The Factor of Moisture in Frost Action

P. F. LOW, Professor of Soils, Agronomy Department, and
C. W. LOVELL, Jr., Assistant Professor of Civil Engineering, Purdue University

Pertinent engineering and scientific literature on the nature and behavior of moisture as related to soil freezing are reviewed. Considered initially is the basic structural nature of water, of ice, and of ionic solutions. This is followed by summarization of the forces responsible for moisture adsorption in clay-water systems, the structure and properties of the adsorbed water, and the consequent effect upon supercooling and freezing of this water.

Having established a basic physical and chemical background, the paper proceeds through a brief review of what is known of in-service moisture conditions under pavements, and how these moisture conditions may change with time. Finally, consideration is given to the techniques of determination of service moisture quantities, and to the principles of control of such moisture quantities.

●THE AUTHORS have considered their function in preparing this paper to be one of review, summarization and systematizing. An effort has been made to meet the diverse demands of brevity, conciseness and completeness.

Discussion of the role of water in frost action proceeds from basic chemical and physical considerations into those applications of science generally considered basic by the engineer. Initially treated are the structures of water, ice and ionic solutions followed by the nature of water in clay-water systems, and the forces responsible for its adsorption.

The theory of supercooling is reviewed, as are certain aspects of the freezing behavior of soil water. Data on the quantities, as well as the sources and mechanisms of change in quantity, of moisture experienced under pavements in service are summarized. In conclusion, methods and principles of measuring, predicting and controlling these moisture quantities are outlined.

THE NATURE OF WATER, ICE AND IONIC SOLUTIONS

Studies of the isolated water molecule (82) have shown that is consists of a V-shaped arrangement of the atomic nuclei, the H-O-H angle being 105°, and the O-H internuclear distance being 0.97 Å (Fig. 1(a)). The dipole moment of the water molecule is 1.83 x 10^{-18} esu, and has been regarded by Bernal and Fowler (11) as being due to the charge distribution depicted in Figure 1(b). This geometry and charge distribution gives rise to a tendency for water molecules to assume a tetrahedral arrangement as shown in Figure 2. Since the positively charged hydrogen ions of a given water molecule attract the negative charge centers of neighboring water molecules, the molecules are said to be held together by hydrogen bonds.

In ice, the water molecules exist in a tetrahedral arrangement with an O-O distance of 2.76 Å (98, 95). The hydrogen nucleus is not midway between the oxygen nuclei, but is 0.99 Å from one oxygen nucleus and 1.77 Å from the other. Most of the water molecules form the maximum of 4 hydrogen bonds and, for this reason, ice possesses rigidity. However, ice retains appreciable entropy (that is, disorganization or randomness), especially near the melting point (98). Accordingly, it is believed that the molecules can re-orient with considerable freedom, and that the hydrogen ions can re-locate by moving 0.78 Å from a position 0.99 Å from one oxygen to a similar position near the other bonded oxygen. If no hydrogen bonding existed in ice, each water molecule would have 12 nearest neighbors instead of 4, and its density would be 1.840 instead of 0.917.

When ice melts, it is estimated that only about 15 percent of the hydrogen bonds are

broken (98). Therefore, the resulting liquid water retains a loose tetrahedral configuration (11, 65, 90), and is said to have a "broken-down ice structure." There is still a tendency for each water molecule to bond itself tetrahedrally to 4 neighbors, but the bonds are continually breaking and reforming so that, on the average, each molecule has slightly more than 4 nearest neighbors but is bonded to fewer than 4 of them. As the hydrogen bonds are broken the resulting fragments tend to pack together as closely as possible so that some of the water molecules acquire more than 4 nearest neighbors. This tendency toward close-packing as bonds are broken explains the volume decrease of about 9 percent on melting, even though the intermolecular distance increases from 2.76 Å to 2.90 Å. As the temperature increases the increased thermal agitation results in the rupture of additional hydrogen bonds. But the increased agitation also results in an increase in intermolecular distances. The former effect of thermal agitation predominates below 4 C; whereas the latter effect predominates above 4 C. The result is that water has a maximum density at 4 C. By the time a temperature of 40 C is reached, somewhat more than one-half of the maximum number of hydrogen bonds are still present. Hydrogen bonding exists even at the boiling point. This bonding is responsible for the unusually high values for the melting point, boiling point, dielectric constant, specific heat and viscosity of water.

The solution of electrolytes in water has an effect like that of increasing the temperature in that the dissolved ions break hydrogen bonds and disrupt the water structure to cause closer packing. It appears, however, that the ions do not appreciably alter the intermolecular distances, because the net effect of electrolyte addition is to increase the density of the water. The disruptive effect of the ions depends on the ionic size; the larger the ion the greater the disruptive effect. These conclusions are based on the X-ray,
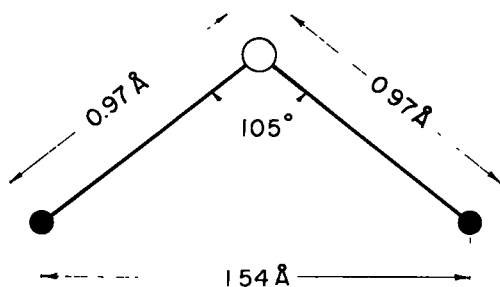

Figure 1(a). Internuclear distances and bond angle of the water molecule. (After Robinson and Stokes, 1955.)
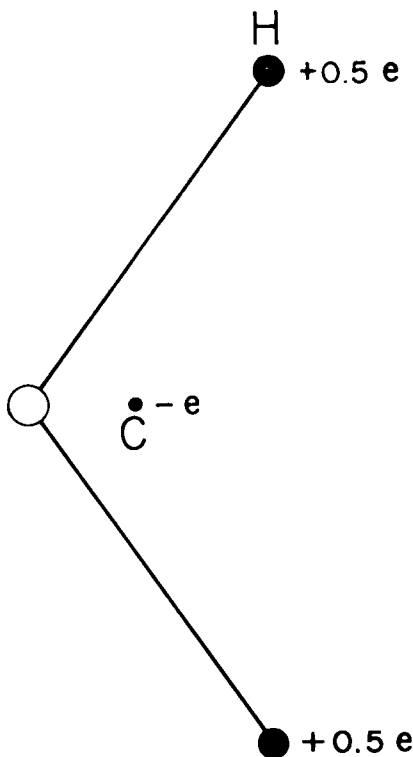

Figure 1(b). Model of the charge distribution in the water molecule. C is taken as the center of the molecule. Distance OC is not drawn to scale. (After Robinson and Stokes, 1955.)

partial molal volume, and compressibility work of Stewart (117, 118, 119, 120) and of Corey (25); the entropy work of Frank and Robinson (40) and of Frank and Evans (41); the dielectric constant work of Hasted, Ritson and Collie (50); and the viscosity work of Wang (126). The disruptive effect of the ions is probably due to the formation of ion-dipole bonds as diagramed in Figure 3. The spacial interference of the ions, however, also plays a part.

