Adsorption on Nonionic Surfactants by Soil Materials

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ABSTRACT

The adsorption of nonionic surfactants by various soil materials from solution was measured. Most studies were on Aqua Gro and Soil Penetrant—surfactants marketed for use on soils. Aqua Gro was generally adsorbed to a greater extent than Soil Penetrant. Essentially all of Aqua Gro was adsorbed from solution until a given amount of surfactant was adsorbed after which there was only a slight increase in adsorption as the concentration in solution increased. Soil Penetrant, on the other hand, was adsorbed to a lesser extent until the concentration in solution was increased to about 500 ppm. At this concentration, there was a very great increase in adsorption to a maximum value after which very little additional adsorption occurred as the solution concentration increased. Equilibrium between the soil and solution was either complete or near completion after one hour. Essentially no Aqua Gro was desorbed as the treated soil was placed in water. Some of the adsorbed Soil Penetrant went into solution as treated soil was placed in water. Since the reaction between soil and surfactant differs for various surfactants, the surfactant which would have optimum properties for a desired effect can be chosen.

Additional Key Words for Indexing: wettabilit, micelle, peat, clay.

NONIONIC surfactants have been demonstrated to be effective when applied to water repellent soils for increasing infiltration, decreasing erosion, and increasing seed germination (3, 5, 6, 7). Water repellent soils which have been wet by a surfactant solution become wettable upon redrying. It is hypothesized that this is accomplished by the hydrophobic end of the surfactant molecule being adsorbed by the soil leaving the hydrophilic end exposed. It would seem therefore that the effectiveness of a surfactant in converting a water repellent soil to a wettable soil would depend upon its adsorption by the soil.

The most effective method of application of surfactants to a soil would depend, in part, upon the adsorption isotherm of the surfactant by the soil. For example, a given amount of surfactant can be applied per unit land surface area in a solution which is very concentrated or in a more dilute solution by varying the amount of solution applied per unit area. The application procedure to follow might well depend upon the adsorption and desorption behavior.

Often layers of water repellent soil occur at or near the soil surface with the remainder of the soil profile being wettable. Estimation of the amount of surfactant to be applied to these soils to make the water repellent layer wettable would depend upon the adsorption of the surfactant. It would be of very little practical value to treat only part of the water repellent layer leaving the remainder of the layer water repellent.

For these and other reasons, it is of importance to have information on adsorption of nonionic surfactants by soil materials.

Law and Kunze (2) measured the adsorption of various surfactants by montmorillonite and kaolinite clays. No reports on adsorption of surfactants on other soil materials have been found. The purpose of this paper is to report the results of our measurements of adsorption of several nonionic surfactants by various soil materials.

EXPERIMENTAL

The surfactants used in the study are listed in Table 1. The most detailed studies were conducted on Soil Penetrant 3685 and Aqua Gro because these are products which have been marketed for use on soils. The soil materials used were Pachappa sandy loam, Waukena clay loam, montmorillonite clay, kaolinite clay, peat, expanded "greenhouse" vermiculite, a water repellent sandy loam soil collected near Morris Dam adjacent to the San Dimas Experimental Forest (referred to as "nonwettable" soil hereafter), the latter soil partially burned causing it to be extremely water repellent, and the same soil burned to a greater extent to make it wettable.

The soils were air dried and passed through a 1-mm sieve. Bulk samples of clays were ground and used for the studies; no separation was made into various size fractions. No prepreparation was made on the peat and vermiculite.

Surfactant adsorption measurements were made by mixing a given weight of soil material with a given volume of surfactant solution, allowing equilibrium, and then analyzing the supernatant solution for surfactant. The change in surfactant concentration after contact with the soil material was assumed to represent the amount of material which was adsorbed by the soil.

Five grams of soil was mixed with 25 ml of solution and 1 g of the bentonite, kaolinite, vermiculite, and peat was mixed with 25 ml of solution in the studies. Most extensive measurements were made with Aqua Gro and Soil Penetrant. The solution concentration ranged from 25 to 10,000 ppm in adsorption studies using the soils and peat. The range in concentration extended to 20,000 ppm for kaolinite and 100,000 ppm for bentonite. Adsorption studies on the other surfactants studied were made using solutions of 1,600 and 3,200 ppm.

