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## SURFACTANTS IN FERTILIZER

# Sorption of Surface Active Agents from Aqueous Solution by Phosphate Rock

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The adsorption of surface active agents from aqueous solutions by phosphate rock suspensions has been investigated as a possible clue to previously reported differences between the behaviors of nonfloated and double-floated phosphate rocks during acidulation. Changes in surfactant concentration as measured by differences in relative surface tensions of the solutions before and after contact with the rock indicate that the anionic, nonionic, and cationic types of surfactants are adsorbed on the surface of rock particles in varying degrees depending on the type and molecular complexity of the surfactant, the particle size and the degree of surface saturation of the rock, and on the previous treatment of the latter with one or more flotation reagents. The presence of the cationic reagent used in the flotation process doubtlessly explains the enhanced reaction rates observed in the acidulation of double-floated rock.

IN A PREVIOUS INVESTIGATION of the use of anionic and nonionic surface active agents in phosphate rock acidulation, double-floated rock behaved like washer pebble rock treated with an effective surface active agent (1, 4). In the double-flotation process, phosphate rock is floated with an anionic-type reagent in the first stage. The cationic surfactant used in the second stage is a flotation agent for siliceous material and a depressant for phosphate rock. It has generally been assumed that relatively little, if any, of the cationic reagent is retained in the rock product. The present investigation was initiated to determine whether the presence of surfactants could be detected in the rock by surface tension procedures. The presence of the anionic-type flotation reagent in single-floated rock has already been demonstrated by other means (3).

### Procedure

In preliminary experiments, aqueous and acetone extracts of double-floated rock exhibited substantially the same surface tension as the pure solvents. Consequently, attempts to demonstrate the presence of surface active agents in the rock by this procedure were ineffective. The procedure of measuring the surface tension of aqueous surfactant solution before and after contact with phosphate rock suspensions, however, showed significant differences and has been used in this investigation of the sorption of different types of surfactants by phosphate rock from several sources.

Aqueous solutions of various concentrations of surfactants, expressed as percentage active ingredient, were prepared and measurements of the solution surface tension were made by the capillary-

rise method. For this purpose graduated thermometer stems open at both ends were used. The capillaries were cleaned with acetone and water after each solution measurement and checked for reproducibility of results against distilled water. Repeated checks agreed within limits of experimental error of about 1% with the surface tension of water at the temperature of observation. Since the results were expressed as relative surface tension, close control over temperature was not necessary, and the surface tension measurements of the surfactant solutions were made at prevailing room temperatures, which varied over the range, 25° to 32° C., corresponding to a change of about 1.4% in the surface tension of water.

Measurements were made by drawing the solutions through the capillaries to wet the walls and expel entrapped air,

**Table I. Chemical Analyses of Phosphate Rock**

No.	Source and Type	Analysis, %		
		CaO	P <sub>2</sub> O <sub>5</sub>	F
3160	Idaho, nonfloated	44.4	33.2	3.4
3163	Wyoming, nonfloated	45.3	32.6	4.1
3169	Florida, nonfloated <sup>a</sup>	46.9	34.1	4.0
3172	Florida, double-floated concentrate	48.0	34.5	5.0

<sup>a</sup> Washer pebble.**Table II. Screen Analyses of Phosphate Rock**

	Wt. % through Tyler Screen (Sample No.)				
	3160	3163	3169	3172	3180 <sup>a</sup>
Dry					
65-mesh	97.2	99.5	93.2	97.1	41.4
100-mesh	88.6	97.0	87.2	84.4	6.6
150-mesh	75.4	91.2	71.0	72.0	
200-mesh	56.7	73.6	57.2	52.8	
Wet					
200-mesh	69.0	86.4	66.8	62.5	

<sup>a</sup> Through 20-mesh, 90.1%; 35-mesh, 67.5%.

after which the tube was vertically mounted with the zero mark at the level of the surfactant solution contained in a small beaker. Observations on the falling level of the solution in the capillary were made at regular intervals and two or more identical readings taken at least 10 minutes apart were required to establish the height of the capillary rise.