For more detailed discussions of water, ice and solutions, the reader is referred to the publications of Bernal and Fowler (11), Llewellyn (72), Pauling (98), Buswell and Rodebush (21), Robinson and Stokes (107) and Owston (95).

NATURE OF WATER ADSORBED
ON SOIL MINERALS

At the present time, all of the forces responsible for water adsorption by soils are not known. It is generally agreed, however, that the exhangeable ions are involved. In the earliest stages of water adsorption these ions form ion-dipole bonds with water molecules (Fig. 4(a)); that is, they hydrate and thereby hold water to the mineral surfaces (125, 93, 53, 104, 43, 89, 66, 83). With the addition of more water, the ions dissociate from these surfaces to form diffuse ion swarms which attract water by osmotic forces (114, 37, 14, 51, 127, 92). Attraction of this kind is depicted in Figure 4(a).

The mineral surfaces also attract water. This attraction is probably due to hydrogen bonding between the water molecules and oxygen or hydroxyl ions in these surfaces (Fig. 4(b)). Hendricks and Jefferson (52) and Macey (79) have proposed

Figure 2. Tetrahedral arrangement of water molecules. (After Bernal and Fowler, 1933.)

possible water structures which might result from such bonding, but other kinds of bonding could be involved. For example, the negative charges in the mineral might attract the positive ends of the water dipoles. This attraction could be between individual charges and water dipoles (Fig. 4(c)) or it could be between the electric field produced by the cumulative effect of those charges and the water dipoles. Or the instantaneous fluctuations in charge distribution of the surface atoms could induce in the water molecules similar fluctuations in phase with themselves (Fig. 4(d)). Regardless of the nature of the bonds, the initial layer of water molecules would be strongly oriented. This oriented layer would, in turn, orient the next layer and so forth. Thus, by relayed action, thick oriented layers of water molecules could be built up.
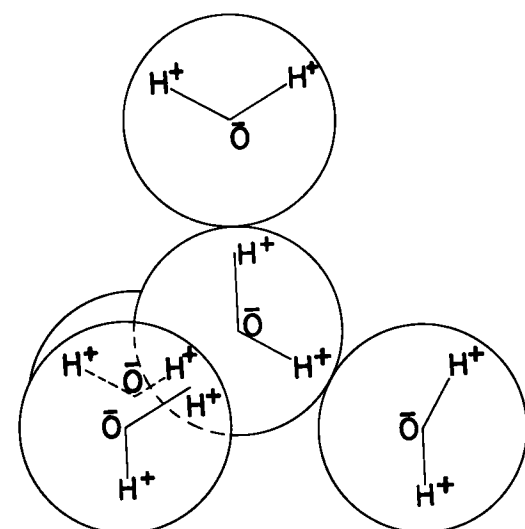
An oriented or ordered structure exists in the water adsorbed on at least a few soil minerals. Anderson and Low (4, 77) observed that the density of the water adsorbed on montmorillonite was less than the density of normal water up to distances of the order of 80 Å from the clay surface. The adsorbed water density decreased with the proximity to the clay surface and with a decrease in temperature. Figure 5 shows the data for potassium bentonite. Since exhangeable cations would disrupt this water structure and tend to increase its density, the clay surface must have been responsible for its development. Evidently, the regularity and extent of the adsorbed water structure increases, not only with a decrease in thermal agitation as the temperature is lowered, but also with an increase in cation dissociation from the clay. This fact is indicated by the following observations:

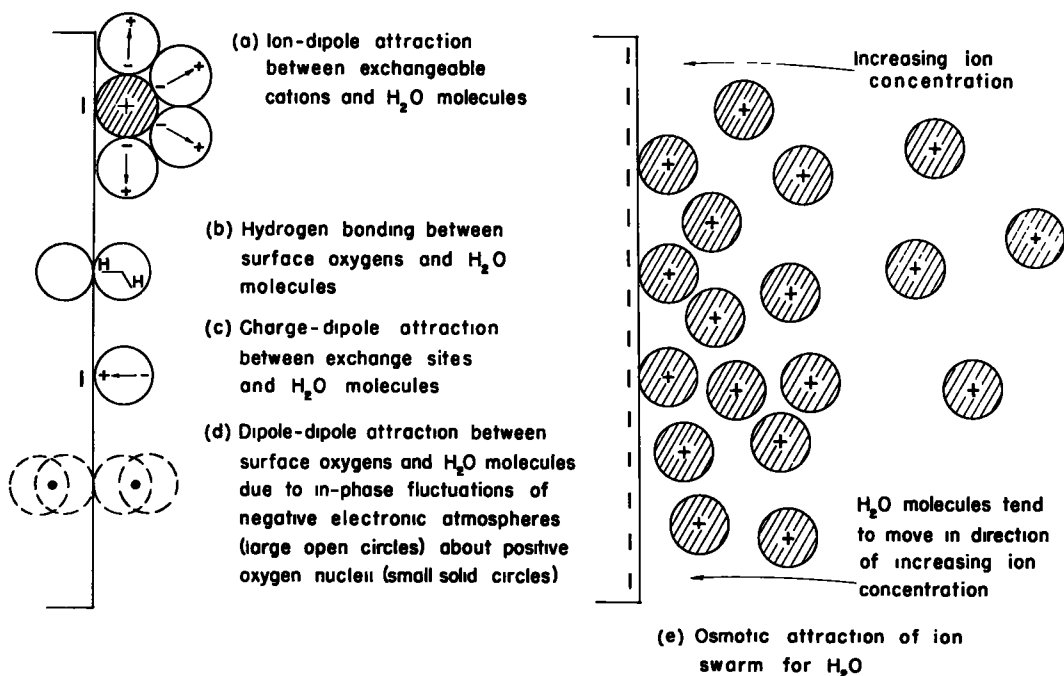Figure 3. Anion hydration (above); cation hydration (below).

Figure 4. Ways in which water might be attracted to mineral surfaces.

1. The activation energy for ionic movement, which depends on the coherence of the adsorbed water structure, increases with increased ionic dissociation from the clay (78).

2. Supercooling of water in clay suspensions, which should be augmented by structural development in this water, increases with increased ionic dissociation from the clay as indicated by zeta potential measurements (33).