The procedure followed was to mix the soil material with the solution and allow to set overnight. The mixture was then shaken for 24 hours. At this time, the solid material was thrown down using an ultra centrifuge and the supernatant solution was analyzed for surfactant using the method described by Valoras and Letey (9).

The time for equilibrium between the solution and adsorbed surfactant was conducted on Aqua Gro and Soil Penetrant using 3,200 ppm solution. The same procedure was followed as described above except that the supernatant solution was analyzed at 1, 2, 4, 6, 24, and 48 hours after contact with the soil. The analyses at the different time intervals were done on separate samples.

Table 1—Nonionic surfactants used in the study

<table>
<thead>
<tr>
<th>Label</th>
<th>Chemical Type</th>
</tr>
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<tbody>
<tr>
<td>Soil Penetrant 3685</td>
<td>Allyl polyoxyethylene ether</td>
</tr>
<tr>
<td>Tergitol 15-S-9</td>
<td>Polyethylene ether</td>
</tr>
<tr>
<td>Triton OF-54</td>
<td>Aminoi-phenoxypolyoxyethylene alcohol</td>
</tr>
<tr>
<td>Aqua Gro</td>
<td>50% polyoxyethylene ether and 50% polyoxyethylene ether</td>
</tr>
<tr>
<td>Sorrec CD</td>
<td>Polyoxyethylene ether</td>
</tr>
</tbody>
</table>

1 Contribution of the Department of Soils and Plant Nutrition, University of California, Riverside. The study was supported by Forest Service, USDA, Washington, D.C. Grant no. 4000. Received Sept. 30, 1968. Approved Jan. 23, 1969.
2 Laboratory Technician, Professor of Soil Physics, and Laboratory Technician, respectively.
The release of adsorbed surfactant was investigated. After samples were at equilibrium with 3,200 ppm solutions, the supernatant solution was analyzed and discarded. Distilled water was added to make up the initial solution volume. The samples set overnight and then were shaken for 24 hours. The samples were ultracentrifuged and the supernatant solution analyzed for surfactant concentration. Distilled water was again added to the samples and the procedure repeated seven times. The quantity of solution remaining in the sample and its associated amount of surfactant was accounted for in the calculations. The surfactant release studies for Soil Penetrant were conducted both by oven drying the sample at 40°C each time before adding water and by keeping the samples moist. This test was conducted to see if the surfactants become more strongly adsorbed (more difficult to replace by water) upon drying.

RESULTS

The quantity of surfactant adsorbed as a function of time after the soil material and solution are brought into contact is presented in Fig. 1 for Aqua Gro. Soil Penetrant gave similar results. Equilibrium was reached with the Waukena clay loam and the Pachappa sandy loam in less than 1 hour for both products. Most of the surfactant had been adsorbed by the water repellent soil in less than 1 hour. There was, however, a slight increase in adsorption by the water repellent soil with increased time. It took longer for equilibrium to be reached with peat than with the other materials. However, 92.5% of the adsorption of Soil Penetrant had occurred within 1 hour, and equilibrium was attained after 6 hours contact between peat and the solution. Equilibrium between Aqua Gro and peat required more than 24 hours; 65% of the adsorption had occurred after 1 hour.

The quantity of surfactant adsorbed by a gram of soil material is plotted as a function of the solution concentration at equilibrium with each material in Fig. 2, 3, 4, and 5. Aqua Gro is completely adsorbed from solution until a critical quantity of surfactant has been adsorbed by the soil material. After this amount has been adsorbed, there is only a slight increase in adsorption as the equilibrium concentration is increased. A maximum amount of adsorption is achieved which is not affected by increasing the concentration in solution.

The adsorption curve for Soil Penetrant is quite different than for Aqua Gro. There is relatively low adsorption at low solution concentrations until a given solution concentration is reached at which time there is an abrupt increase in the quantity of surfactant adsorbed. As the solution concentration is increased beyond that point, there is no further increase in quantity of adsorption. This type of adsorption curve has been observed in studies on the adsorption of surfactants by textiles, for example, Schott (8). The large increase of adsorption at a given surfactant concentration occurs at the critical micelle concentration (The concentration of surfactant at which the molecules "aggregate" into micelles).