Fifty milliliters of surfactant solution and 25 grams of rock were normally mixed and continuously agitated for a period of 10 minutes before filtering through No. 42 Whatman filter paper. The filter paper had no significant effect on adsorption measurements. In a few instances due to filtration difficulties, separations of the rock and surfactant solution were made by centrifuging the supernatant liquid.

### Materials

The chemical and screen analyses of four phosphate rocks used in this study are given in Tables I and II. The non-floated rocks from Florida, Idaho, and Wyoming were used in the previously reported laboratory investigation (7), while the double-floated Florida land pebble concentrate was used in recent plant scale tests (2). The test surfactants are listed in Table III. Surfactants, A, B, C, D, E, G, and H were used in the laboratory tests, and C, in the plant tests.

### Experimental Results

Adsorption of cationic surfactant *J* by phosphate rock suspensions is shown in Figure 1. Curve *a* shows the characteristic surface tension lowering produced by increasing concentrations of this surfactant. Curves *b* and *c* show the relative surface tension of the surfactant solution after contact with commercially ground nonfloated and double-floated Florida land pebble rocks, re-

spectively, while curve *d* is for the unground double-floated rock concentrate. The lateral shift of curves *b*, *c*, and *d* from the position of curve *a* is a measure of the amount of surfactant adsorbed from various concentrations of surfactant solutions shown along the abscissa.

Table IV shows an estimate, based on the data of Figure 1 of the amounts of surfactant *J* adsorbed in grams per kilogram of rock. In all cases 99%, or more, of the surfactant added in solution was adsorbed by the rock suspensions. The amount adsorbed cannot be determined by this method when the concentration left in solution exceeds 0.002%, which concentration corresponds to the minimum relative surface tension produced by this reagent.

### Differences between Surfactants.

Figure 2 shows a comparison of the relative surface tensions of 0.10% aqueous solutions of several different anionic, nonionic, and cationic surfactants before and after 10-minute contact time with ground washer-pebble and double-floated Florida rock in the proportions of 50 ml. of solution per 25 grams of phosphate rock. The relative surface tension of the aqueous surfactant solution before contact with the rock (Bar 1) was always less than that observed after contact with the rock. Figure 2 also shows that various surfactants even of the same type are not all equally effective in lowering the surface tension of the solution. Thus, in the case of the anionic surfactants, the relative surface tension of 0.10% solutions varied from 50 to 97%; in that of the nonionics, from 43 to 54%; and in that of the cationics, from 35 to 60% of the surface tension of pure water. These differences may be attributable, at least in part, to variations in the molecular weight of the surfactants as shown by comparing the relative surface tension of decylbenzene sodium sulfonate solution (surfactant B) with those of the sulfonated residues of petroleum distillation (surfactants S and T). The latter, doubtlessly, are compounds of very high molecular weight. Therefore, the 0.1% solutions of the compounds that have a relatively low molar concentration show little lowering of the surface tension. At 1.0% concentration the relative surface tension of surfactant S (47%, Figure 4) is equal to that of a 0.1% solution of nonionic surfactant C (Figure 2). These observations indicate that the effect of surfactants on the surface tension of

**Table III. Surface Active Agents**

Key Letter	Compound as Listed by Producers
Anionic	
A	Dodecylbenzene sodium sulfonate, 100%
B	Decylbenzene sodium sulfonate, 100%
H	Alkylbenzene trimethanolamine sulfonate, 60%
K	Alkyl aryl sodium sulfonate, 37%
L	Alkyl aryl sulfonic acid (unneutralized), 85%
M	Alkyl aryl sodium sulfonate, 40%
N	Alkyl aryl sodium sulfonate, 85%
O	Alkyl aryl sulfonate, 92.5%
S, T	Sulfonated residues of petroleum distillation
Nonionic	
C	Alcohol-ethylene oxide condensation product, 85%
D	Mercaptan-ethylene oxide condensation product, 100%
E	Alkylphenyl polyethylene glycol ether, 95%
G	Alkyl phenoxy polyoxyethylene ethanol, 100%
Cationic	
I	Alkyl dimethyl benzyl ammonium chloride, 50%
J	Lauryl dimethylamine oxide, 20%
P	<i>tert</i> -Alkyl primary amine acetate
Q	Rosinamine-ethylene oxide condensation product
R	Imidazolium hydrochloride compound