3. Unfrozen water in clay pastes at -5.0 C increases with increased ionic dissociation from the clay, even though the ions are not sufficiently concentrated to prevent freezing at this temperature (51).

4. Unfrozen water in clay pastes at -5.0 C increases with clay swelling, and is more extensive on external surfaces than on internal surfaces[1] (51).

It can be postulated that structural development in the adsorbed water is enhanced by increased ionic dissociation from the clay, because the disruptive effect of the ions is less when they are distributed through a relatively large volume than when they are concentrated at the surface where the structure is "anchored." Figure 6 illustrates this concept. The structure imparted to the water by the clay surface is not that of ice, because the adsorbed water supercools extensively; nor is it entirely rigid, because ion exchange occurs readily.

Several investigators (89, 92, 19, 133, 39) have used X-ray diffraction techniques to measure c-axis spacings of clay samples at various degrees of hydration, and have observed that expansion of the lattice layers occurs in definite increments. These increments approximate the diameter of the water molecule, or multiples thereof, up to spacings of 18 Å for montmorillonite. The general conclusion drawn from the results is that successive layers build up on the clay surface as it hydrates. Since it is not yet possible to locate individual water molecules by X-ray measurements on clay-water systems, no conclusions regarding the exact arrangement of the adsorbed water molecules are justified.

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[1]Note that the dissociation of cations from clay surfaces should depend partly on the proximity of adjacent surfaces; the nearer the surfaces, the less the dissociation.

Measurements of the dielectric properties of clay-water systems have indicated that the structure of the adsorbed water is different from that of normal water. Muir (91) examined the dielectric properties of hydrated samples of kaolinite, halloysite, metahalloysite and talc at different frequencies and at different degrees of hydration. He found that the frequency of maximum dielectric adsorption for the first layer of water was relatively low, and was nearly the same for all the minerals tested. Hence, he concluded that the first layer of water was strongly adsorbed with about the same intensity regardless of mineral type. As successive layers of water were added the frequency of maximum adsorption increased, suggesting reaction of the less organized outer layers with the first. Palmer, Cunliffe and Hough (96) observed that the dielectric constant of water on mica decreased with calculated film thickness, from more than 20 for films about 5 microns thick, to less than 10 for films about 2 microns thick. They also observed that, as in ice, the dielectric constant of the adsorbed water changed rapidly as the frequency was changed from 2 to 2.5 megacycles per second. Since neither the dielectric properties of free water or mica are frequency sensitive over this range, they concluded that the adsorbed water approached the same degree of crystallinity found in ice. Cownie and Palmer (28) and Palmer (97), using an unspecified wet clay, found that the dielectric constant increased from a value of about 3 to a value of about 50 in moving from zero moisture to 80 percent moisture (Fig. 7). Thus, the evidence from measurements of the dielectric constant indicates that water
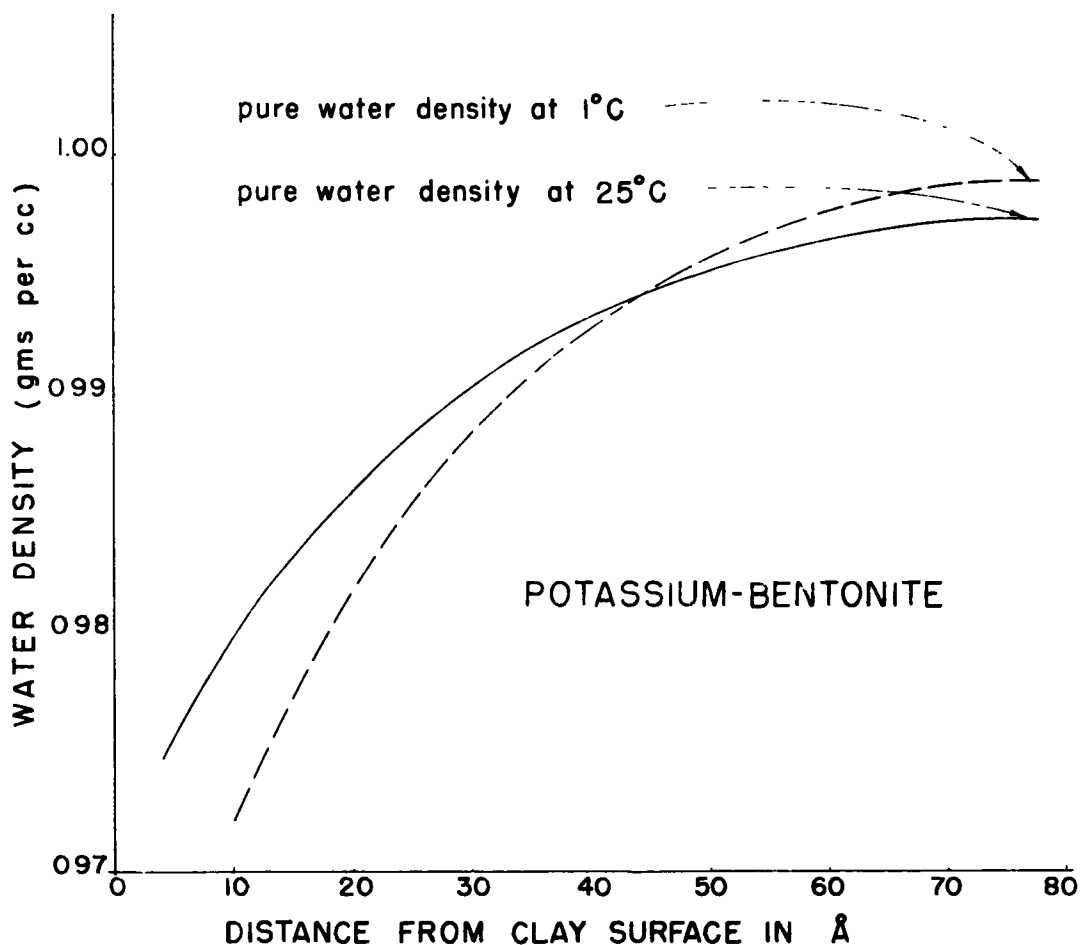

Figure 5. Change in water density with distance from the surface of potassium bentonite at two temperatures. (From data by Anderson and Low, 1958).

(a)

IONS SLIGHTLY DISSOCIATED
FROM CLAY SURFACE

(b)

IONS HIGHLY DISSOCIATED
FROM CLAY SURFACE

◯ = WATER MOLECULE

⊕ = CATION

Figure 6. Effect of ion dissociation on the surface-induced water structure. (Illustrative only. Not intended to represent actual molecular arrangement.)

is strongly ordered at mineral surfaces, the degree of order decreasing with distance from these surfaces.

