would not be detected in this data due to the fact that the data represents flow after four minutes. The higher activation energy for SPA than SHA-III would not be expected on the basis of the contact angle forming an energy barrier. However, it does agree with the desorption data in which SHA-III loses a greater quantity of water at a given tension than the SPA.

Figure 10 represents the water vapor adsorption isotherm of DPA and DHA-III. These appear to be contrary to the expected isotherms. One would expect a greater difference at low pressures where the water molecules are more subject to surface forces. One explanation would be the small amount of water adsorbed at these low pressures. However, a more contributing explanation would lie in the cations that are on the exchanger. In order to assure that none of the extract would leave the dickite during the experiments, it was leached with a low calcium concentration solution and checked with a tensiometer until comparable readings were obtained between the effluent and inffluent. Hence, there are two opposing forces acting on the ion: one is energy of hydration and the other is the electrostatic bond between the clay and ion. It is conceivable that the organic coatings do not exert an influence on either of these forces. The fact that there is little or no differences in the adsorption isotherms below $P/P_o = 0.8$, one concludes that ion hydration is occurring in this range. Therefore, no differences would be expected. This is in excellent agreement with Martin's (1957) statement that capillary condensation does not begin below $P/P_o = 0.8$ on kaolinite. It is evident that surface forces would exert an in-