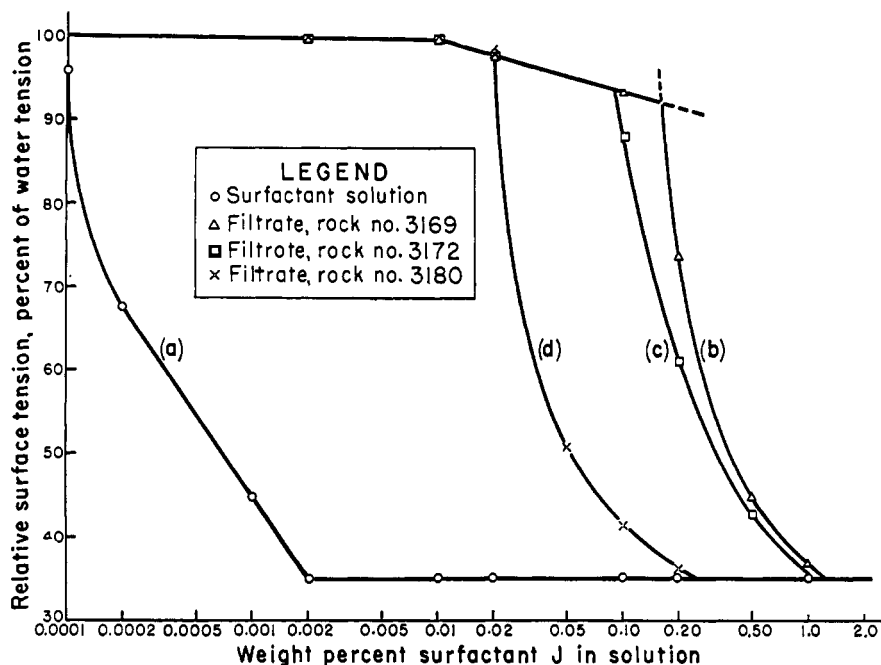


Figure 1. Influence of phosphate rock adsorption of cationic surfactant J on relative surface tension of aqueous solutions

water is a function of surfactant composition.

**Differences between Washer Pebble Rock and Flotation Concentrate.** A further observation made from data shown in Figure 2 pertains to the difference in the influence of floated and non-floated rock on different types of surfactants. In the case of most of the

in part, the fact that in phosphate rock acidulation the anionic type surfactants do not yield as good results with floated rock as they do with nonfloated rock (1, 2).

**Influence of Phosphate Rock from Different Sources.** Figure 3 shows the influence of source, ore dressing treatment, and rock grinding on the adsorption of typical anionic, nonionic, and cationic surfactants from 0.01, 0.10, and 1.0% solutions. Bar 1 shows the relative surface tension of the anionic, nonionic, and cationic surfactant solution before contact with the rock. Bars 2, 3, and 4 show the relative surface tension of the same solutions after contact with ground

Table IV. Distribution Based on Figure 1 Data of Cationic Surfactant J between Aqueous Solution and Phosphate Rock Suspensions

Contact time 10 minutes

Residual Tension, %	Solution Concentration, %	Surfactant Adsorbed by Rock, Grams/Kg.		
		3169	3172	3180
67.5	0.0002	4.2	3.2	0.6
54.6	0.0005	6.2	5.0	0.8
45.0	0.0010	9.8	8.6	1.4
40.0	0.0014	14.8	12.8	2.4
36.3	0.0018	20.6	18.0	3.8
35.0	0.0020	24.4	22.0	5.0