If the adsorbed water possesses a structure which is more ordered than that of normal water, its viscosity should be greater than the viscosity of normal water. Very little direct information is available in this regard. Macey (79), however, observed that none of the existing theories on water flow through porous media could be applied to clays without assuming that part of the water was immobile; that is, that its viscosity was infinitely high. Carman (23) and Von Engelhardt and Tunn (124) were obliged to make the same assumption to explain their data. Macey also found that the conductivity of clays for non-polar liquids was of the order of 10^4 to 10^6 times that for water, suggesting that, despite differences in clay packing, the viscosity of the water was unusually high. The work of Rosenqvist (109) supports these observations. By making certain assumptions relative to the geometry of the pores and using experimental data, Rosenqvist calculated a diffusion coefficient for deuterium oxide in the pores of a clay paste which was only about 5 percent that of pure water. Recently, Low (78) has shown

that the activation energy for ion movement in the adsorbed water is higher than the activation energy for ion movement in pure water. The available evidence indicates that clay-adsorbed water has an unusually high viscosity. But it should be noted that electroviscous effects (36) or counterelectro-osmotic effects (87) might account for part of the retardation of water flow in porous media. It is unlikely that they account for all of it (54). A hypothetical viscosity vs distance curve is shown in Figure 8.

The thermodynamic properties of water adsorbed on soil minerals are also different from those of normal water. For the equation,

$$\bar{F} - \bar{F}^0 = -\bar{v}\,\pi$$

where $\bar{F}$ and $\bar{F}^0$ are the partial molar free energy of the soil water and pure water, respectively, $\bar{v}$ is the partial molar volume of the soil water and π is the swelling pressure. It may be seen that the partial molar free energy of the soil water is less than that of pure water as long as the soil swells in pure water. Clay soils will swell in pure water until films as thick as 200 Å have developed on the particle surfaces (114, 37, 14, 51, 127, 92).

The heat content of this water is also less than that of normal water. There is considerable evidence (19, 133, 109, 116, 88, 47) which shows that heat is lost on the adsorption of water by clays until water films of appreciable thickness are formed. The initially adsorbed water has a heat content less than that of ice (109).

The data on the entropy of soil water are limited. However, they show that the soil water has a higher degree of order than normal water, up to water contents as high as the field capacity (106, 6). The water in the first monolayer on kaolinite is more ordered than ice (45).

For additional information on the nature of adsorbed water, the reader is referred to the discussions of Grim (47), Williamson (128) and Mackenzie (80).

SUPERCOOLING AND FREEZING OF ADSORBED WATER

The evidence presented in the previous section shows that the structure and properties of water are altered when adsorbed on soil minerals. Now the consequences of this alteration on the supercooling and freezing of the water may be examined. The discussion will be brief because the subject of freezing will be treated in greater detail elsewhere in this symposium.

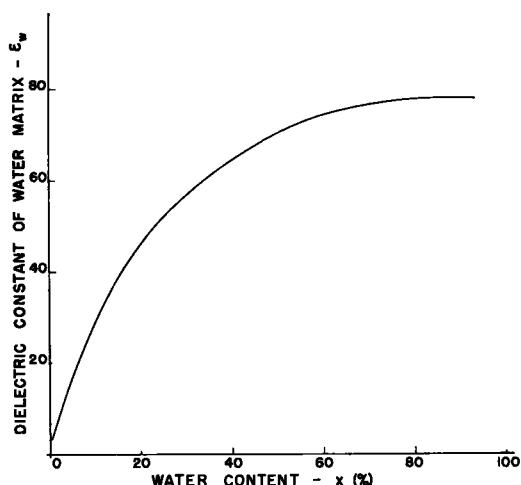According to the nucleation theory of Turnbull and Fisher (122), as applied to water by Mason (85, 86),

Figure 7. Variation of the dielectric constant of water in a wet clay with the water content. (After Palmer, 1952.)

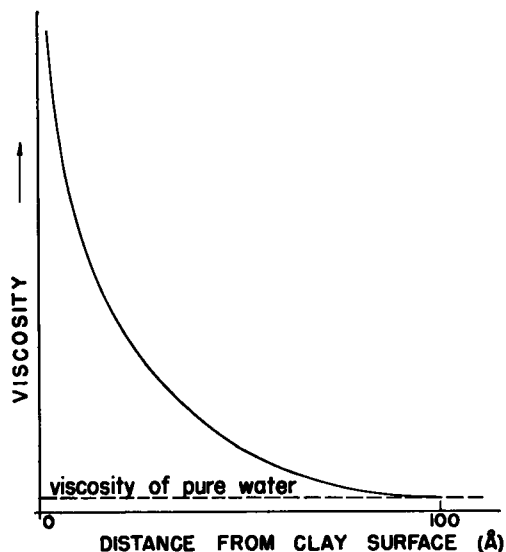Figure 8. Hypothetical decrease of water viscosity with distance from the clay surface.

$$\log J = 32.84 + \log T - \frac{U}{2.303kT} - \frac{760\,\sigma^3}{(T_0 - T)^2 T}$$

in which

> J = rate of production of ice nuclei of critical size;
> T = absolute temperature;
> U = activation energy for the diffusion of water molecules across the water-ice interface;
> σ = interfacial energy between water and ice; and
> T_0 = thermodynamic freezing point.

A nucleus of critical size is one which is just large enough to grow to an ice crystal rather than evanesce. Now U is related to the viscosity η by the expression (5, 44),

$$\eta = Ae^{\frac{U}{kT}}$$

in which A is a constant; hence, the rate of production of ice nuclei of critical size is expected to be small; that is, there will be a tendency for the water to supercool if the viscosity of the water is high and if its interfacial tension against ice is large. There is evidence that the viscosity of the adsorbed water is unusually high. In addition, evidence exists that the adsorbed water has a different structure from normal water and, for this reason, should have a different interfacial tension against ice. If it is assumed that this interfacial tension is increased by the clay-induced modification in the water structure, the observed supercooling of water in clays and soils can be explained.

The freezing point of water can be lowered by increasing the ion concentration and pressure (110, 35) and by lowering the potential energy of the water relative to that of ice (6). Undoubtedly, the ion concentration and hydrostatic pressure are greater in the region of the charged mineral surfaces than in the bulk of the soil solution. If an attractive force exists between the water and mineral surfaces as indicated, the potential energy of the water should be lower in this region. It is not surprising, therefore, that all the water in a clay or soil system does not freeze at the same temperature; the adsorbed water can freeze only at a lower temperature (51, 15, 3, 20, 76).

