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Publisher: Taylor & Francis

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## Journal of Dispersion Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/Idis20>

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Published online: 27 Apr 2007.

To cite this article: Stella M. Zabala & R.M. Torres Sanchez (2000) WATER MOVEMENT CAUSED BY SPREADING SURFACTANTS IN UNSATURATED SYSTEMS OF PARTICLES OF NONUNIFORM SIZE, Journal of Dispersion Science and Technology, 21:7, 957-968, DOI: [10.1080/01932690008913323](https://doi.org/10.1080/01932690008913323)

To link to this article: <http://dx.doi.org/10.1080/01932690008913323>

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**WATER MOVEMENT CAUSED BY SPREADING SURFACTANTS IN UNSATURATED SYSTEMS OF PARTICLES OF NONUNIFORM SIZE**

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**ABSTRACT**

The movement of water originated by the spreading of two surfactants was analyzed in glass beads as well as on soil systems, both of particles of nonuniform size

The higher difference of surface tension produced in the system by 1-hexadecanol compared to that of 1-tetradecanol led therefore to a higher amount of water moved. Decreased proportion of the smaller sized particles in glass beads system produced a decrease in the total water moved by both surfactants.

Organic matter acted in soil as a second surfactant in glass beads. This effect was compared in glass beads systems once 1-hexadecanol was evenly distributed among the particles as continuous film, which played a role alike that of organic matter in soil and then a second surfactant 1-tetradecanol was added. These additional surfactant effect diminished the difference between initial and final surface tension (surface tension depression) of the system and so the total water moved.

The soil organic matter (1.7%) modified the water movement curve in the presence of low (0.2g) content of 1-hexadecanol, whereas for high content of either alcohol (0.4g) or low content of 1-tetradecanol content (0.2g) the water movement curves were the same.

**Keywords:** surfactant spreading, water movement, heterogeneous particle size system, soil.

## INTRODUCTION

The water movement promoted by surfactants spreading is well-known and was studied in bulk water systems (i.e. water reservoirs, lakes, etc.), the layer of water moved being some mm thick [1-2].

In unsaturated particulate materials the spreading of some insoluble surfactants in water (e.g., long-chain aliphatic alcohols,  $C > 10$ ), also produces a movement of the underlying water. The water movement occurs from the place where the surfactant is toward the surfactant-free region. The best condition for water movement was found on forming continuous water film, of few Å thick, on the system [3]. It occurs at the so-called maximum initial water content, which increases as the system particle size decreases [3].

The water moved by surfactant spreading has been studied mainly in simple, uniformly sized [3-5] systems, where surfactants with low surface tensions proved to be most effective. The water movement in these systems is produced by a pressure drop generated by differences in particle size and surface tension [3,5], according to the equation of Young and Laplace [6]:

$$\Delta P = 2 \gamma / r \quad \text{eq. 1}$$

where:  $\gamma$  is the surface tension of the liquid and  $r$  the radius of curvature of the interface.

The objectives of the present work (following precedent works [7-8]) are; (1) to analyze the water movement originated by different surfactants in relation to the influence of particle size in systems of glass beads, and (2) to compare the behavior found to that of a more complex non-uniform sized particle system as natural soil.

## MATERIALS AND METHODS

The soil used in this work was a typical Hapludoll gathered from horizon A, original from Anguil (La Pampa province). The soil was crushed and sieved (<1mm) to remove plant residues and gravel, leached with distilled water and air-dried. Table 1 shows the organic matter (OM) content and texture of the soil.

Two types of spherical glass beads were used (Dragon-Werk, Bayruth, Germany) with nominal diameter ranges of 510-700 (type I) and 80-110 $\mu$ m (type II). Glass beads were allowed to remain in concentrated HCl for 1 day and then washed with distilled water.

Alcohols 1-tetradecanol and 1-hexadecanol (Fluka AG) were chosen as surfactants and used as received. Their surface tensions (in 0.01 N HCl) were 45.4 and 37.7mN/m, respectively.

After 24hs and 5ml water addition, the surface tension of each part of the system was measured on the centrifuged liquid by the du Nöuy method.

Water movement was studied in horizontal closed columns, made of 3 acrylic rings (diameter 2cm and height 1.5cm each).