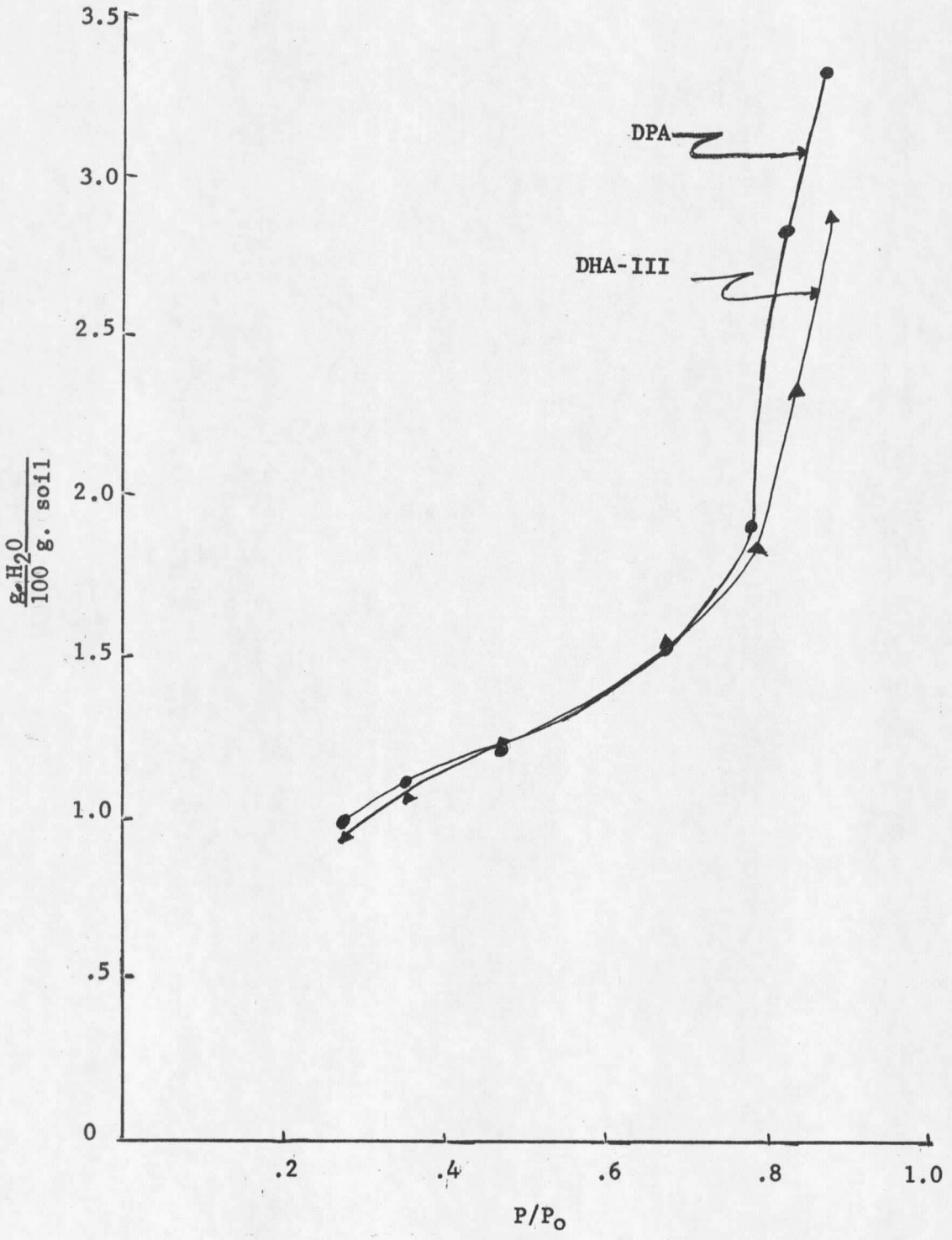

Figure 10. Water vapor adsorption isotherm at 20° C.

fluence in the capillary condensation range; and if the added extracts have influenced surface forces, more water would be adsorbed on the DPA than the DHA-III. It would be well to note again that the data is in agreement with desorption data in the upper vapor pressure range.

Figure 11 is the BET plot of the data presented in Figure 10 in the usual BET vapor pressure range, 0 to 0.47. In this range the points appear to give a linear relationship. BET 'C' values for the DHA-III and DPA are 33.6 and 44.5, respectively. Martin (1957) found C values of 33.0 for Li and K kaolinite clay and estimated that this corresponded to 75% of a completed monolayer before a second layer forms. It is evident that a C value of 44.5 would correspond to a monolayer of something greater than 75% complete, perhaps 80 to 90%. Brunauer et al. (1938) state that a completed monolayer corresponded to C values of 100. It would appear that a high contact angle surface adsorbs vapor around a fixed site (hydrated ion) and a second adsorbed layer forms at these sites before 75% of a monolayer is complete. On the other hand, a wetting surface will almost completely adsorb a monolayer before starting a second layer.

It will be granted that Figure 11 shows a very small difference between the two lines; however, the DPA points are all below the DHA-III line.

Since $C = \exp.(\Delta Q/RT)$, one can obtain ΔQ values for both DPA and DHA-III. Then since $\Delta Q = (Q_1^o - Q_L)$ and

$$Q_L = RT \ln \frac{23.756}{760} \qquad [33]$$

which is the Gibbs free energy and as used by Goates and Hatch (1953), Q_1^o can be calculated and represents the affinity of the surface for water mole-