In view of the ion concentrations and probable hydrostatic pressures in the systems studied thus far, it appears that these factors alone cannot account for the observed amounts of water remaining unfrozen. Consequently, the reduction in the potential energy of water near the mineral surfaces must also be a factor. This factor has not been generally recognized.

QUANTITY OF MOISTURE UNDER PAVEMENTS

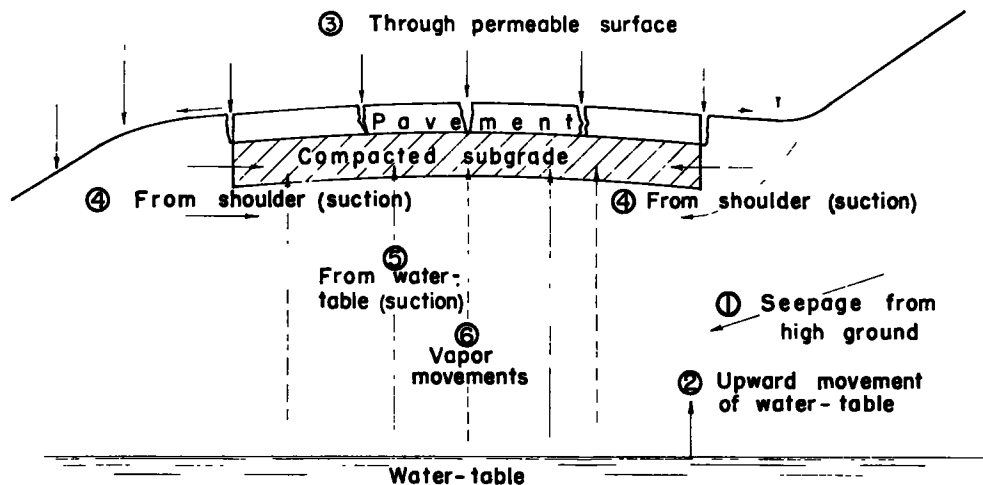Prediction of the moisture content or degree of saturation to be expected beneath a

Figure 9. Ways in which moisture can enter road subgrades. (After Road Research Laboratory, 1952.)

pavement at a given time is in general a complicated matter. The multitude of variables and uncertain boundary conditions have limited the scope and conclusiveness of both the field measurement and rational or calculation type of approach.

In this regard, consider first the variable of initial or compaction moisture content, which is influenced by the soil texture, the type and magnitude of compactive effort, and the efforts of the engineer to specify and control it. As a result of a number of recent studies it is anticipated that progressively less emphasis will be placed on the simple achievement of high densities, and more on the specification of compacted moisture-density conditions capable of producing desired, predetermined properties in the service subgrade or embankment.

For example, Foster (38) and Turnbull and Foster (123) have shown that the strength of a compacted silty material can decrease with increase in density, unless the compaction moisture content is properly controlled. Wilson (129) demonstrates that for cohesive soils the properties of strength, resistance to deformation, permeability, and compressibility can be greatly influenced by variation of only the molding water content. Discussions of these papers point out the manner in which high densities and low molding water contents serve to increase swelling of clays.

Lambe (70a, 70b) has taken a fundamental approach to the matter of compaction moisture content, suggesting that the difference in soil properties wet and dry of optimum is logical in view of the differences in soil particle orientation for the two conditions. Seed (114a) in as yet unpublished research has successfully applied the flocculent vs dispersed structure concept in interpretation of laboratory data on compacted clays.

The observations of Hveem and Vallerga (59) and of Hveem (60)—with discussion, lend additional support to the belief that compaction specification must become increasing definitive of desired service properties. The trend to better control compaction moisture contents should, as a by-product, aid efforts in measurement and prediction of service moisture conditions.

Prominent among the studies of actual moisture conditions under pavements are those by Kersten (68, 69), Hicks (55), Corps of Engineers (26, 27), Redus and Foster (102) and Redus (103). This listing can be supplemented rather extensively if one includes work where, (a) the data reported are more limited, (b) the moisture measurements are much subordinated to another investigational endpoint, and (c) the observations are made under other than a pavement cover. The data reported serve to emphasize the relative importance of such factors as: type of pavement (including base and subbase layers); loading and its capacity to produce densification; age and condition of the pavement; texture and initial condition of subgrade or embankment; the environment—topographic position, ground water level, climate, season, severity of frost action; and depth, position and frequency of sampling.

These investigations show: (a) that the more clayey soils achieve higher degrees of saturation in service than do soils of low plasticity; (b) that climate, and more particularly precipitation has the anticipated effect at shallow depths; (c) that the moisture quantities show continuous, if small, variation with the seasons, but with an increase trend to some critical age; and (d) that moisture gradients exist laterally with respect to the pavement, as well as with depth under the pavement. Beyond this area of general agreement in data are important differences, assumed to be peculiar to the study sites and perhaps also to the investigational perspectives.

A generalized concept of the sources of sub-pavement moisture is presented in Figure 9 in which the following may be noted:

1. Moisture may permeate from the sides, particularly where coarse-grained layers are present or where surface drainage facilities in the immediate vicinity are inadequate.
2. The water table may rise, and indeed may be depended upon to do so in the winter and spring seasons.
3. Surface water may enter joints and/or cracks in the paving, penetrate at the edges of the surfacing, or percolate through the surfacing and shoulders.
4. Water may move laterally.

5. Water may move vertically in capillaries or interconnected water films.

6. Moisture may move in vapor form, depending upon the existence of adequate gradients and air void space.

Moisture can be removed from the soil by reversing the above actions and substituting evaporation for (3).

The study of mechanisms by which moisture moves in a porous medium is basic to a number of scientific and engineering disciplines. Certain quantities are "free" to move by gravity flow; other moisture is "held," and can move only in response to more complex energy gradients. Suction differences are capable of producing considerable liquid flow when the soil is saturated or nearly so. Temperature gradients provide prime motivation for vapor movement, particularly when soil texture and water table position combine to produce a relatively low degree of saturation.

The topic of moisture migration is one extensively studied with a primary reference to highway problems—Russell and Spangler (113), Winterkorn (131), MacLean and Gwatkin (81), Croney and Coleman (29), Road Research Laboratory (105), Wooltorton (132), Rollins et al. (108), Johnson (61); as well as the papers of the International Symposium on Moisture Conduction in Soils and Similar Systems (134).