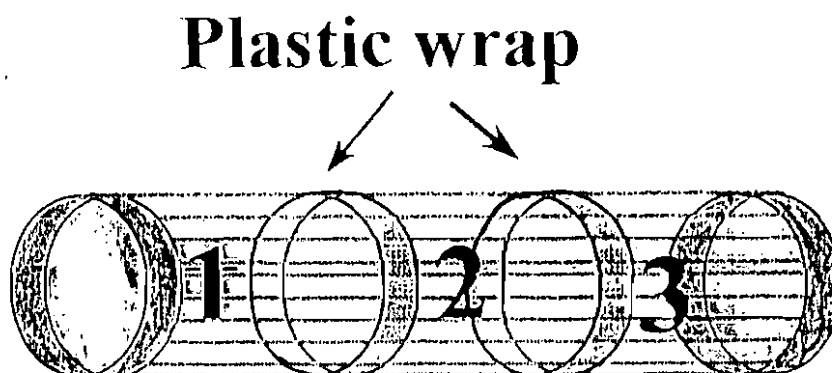
The method is as follows: a weighed amount of solid material was added with water and thoroughly mixed to achieve a given initial water content. The mixture obtained was divided into two parts: one was used to fill the rings 2 and 3 of the column, and the other part was added with a weighed amount of surfactant before being placed to fill ring 1. The rings were assembled together as a column by using plastic wraps and then it was weighed to determine the amount of wet material.

The figure 1 shows a scheme of the column.

After a determined contact time (24h), the column was weighed to verify that evaporation losses were negligible. Then plastic wraps

**TABLE 1:** Soil organic matter and texture.

OM (%)	1000-50 $\mu$ m (%)	50-5 $\mu$ m (%)	<5 $\mu$ m (%)
1.7	30	53	17

**Figure 1:** Scheme of the column utilized for measuring the water moved after surfactant spreading.

were removed from the column to weigh each ring. Water content of the samples were determined by drying to constant weight in an oven set at 100°C; results were expressed as g of water per 100g of dry material (% w/w dry basis).

## RESULTS AND DISCUSSION

### Glass beads system

Table 2 shows initial and final surface tensions and water contents values for a glass bead system (Type I) and 0.2g of

**TABLE 2:** Glass beads system (Type I). Initial and final surface tensions and water contents, for both surfactants (A, 1-tetradecanol and B, 1-hexadecanol).

Ring Number r	Initial Surface Tension (mN/m)		Final Surface Tension (mN/m)		Initial Water Content (%)		Final Water Content (%)	
	A	B	A	B	A	B	A	B
	1	56.5	54.5	51.0	47.0	12.0	12.0	7.2
2	72.0	72.0	50.0	50.0	12.0	12.0	11.6	11.6
3	72.0	72.0	52.0	47.0	12.0	12.0	19.0	18.5

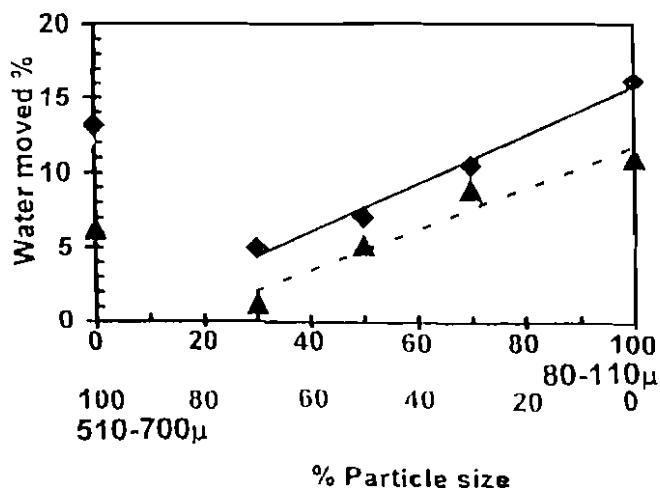
surfactant. The initial water content chosen (12%) allows maximum water movement in these systems [3].