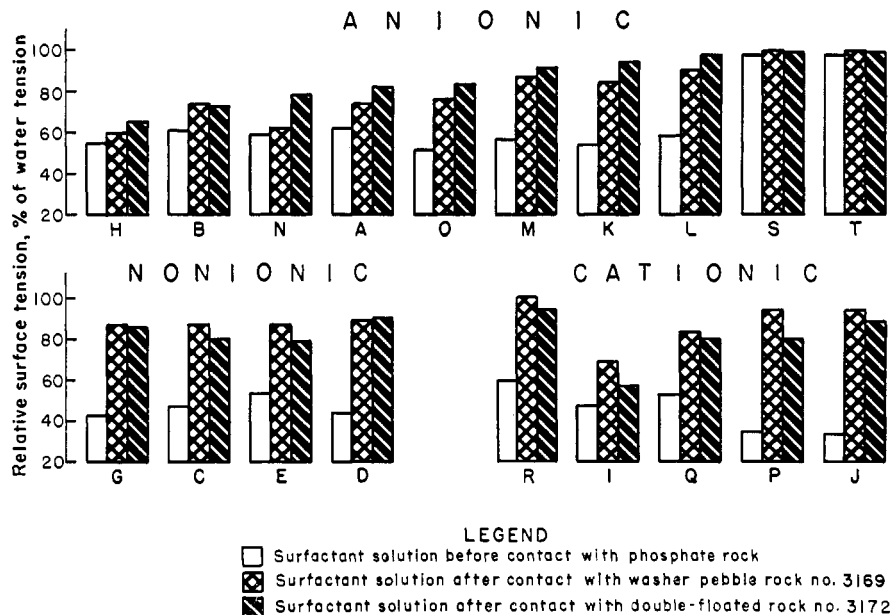
anionics, floated rock (bar 3) removed more of the surfactants from solution than nonfloated rock (bar 2), whereas in the case of the nonionic and cationic surfactants, the nonfloated rocks were the better adsorbers. This could signify that the capacity of the rock for cationic surfactants was already partially satisfied by the flotation agent, which decreased its capacity for further adsorption of both the cationic and nonionic agents, but increased its capacity for the anionic type which is chemically opposite to the cationic type. The neutralizing effect of the flotation agent on the anionic type surfactants doubtlessly explains, at least

nonfloated phosphate rocks from Idaho (No. 3160), Wyoming (No. 3163), and Florida (No. 3169), respectively. Bars 5 and 6 are for ground and unground double-floated Florida land pebble concentrate (No. 3172 and 3180), respectively. Anionic surfactant A produced no significant lowering of the surface tension in 0.01% solution. Consequently there was no significant difference between it and the surface tension of the same solution after contact with the several rocks. In the case of the nonionic and cationic surfactants, C and J, respectively, all of the rocks were about equally effective in removing the surfactants from the 0.01% solution, but show different degrees of effectiveness in removing the surfactant from 0.10 and 1.0% concentrations.

**Influence of Surfactant Solution Concentration.** Figure 4 shows a comparison of surfactant adsorption by nonfloated and double-floated ground phosphate rocks from various concentrations of typical anionic, nonionic, and cationic surfactants covering the range of concentrations in which significant differences were observed in the surface tensions of the solutions before and after contact with rock. Thus, anionic surfactants of high molecular weight showed significant differences only in the concentration range, 0.1 to 1.0%, while all of the others showed significant differences over the range, 0.01 to 1.0%. The cationic surfactants were sensitive from 0.0002 to about 1.0% solutions (Figures 1, 4).

**Influence of Contact Time and Rock-Surfactant Ratio on Surface Tension Measurements.** Figure 5 shows the influence of varying the time of contact between rock and surfactant solution, and the ratio of rock to surfactant solution on the surface tension of a 0.20% solution

Figure 2. Change in surface tension of 0.10% solutions of various surfactants due to sorption by nonfloated and double-floated phosphate rock