The great capacity of the soil freezing process to "pull" moisture into the freezing zone has long been recognized and reported for both laboratory and field studies—Taber (121), Beskow (12), Shannon (115), Lund (74), Haley and Kaplar (48), and Lovell and Herrin (75). Within the last few years intensive investigations of the details of these moisture-moving potentials have appeared in engineering literature—Penner (100, 101), Gold (46), Jumikis (62, 63, 64), and Martin (84). It is found that very considerable suctions are operative for liquid flow to the area of crystallization.

DETERMINATION OF QUANTITY OF MOISTURE

The primary approach to determination of moisture quantities has been experimental, that is, measurement of in-service conditions. The oldest, and still dominant, measuring technique is the gravimetric method of sampling and oven drying. This technique has very pronounced and obvious deficiencies when applied to the problem at hand.

A variety of techniques of in-place moisture measurement have been subjected to experimental or to practical use. Perhaps the best known of these are the electrical resistance cells of Bouyoucos and Mick (16), Bouyoucos (17, 18), and Colman (24). The porous material of these units (plaster of paris, nylon or fiberglas) tends to remain in moisture equilibrium with the surrounding soil. The electrical resistance of the "block" changes with its quantity of moisture, and upon calibration becomes a measure of the moisture in the soil.

Another method, and one of considerable promise, is the neutron method of counting hydrogen nuclei—Belcher et al. (7), Belcher (8), Carlton (22), Horonjeff and Goldberg (57), Horonjeff and Javete (58), and Roy and Winterkorn (112).[2] In this method, neutrons are emitted, scattered, lose energy and become "slow" after collision with the hydrogen atoms in the soil-water system. As the quantity of moisture (in any form—solid, liquid or vapor) increases, the count of slowed neutrons increases. Upon calibration, the count becomes a measure of the average moisture content over a small sphere of influence.

Further possibilities are the heat diffusion technique, reported to have strong practical limitations by Aldous and Lawton (2), and the evaluation of moisture content by measurement of dielectric constant or capacitance—DePlater (34), Cownie and Palmer (28), and Palmer (97). The latter technique should be viewed as very much in the experimental stage. In addition, a recent modification of the electrical resistance method utilized an ionic moisture barrier to filter salts from the moisture being measured. Engineering development of this device has had primary reference to the moisture in hardened concrete—Blythe (13) and Klein (70).

A summary view of moisture measurement methods may be attained by review of

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[2] Contains a very extensive bibliography.

Penner et al. (99), Lull and Reinhart (73), and the references of the HRB Bibliography (56). The development and use of all the in-place measuring instruments pose, to varying degrees, similar questions and problems. These are concerned with: the range of moisture sensitivity, the need for length calibration periods, definition of exactly what the instrument measures, the effective zone of measurement, the effect of salts and of temperature, the intimacy of contact of the sensing element with the soil and the rapidity of response to moisture change, and others.

An interesting supplementary capacity of the electrical resistance method is that of determination of time or duration of soil freezing—Rowland et al. (111) and unpublished work at the AASHO Test Road in Illinois.

The approach of prediction through calculation for equilibrium of maximum moisture contents has been spearheaded by English investigators, using the suction concept—Croney et al. (30), Croney (31), and summarized by Croney et al. (32). With reasonable limitation on the boundary conditions, calculated moisture values have been found to check actual moisture conditions rather well. Wooltorton (132) has recommended as prediction alternates the use of density-moisture change curves or the field moisture equivalent.

CONTROL OF MOISTURE QUANTITIES

Reference is again made to Figure 9 and to the previous discussion of sources and mechanisms for moisture increase of subgrades and embankments.

Drainage is an obvious method of control for the gravitational water. Much of the water in the pores of the coarse-grained soils is in this category, and it is commonly possible to greatly reduce the degree of saturation of such soils by conventional subdrainage. For example, lateral seepage in granular layers can be intercepted, open-graded bases and subbases can be drained, and free water perched in a sandy stratum by a relatively thin layer of low permeability can usually be disposed of by subdrainage. The water table can be lowered by subdrainage in fine-grained materials also; but as the soil becomes more clayey, the time required to achieve significant lowering becomes progressively more impractical, and the reduction in degree of saturation effected by the removal of gravitational water becomes rather insignificant.

A number of investigators have addressed the problem of definition of a limiting initial moisture content or degree of saturation, below which ice segregation and frost damage are unlikely. These include Taber (121), Winn and Rutledge (130), Corps of Engineers (26), and Haley (49). This critical quantity of moisture varies with a number of factors, such as the availability of additional moisture and the rate of freezing.

Field observations have revealed that even though the water table often cannot be lowered sufficiently to eliminate frost damage, this damage can be very significantly reduced by lowering the order of several feet—Beskow (12), Keene (67), Road Research Laboratory (105), and Lawson (71). Experience also favors, as an alternate or supplement to ground water lowering, the use of an elevated grade line.

Certain profile situations need particular drainage attention, due to their tendency to "trap" free water—Aaron (1). The same is often true of situations where rock underlies the pavement at shallow depth—Bennett (10), Otis (94), and Fuller (42). Drains must, of course, be open and able to function during the critical thawing period.

Finally, it seems pertinent to mention the use of "barriers" to reduce capillary or vapor movement. The idea of interposing a granular layer which "cuts off" capillary flow is an old one—Beskow (12). Membranes capable of also sharply reducing vapor transmission have received increased recent attention. Particularly interesting, although beset with sizable practical difficulties, is the use of plastic films—Bell and Yoder (9).

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Discussion

A. R. JUMIKIS, Professor of Civil Engineering, Rutgers, the State University, New Brunswick, N. J. —Judging by their contributions to HRB activities in furthering the dissemination of basic knowledge for the purpose of good road and earthwork design in the past years, it can be observed that the efforts of engineers, scientists and researchers have stood the fundamental test of time and acceptance. Scientific ideas and methods of research and construction now seem to have penetrated through the once apparently impermeable barrier of ignorance and indifference, and basic knowledge and research personnel are now being appreciated at their true value. Hence one suddenly finds himself in the midst of a situation where it is recognized that there is not enough of basic knowledge available to explain one or another phenomenon. This is encountered not only in highway research in general, but also in frost action research in particular. In other words, it is realized that there exists a need for more basic

knowledge in order that researchers can investigate and explain a new problem on phenomena met in highway engineering. The need for more basic knowledge is now also being accentuated by the new U. S. A. highway construction program.

The Freezing Soil System Not Fully Understood

One such phenomenon where much basic science can certainly be used is that of soil freezing with its associated moisture migration in soil.