Table 2 indicates that the highest surface tension difference (in ring 1) was originated by the 1-hexadecanol ( $\Delta\gamma=7.5\text{mN/m}$ ) which produces a stronger water movement (13.12%) compared to that caused by the 1-tetradecanol ( $\Delta\gamma=5.5\text{mN/m}$  and 11.78% water moved). These results are in agreement with that reported by Karkare et al [5] and indicated by eq. 1.

Figure 2 shows the water moved by both surfactants, for systems with several proportions of glass beads of different size, at 12% initial water content.

The surface tension values obtained for these systems match those of Table 2.

Parallel linear trends (slope=0.15) were obtained for both surfactants (solid line, 1-hexadecanol; dashed line, 1-tetradecanol) showing that, as in the uniformly-sized particle system of Table 2, a



**Figure 2:** water moved (%) for different proportions (% w/w) of glass beads of different diameters for 1-tetradecanol (dashed line) and 1-hexadecanol (solid line).

lower difference in surface tension (lower surface tension depression) produces a lower water movement. In each surfactant system, the amount of water moved was decreased when reducing the proportion of the smaller particles (type II). This fact evidences the influence of pore size (originated by the particle size system), at constant surface tension difference, in agreement with that found for homogeneous particle systems [5].

To compare the heterogeneous particle system of glass beads with that of natural soil, the effect of soil organic matter must be taken into account. As shown elsewhere [9], the soil organic matter also acts as surfactant, the decrease of surface tension of the soil water extract being dependent on the amount of organic matter present. It was

pointed out [9] that soil lixiviation with ethanol decreases surface tension by about 2-4mN/m [9]. In turn, soil suspension treatment with 1-tetradecanol and 1-hexadecanol decreases soil surface tension by about 20 and 15mN/m, respectively (Table 4).

To account for the effect of soil organic matter as surfactant in soil systems, to be analyzed later, 1-hexadecanol was thoroughly mixed with the glass beads (to play the role of soil organic matter) and 1-tetradecanol was added only to ring 1.

Table 3 lists initial and final surface tensions and water contents for the glass bead system (type I).

The surface tension decrease (initial-Final) listed in Table 3 are lower than those of Table 2, so the total water movement was reduced from 11.8 (Table 2) to 8.4%. Similar results were found when mixing 1-tetradecanol with the glass beads, while incorporating 1-hexadecanol only to ring 1. By analyzing the data of Figure 2, it becomes clear that increased proportions of the smaller particles (as it is the case in soil systems) will also increase total water movement in the presence of a surfactant in the system.

### **Soil system**

Table 4 presents values of initial and final surface tensions and water contents for the soil system at 42% initial water content (assumed to be the maximum initial water [7]).

In the soil system treated with 1-tetradecanol, the presence of organic matter (1.7%) depressed the initial surface tension in ring 1 from 50.0 to 48.0, i.e., by 2.0mN/m. This depression was lower than in glass beads (from 56.5 to 51.0, i.e., 4.5mN/m, see Table 2). The surfactant behavior of organic matter (additional surfactant effect) was similar to that found for the glass beads system treated with both



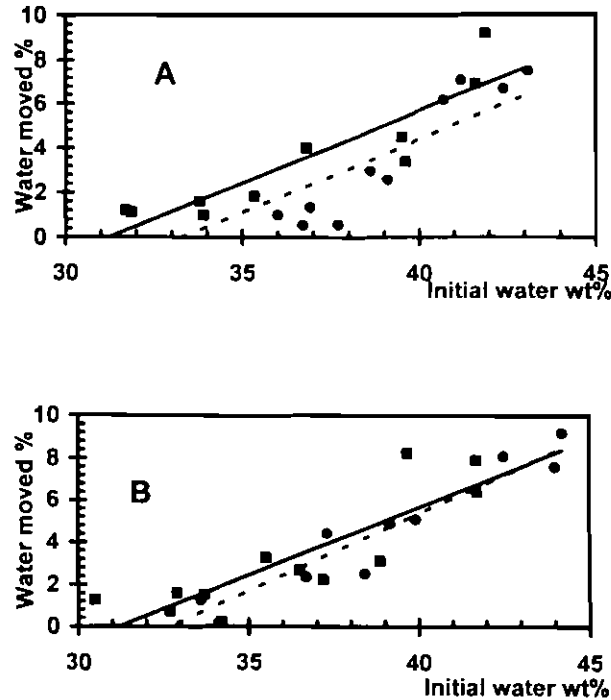
**TABLE 3:** Glass beads system (Type I). Initial and final surface tensions and water contents for 1-hexadecanol mixed in all columns and 1-tetradecanol added only in ring 1.