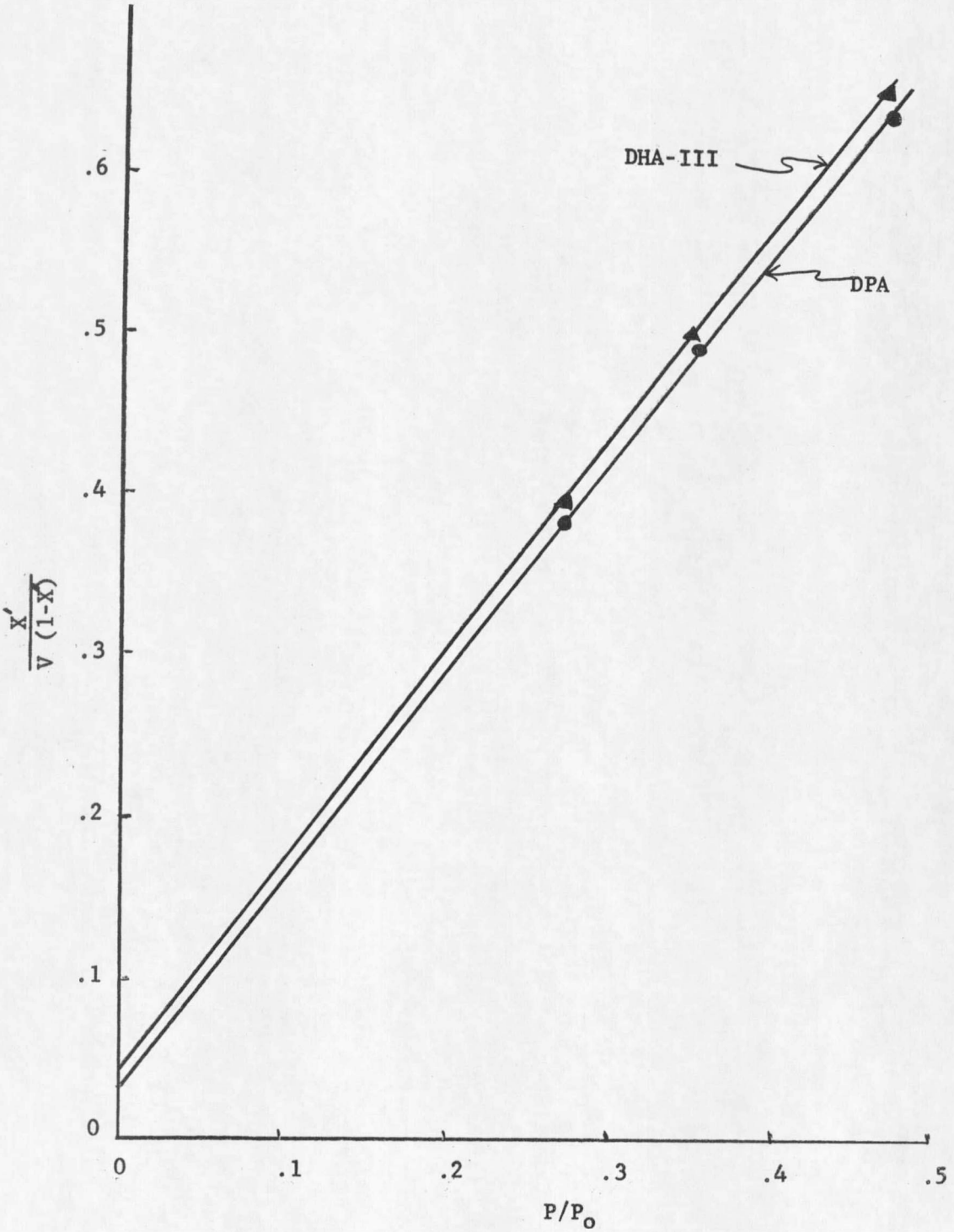

Figure 11. BET plot.

cules. The values of Q_1^o for DPA and DHA-III are -1172 and -1342 cal. per mole. It appears that DPA has a greater affinity for water molecules than the DHA-III surface. This would indicate that vapor adsorption ahead of the wetted front would adsorb more readily on the untreated soil than on the treated soil. Hence, if a dry soil requires a minimum moisture content for liquid movement, vapor adsorption may be the rate-limiting step in unsaturated flow. This would also explain the depress initial water entry into the treated silt.

However, Anderson et al. (1963) concludes from vapor flow studies that the rate of evaporation at the wetted front is the rate-limiting step in water movement through unsaturated soils. Moreover, they state that vapor adsorption is not an activated process, i.e., the process is not temperature dependent; hence, it has no effect on the apparent activation energy for vapor flow. Dacey et al. (1958) found water vapor adsorption on charcoal to be temperature dependent and, further, calculated the activation energy to be 3.4 kcal. per mole. However, there has been no experimental evidence to show the apparent activation energy for vapor adsorption on clays.

From published experimental data on vapor adsorption on Millville loam, one can calculate the activation energy for evaporation and vapor adsorption. Langmuir adsorption isotherms at various temperatures can be drawn from data obtained by Kohl[5/] (1962, page 56) in the vapor pressure

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[5]Kohl, Robert. Utah contributing project report to the technical committee. Western Regional Research Project W-68. 1962.

range of 0 to 75 mm. oil. The Langmuir equation is derived from the assumption that at equilibrium the rate of evaporation is equal to the rate of adsorption and is given by