While many processes and factors in a freezing soil system have been clarified during the past few years (moisture transfer in soils by various potentials, the classification of the existence and classification of various soil moisture transfer mechanisms, rhythmic ice banding in soil, the effect of additives to soil to reduce or increase the magnitude of frost heave, some properties of water and ice—to mention a few), there are still some important phenomena, processes, and factors occuring in a freezing soil system which are as yet neither understood nor explained. This is, probably, one of the reasons why up to now there is no satisfactory continuity and systematic treatment of the subject which this discussion terms the "Freezing Soil System" within the scope of thermal soil mechanics.

General Remarks

Realizing the importance of the problem of more basic knowledge, the HRB Committee on Frost Action in Soils organized this symposium to review the available knowledge as it may apply to frost action research in soils and to highway pavement design in frost areas.

The paper under discussion is one within the scope of this symposium which briefly reviews and summarizes in one place some of the knowledge now scattered in the many branches of the various sciences. The paper can be characterized as the exposition of the factor of moisture in frost action in soils. It makes the highway user conscious of the state and importance of the knowledge needed and/or available for good road design, and it should stimulate the work in frost action research in soils, the studies of the properties of soil moisture, and highway construction methods in frost areas. The organization and presentation of the material are clear enough to make the concepts of the authors and the discusser easily understood by a wide circle of highway, foundation and earthwork engineers, the young generation still in college, and the highway owner and user. The review also contains a rich list of reference sources, most of them from the last twenty years, and describes the essential features contained in these references. Hence this list may also serve in orienting one's self in pursuing a particular research topic. Obviously, to keep the paper down in volume, it has been necessary to make a severe selection of the material presented.

Nature of Paper

In view of the topic of the paper, the authors start out with describing the nature and some of the properties of water in bulk in general. After that, consideration is given to principles and methods of predicting, measuring and controlling the soil moisture regimen in connection with highway engineering.

Hence the nature of the paper can be characterized as presenting a two-fold discussion of:

1. The theoretical aspect of the nature of water, and
2. Soil moisture under a pavement which reflects a research phase with its practical aspects.

Theoretical Aspects of the Nature of Water

Hydrogen Bonding. Water is the only liquid with which there is any degree of familiarity. In much of its functioning water is commonplace. However, odd as it sounds commonplace things usually are the least appreciated and the most difficult to understand. It is known that the substance, water, is the most abundant liquid on the earth,

and that it is used and exploited daily because it is an absolute necessity for sustaining life as well as well-being.

However, when it comes to the studies of freezing soil systems and their associated soil moisture migration, water, particularly in the film phase, turns out to be the least understood factor pertaining to the freezing process.

In describing the nature of water the authors are trying to explain some of the properties of water. They point out clearly that water is a polar liquid, and that hydrogen bonding (like a link) between the water molecules is the main reason for the high values of its melting point, boiling point, dielectric constant, specific heat, and viscosity. The bonding concept is illustrated by appropriate drawings. The explanations of these properties of water are buttressed by rich sources of reference, which reveal that the basic knowledge for the explanation of water properties was derived from recent research and by the application of modern research techniques and equipment.

In connection with the description of the nature of water and hydrogen bonding it is felt desirable to mention in this paper that much of this understanding is based on Debye's important work on polar molecules and on the structure of matter ($\underline{1}$, $\underline{2}$, $\underline{3}$, $\underline{4}$).

This available knowledge on water helps one to understand the induced changes in density of water, viscosity, dielectric constant and other factors when a soil system is subjected to a thermal potential, that is, to freezing.

The structure of ice itself is reasonably well understood, although certain details are still in doubt, particularly when ice is under pressure.

Water Adsorbed on Soil Mineral Particles. The review on the nature of water adsorbed on soil particles reveals that at the present time not all of the forces partaking in the interaction between soil water and the surfaces of the soil particles are known. Thus, much work lies ahead to study this problem.

However, by now there is a good concept that water molecules forming moisture films are not the only factors that are adsorbed on the surfaces of solid particles. It is one of the conspicuous characteristics of a dispersed soil particle in a medium of water that under certain conditions it carries an electrical charge which, in contrast to heat, tends to reside on its surface. It is helpful, indeed, to consider soil as a disperse system. It should be understood that at the present time there is no satisfactory explanation available of the manner by which soil colloidal particles acquire their electric charges, a process which seems to be very complex indeed. There is also interest in how water adsorption at the interface affects such properties as phase boundary potentials. Unfortunately, in accord with the authors, one must regret that at the present time it is not yet possible to locate individual water molecules in the clay-water system, and therefore, no plausible conclusions as to the configuration of the adsorbed water molecules can be drawn.

The science, however, has presented an important fragment of knowledge, namely, that the amount of adsorbed moisture in a unit of given volume (or weight) of soil is proportional to the specific surface area of the soil particles. In other words, the finer the soil particles, the greater the possibility of having in a unit of volume more adsorbed moisture films.

Dielectric Constant. The factor, dielectric constant, was introduced in the Helmholtz electrical double layer theory in 1893 by Smoluchowski ($\underline{5}$). This constant has since proved an important factor in studying the freezing soil system. The value of the dielectric constant, expressed in electrostatic units, is defined as the ratio of the mutual electrical capacity of a given pair of equipotential surfaces , fixed with reference to each other, when immersed in the dielectric to their capacity when immersed in a vacuum. The dielectric constant of water below 600 megacycles per second is about D_w = 81.5 electrostatic units at +17 C ($\underline{6}$), and that of soil particles is D_s = 5 to 6 esu.

Therefore, in studying freezing soil systems it is necessary to know the values of the dielectric constants of soil, water and ice at different temperatures. As outlined by the authors, the appreciation of the importance of understanding the value of the factor of the dielectric constant has progressed in a fairly satisfactory manner.

Viscosity. The review under discussion also reveals that clay-adsorbed water has

an unusually high viscosity. It is known that the viscosity of water varies inversely with temperature. Thus, upon freezing, the viscosity of the free soil water would change. It would be highly desirable to know what is the viscosity of film moisture, how the viscosity of film moisture varies upon freezing, whether such a moisture with such a viscosity facilitates the amount of soil moisture transferred from the groundwater to the cold front, and how to measure the viscosity of film water. The hydrodynamic process induced by the thermodynamic process in soil, and their mutual interaction, is complex and no effort should be spared in learning to understand these two flow processes and the change in properties of water and ice.