There is considerably less adsorption of Soil Penetrant as compared to Aqua Gro at the lower solution concentrations. At the higher solution concentrations, there is
There is a difference between the quantity of material adsorbed per unit weight of soil material for the various materials tested. For example, there is more adsorption on Waukena clay loam than on Pachappa sandy loam. This behavior is to be expected because of the larger surface area of the Waukena soil as compared to the Pachappa. McNeal and Coleman (4) report the surface area for Waukena and Pachappa soil to be 145 and 50 m²/g respectively. The ratio of surface area of these soils is approximately 3 to 1. This is the approximate ratio of adsorption of Aqua Gro on these two soils. However, there is not as much difference between the adsorption of the soils for Soil Penetrant.

It can be noted in Fig. 3 that there was about twice as much Aqua Gro adsorbed on the partially burned soil as compared to the completely burned soil. De Bano measured the surface area of these soil materials by the ethylene glycol monoethyl ether technique (1) and found the ratio of the surface areas to be approximately 2:1, so again it appears that the amount of Aqua Gro adsorption is proportional to the surface area. The difference in the amount of adsorption of Soil Penetrant for the two materials is not as great as would be indicated by the surface area measurements, so again it appears that Soil Penetrant is only partially affected by the surface area of the material.

There is considerably more adsorption of surfactant on peat as compared to the mineral soil materials. Approximately 80 mg of surfactant can be adsorbed per gram of peat. The adsorption of both surfactants by vermiculite is unusual (Fig. 5). There is an initial increase in adsorption with an increase in concentration followed by a slight decrease in adsorption and then a rapid increase in adsorption as the concentration is increased further. This behavior is not readily explained.
Fig. 7—Quantity of Soil Penetrant adsorbed by four soil materials after various washings with water.

A comparison between the various surfactants tested is presented in Fig. 6. The data obtained with the 1,600-ppm treatment indicates that the ester type surfactants are adsorbed to a greater extent than the other types. This is also demonstrated by the 3,200-ppm treatment with some exceptions.

The concentrations of adsorbed surfactant after “washing” with distilled water are illustrated in Fig. 7 for Soil Penetrant. Aqua Gro appears to be irreversibly adsorbed as essentially none of the adsorbed material is removed by water. Soil Penetrant on the other hand is removed by distilled water until a given adsorbed concentration is reached after which very little is removed by further “washing.” There was no significant difference between samples which were dried each time and those which were not.

DISCUSSION

The results indicate that there are basic differences between the behavior of Soil Penetrant and Aqua Gro. This is fortunate because it provides flexibility in choosing surfactants based upon the desired results.

In the use of surfactants on water repellent soils, water penetration and/or rewet properties are desired. If priority is given to obtaining deep water penetration at minimum time, a surfactant with low adsorption would be chosen. On the other hand, if one is primarily interested in treating a water repellent soil for rewet properties (converting the water repellent soil into a wettable soil upon drying) he would choose a surfactant which is adsorbed by the soil. The surfactant which is greatly adsorbed by the soil is not as effective for deep penetration because the molecules are adsorbed from solution by the soil and thus the water near the wetting front may be very low in surfactant concentration.

Based upon the adsorption data presented in this paper, one would expect that Soil Penetrant would be more effective than Aqua Gro in getting deep water penetration. On the other hand, Aqua Gro would be better than Soil Penetrant in converting a water repellent soil into a wettable soil. Furthermore, the longevity of the treatment should be greater for Aqua Gro than Soil Penetrant because the molecules were not desorbed from the soil. These conclusions are in agreement with observations which we have made in our laboratory over the last several years. We find that Soil Penetrant gives better initial wetting but that Aqua Gro gives better rewet properties.

Another consideration which should be given to the use of surfactants on soils is their possible toxicity to plant life. We have found that very low concentrations of surfactants in solution culture can be detrimental to plants. On the other hand, much higher concentrations can be applied to soil without any apparent damage to plants. Again, based upon our adsorption data, we would predict that we could use larger concentrations of Aqua Gro in a soil system as compared to Soil Penetrant without damage to the plant, because Aqua Gro would be adsorbed by the soil and not be as effective as a plant toxin. We have also observed in our greenhouse that this is the case.

These observations indicate that data on adsorption of various surfactants by given soil materials can be used to predict relative effectiveness of a treatment for wetting, rewet properties, and possible plant toxicity factors. Adsorption data will also be useful in establishing rates of application to a particular soil to achieve the desired results. Fortunately, surfactants have different properties which allows one to choose the specific surfactant which will give the optimum desired result.

LITERATURE CITED