Ring Number	Initial Surface Tension (mN/m)	Final Surface Tension (mN/m)	Initial Water Content (%)	Final Water Content (%)
1	44.0	48.0	12.0	10.0
2	54.0	49.0	12.0	9.8
3	54.0	49.0	12.0	16.2

**TABLE 4:** Soil system. Initial and final surface tensions and water contents, for both surfactants (A, 1-tetradecanol; B, 1-hexadecanol).

Ring Number	Initial Surface Tension (mN/m)		Final Surface Tension (mN/m)		Initial Water Content (%)		Final Water Content (%)	
	A	B	A	B	A	B	A	B
1	50.0	54.0	48.0	55.0	42.0	42.0	36.9	37.8
2	70.0	71.0	52.0	52.0	42.0	42.0	43.9	43.8
3	70.0	71.0	47.0	70.0	42.0	42.0	44.2	44.1

(alcohols) surfactants added (Table 3) where a decrease of the surface tension value also was produced. The difference between initial and final surface tension values, observed in rings 2 and 3 was also close to that found in glass beads system. The total water moved in the soil system (9.2% for 1-tetradecanol and 8.1% for 1-hexadecanol) agreed



**Figure 3:** water moved (%) as a function of the initial water content (%), in the soil system added with alcohol (A), 1-tetradecanol and alcohol (B), 1-hexadecanol, for (●) 0,2g and (■) 0,4 g of either alcohol.

to that found for heterogeneous glass bead system in both surfactants (8.84% for 1-tetradecanol and 9.44% for 1-hexadecanol), for equal proportions of differently-sized particles (Figure 2, point corresponding to 30% proportion of particles sized between 80 and 110 $\mu$ )

However, the difference of initial surface tensions in ring 1 between the soil system treated with 1-hexadecanol and glass beads (54.0 and 54.5mN/m, respectively) did not evidence the presence of

organic matter. It must be pointed out that the final surface tension obtained for the ring 3, indicated a very low decrease after the surfactant spreading, which was within the experimental error ( $\pm 1\text{mN/m}$ ).

Notwithstanding, the amount of water moved was alike (around 8.0%) that found for 1-hexadecanol, at 42% initial water content.

The figure 3 shows the amount of water moved in the range of initial water contents for 0.2 and 0.4g of both alcohols.

The linear regression for each series of data in both alcohol systems had a coefficient of determination ( $R^2$ )  $\approx 0.8$ . It must be indicated that the regression lines for 0.4g of either 1-tetradecanol or 1-hexadecanol coincided exactly ( $y=0.65x-20.1$ ). In 1-tetradecanol, the straight lines at 0.2 and 0.4g were parallel, so the water moved increased when increasing the amount of alcohol. In turn, water moved by 1-hexadecanol gave regression lines with different slope (0.65 and 0.74 for 0.4g and 0.2g of alcohol, respectively), which may indicate some association of 1-hexadecanol with organic matter. This was also evidenced by the similar surface tensions obtained in rings 1 and 3 (Table 3). Nonetheless, the association hypothesis requires new experiments to be confirmed, which are to be done in a subsequent work.

## CONCLUSIONS

In a soil system at maximum initial water content, the amount of water moved (by the action of surfactant spreading) was close to that found in glass beads system and can be compared to the behavior of systems with particles of different sizes.

In soil systems, water movement followed the same lines for 0.4g of either 1-hexadecanol or 1-tetradecanol. The fitting line at 0.2g

1-tetradecanol was parallel but indicated lower water movement. The line obtained for 0.2g of 1-hexadecanol had different slope. This, together with the fact that the surface tension depression in 1-hexadecanol was lower than in 1-tetradecanol, would indicate organic matter association with 1-hexadecanol.

#### ACKNOWLEDGMENT

The authors thank the financial support provided by CONICET through the Project IP 0217.

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*Received:* 11/8/99

*Accepted:* 3/28/00