Another aspect relative to viscosity is the behavior of water under high pressure. It is known that Bridgeman found that the coefficient of viscosity increases rapidly with pressure. It is noteworthy that the effect of pressure on viscosity of water is greater than on any other physical property. Besides, viscosity varies exponentially with pressure. One sees that, as in other respects, in respect to viscosity water shows an exceptional behavior.

It is generally known that the effect of the increase in pressure from 1 to 2,000 kg/cm^2 upon the viscosity of water is considerable, namely, at 0 C the viscosity of water increases to about three times its normal value. However, it is of great importance to know what is the role of pressure upon water, and particularly film water, in a freezing soil system. If there is one, how is the pressure built up in a freezing soil system and why does it happen? And, how do the various phases of soil water and pressure under freezing temperatures in soil develop? These and other questions lead to the problem of undercooling of soil moisture in the voids of the soil and migration of soil moisture phenomena which are also still not satisfactorily understood.

Conclusion

The evaluation of the authors' review reveals to the engineering profession that:

1. There is already a rich store of knowledge available for the explanation of some of the properties of water and ice which is applicable in highway research, design and construction.

2. Still more basic knowledge about the properties of water and ice, and their behavior in soil under freezing conditions is needed.

3. More and better interpretation and explanation of the existing knowledge in these matters are needed in order to convey their meaning to larger circles engaged in highway research and design.

4. The application of this knowledge to soil technology must be clearly shown. This would be, among other things, the next immediate work to be done in frost action research.

To achieve this it is expected that the Highway Research Board will continue in the future its liberal policy of sponsoring highway research and encouraging and publishing researchers' contributions no matter how big or small they may be. It is at this early stage of development of scientific frost action research that such an appreciative understanding and tolerance for contributions should be cultivated; it facilitates the development of a field of science more rapidly, and it also encourages more people to engage in scientific work so badly needed. It is evident that nowadays science in engineering is being more and more greatly appreciated and it is hoped that this tendency will continue. Of course, science alone will not guarantee good roads. But knowledge will make it possible for engineers to do good work.

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W. L. DOLCH, Research Associate, Joint Highway Research Project, Purdue University, Lafayette, Indiana—The review of Low and Lovell and the great amount of work that it summarizes is further evidence of the growing importance of the application of physico-chemical principles to the nature and behavior of engineering materials. The nature of water in a soil system is a complicated matter and the authors are to be complimented for their concise and inclusive presentation.

They have particularly emphasized the importance of the water film adjacent to the clay particle in determining many of the properties of such systems. Leonards (1) has also pointed out that certain physical properties of clays can be interpreted by the assumption of rather extensive films of water that have properties different from bulk water. The authors have cited many different kinds of evidence. The conclusion seems to be, stated very qualitatively, that in clay-water systems there exists on the surface of the clay minerals a water layer that has some structural order greater than that in bulk water. This order is not that of ice but is energetically roughly equivalent to it. Such films extend for distances of many molecular dimensions and gradually become indistinguishable from bulk water as the distance from the solid surface increases. Many properties of this film are, furthermore, stated to be independent, to a certain degree, of its electrolyte content.

The purpose of this discussion is to reinforce this picture of the clay-water by pointing out that it is a specialized, although spectacular, case of a more general concept concerning the nature of surface zones and thin films of liquid.

Henniker (2) has given an excellent review of the subject that should be consulted for original references and details. He presents a large amount of evidence from the literature. Some of this evidence is "optical" in nature, such as the birefringence of films on solids, x-ray diffraction studies of clays and soap micelles, and contact angles of liquid drops on films of the same liquid. A case in point for this last is the observation of Terzaghi (3) of difficulty in wetting moist clay with additional water. Included also in this category are the results of experiments that show an orienting effect of a surface on crystals deposited thereon even though rather thick films of amorphous material intervene.

Other results are from what might be called "strength" measurements. These include determinations of adhesion of such films. Experiments on the strength of adhesive joints are examples. Also the very existence and stability of foams from solutions of surface active agents show the strength imparted to these fairly thick layers by the oriented solute molecules in the surfaces.

Dielectric measurements have been mentioned in the main paper. Other electrical measurements (for example, the large conductivity increases for thin films of oils that are insulating in the bulk phase) show structural changes to occur in thin films.

Of particular interest to persons concerned with freezing phenomena in soil systems are possible viscosity changes in the water films that would lead to a lowered permeability. Many measurements have been made showing anomalously decreased flow through finely-pored structures, especially in the case of water transmission. Viscosity measurements have been made with rotating plane surfaces between which is the liquid in question. All these fluid flow measurements are difficult to interpret because of the possibility of other effects influencing the results. Examples are the effect in porous media of gas bubbles that might be liberated into the system and block pores by meniscus effects, the influence of surface roughness or foreign matter in trapping

stagnant volumes of fluid, and electrokinetic effects that cause an osmotic flow counter to that caused by the pressure gradient. Instances in the field of soils of the last two mechanisms are the papers by Schmid (4) and Michaels and Lin (5), respectively. However, the experiments that show viscosity increases in thin films where one bounding phase has been gaseous are more difficult to refute.

It should be emphasized that the work on the nature of thin films has involved a wide range of "liquids"—synthetic polymers, waxes, oils, polar and non-polar organic compounds, aqueous solutions, and water, among them—and a wide range of bounding phases such as gases, ionic crystals, metals, and liquids. The general conclusion that has been drawn can best be stated by quoting part of Henniker's summary.

"The surface zone of a liquid is not merely a monomolecular layer with unaltered liquid immediately underneath it, but it is a region in which orientation extends effectively to many molecular lengths. The effective depth of the surface zone in tens or hundreds of angstroms in low molecular weight liquids, thousands of angstroms in long-chain molecules."

The forces responsible for such orientation over comparatively long distances are probably not all known, as is stated in the paper. The Van der Waals forces that decrease in magnitude with the seventh power of the intervening distance are too weak to be effective between isolated molecules separated by the distances in question here. The explanation may lie in a transfer or polarization process that proceeds from molecule to molecule in much the same manner, to use the analogy given by McBain (6), as a magnet's effects are transmitted by a chain of iron filings to a particle at a distance so great that without the intervening structure there would be a negligible interaction.

Such action in liquid layers is greatly influenced by the nature of both the liquid and the bounding phases. Polarization effects must be important as must special bonding processes, e.g. hydrogen-bonding. Illustrative of this is the point made by Rosenqvist (7) that clays form plastic mixtures with polar liquids but not with non-polar liquids unless there is the possibility of hydrogen-bonding (e.g. dioxane).

Other sources of information on the above topics are the texts by McBain (6) and Bikerman (8), the 1948 symposium of the Faraday Society (9), and the review by Williamson (10).

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