$$\frac{P}{y} = \frac{a}{ym} + \frac{P}{ym} \qquad [34]$$

where P is the pressure, y is the volume of water adsorbed, ym is the volume adsorbed at the monolayer point and 'a' is equal to K_1/K_2. K_1 and K_2 represent the proportionality constants for rate of evaporation and rate of adsorption, respectively, (Barrow, 1961). It is evident that a linear plot of $\frac{P}{y}$ versus P will produce a slope of $\frac{1}{ym}$ and intercept of $\frac{a}{ym}$. In the pressure range studied excellent Langmuir isotherms were plotted and 'a' values were calculated. At this point, it would be advantageous to quantitatively describe both K_1 and K_2. Data obtained from Wiegand and Taylor (1960) enables one to compute the values for K_1 (rate of evaporation) on Millville loam at the temperatures 14.8, 24.8, and 34.8° C. used by Kohl (1962). Since Wiegand and Taylor (1962) indicate that the evaporation rate was calculated after 160 to 200 hours, it would appear that the soil surface would be fairly dry and would correspond to the pressure range being studied. Then, plotting log K_1 versus 1/T, one can calculate the activation energy for evaporation. Similarly, since K_2 values can be found from the corresponding 'a' and K_1 values, activation energy for adsorption can be calculated. In so doing, one must assume that the evaporating surface is covered with a monolayer or less of water and the fraction of surface covered remains fairly constant over the pressure range studied. Apparent activation energy for evaporation and vapor adsorption were found

to be 9.6 and 6.6 kcal. per mole. However, one must add the activation energy for vapor diffusion through air (1.1 kcal. per mole)[6] to the activation energy for vapor adsorption. Then, according to Anderson et al. (1963), an average of the two activation energies (9.6 and 7.7 kcal. per mole) would describe the apparent activation energy for vapor flow. Their value for vapor flow is 9.7 compared to 8.7 kcal. per mole obtained above. An average value may have no real physical meaning. It should be noted that the activation energy for evaporation (9.6 kcal. per mole) corresponds to the heat of vaporization of water (i.e., 9.7 kcal. per mole) and that Anderson et al. value of 9.7 kcal. per mole for vapor flow corresponds closely with the calculated value of 8.7 kcal. per mole. It would appear that both evaporation and vapor adsorption are activated processes and, hence, both may contribute to the apparent activation energy for vapor flow. Furthermore, evaporation appears to be the rate-limiting step.

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[6]Anderson, D. M. and Linville, F. A. Arizona contributing project report. Water Movement in Soils. Western Regional Project W-68. 1960.

CONCLUSION

There appear to be many natural soils that exhibit a hydrophobic nature, either temporary or permanent. These soils are observed mostly in sandy soils primarily because visual observations are most noticeable on these soils. However, this does not mean that hydrophobic properties do not exist in clay soils. Another source of water resistant soils lie in burned-over land.

The source of hydrophobic soils probably arise from the organic fraction. In ethanol extracts from hydrophobic soils, nonpolar groups which can cause non-wetting were observed. However, an extensive search for the specific groups was not carried out.

The water contact angle was used as an index of the hydrophobic characteristics of the ethanol extracts and significant differences were found between two forest soils. Contact angles as large as 122.8 degrees were found. Moreover, cold ethanol contact angle was formed on a hot ethanol extract indicating that ethanol does not wet all surfaces as reported by Letey et al. (1962).

Data obtained from desorption curves indicate that the relative adhesion between the soil particles and water become important in hydrophobic soil-water relationships, e.g., runoff, evaporation, capillary rise from a water table, irrigation and water-holding capacity. Moreover, differences in desorption curves were observed at relatively high moisture contents.

Data show that increasing relative humidity tends to decrease the liquid-solid contact angle. However, even at high relative humidities,

some extracts exhibit contact angles as large as 99.4 degrees. It is conceivable that a hydrophobic soil at 15 atmosphere tension (98% relative humidity) will still exhibit hydrophobic properties.

Unsaturated flow studies indicate that a minimum moisture content is necessary before liquid movement will occur. This appears to be a manifestation of liquid movement through thin films over the soil particles. Since a monolayer will not form over a hydrophobic soil, multilayer adsorption must first occur. Moreover, unsaturated flow appears to occur in "jumps" and enhance sudden filling and emptying of pores causing disintergration of aggregates.

Kinetic theory applications to vapor adsorption studies indicate that the surface of a hydrophobic soil has less affinity for water molecules than hydrophilic soils. It appears that the rate-limiting step in unsaturated soils may be associated with the vapor phase. This would be in agreement with Anderson et al. (1963) conclusion that evaporation at the wetted front is the only rate-limiting step to unsaturated flow. However, calculated data from Millville loam indicate that the activation energy for adsorption is not zero as assumed by Anderson et al. (1963) but almost equal to the activation energy for evaporation. Since the contact angle influences both evaporation of water from a soil particle and adsorption of water vapor, it would appear that the wetting properties of a soil are important in unsaturated flow studies.

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