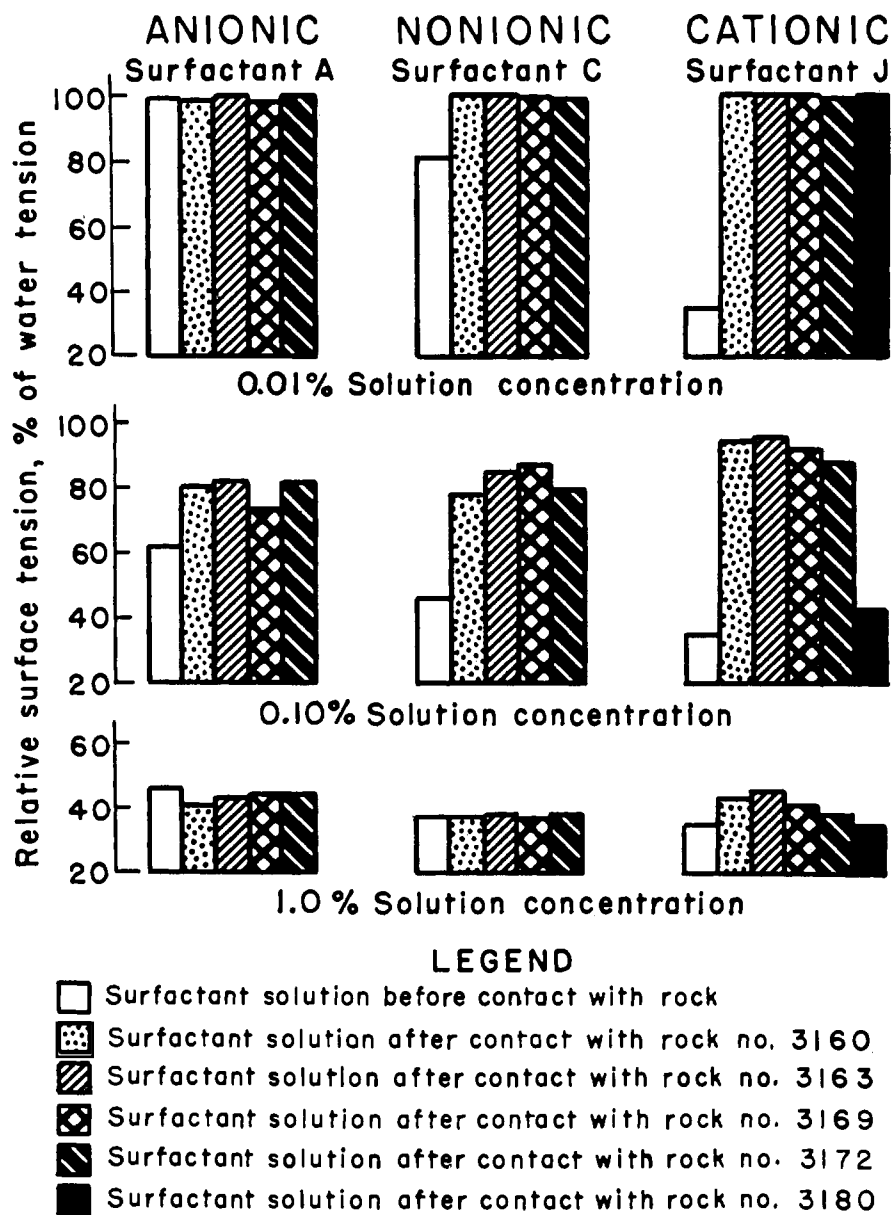


Figure 3. Influence of source, treatment, and particle size of phosphate rock on sorption of typical surfactants of different types from solutions of various concentrations

of cationic surfactant J. The adsorption of surfactants by washer-pebble rock No. 3169 increased with time over the range, 0 to 15 minutes, while with double-floated rock No. 3172, it increased with time over the range, 0 to 10 minutes (the normal contact time used in these tests). Adsorption of the surfactant by the rock increased with increasing ratio of the rock to surfactant solution. The difference between the amounts adsorbed by floated and non-floated rock increased with time of contact and with increasing ratio of rock to surfactant solution.

**Influence of Degree of Surface Saturation on Surfactant Distribution.** Figure 6(a) shows the results of successive treatments of 25 grams of ground Florida rock with 50 ml. each of 0.20% solution of surfactant J, followed by washing and aqueous extractions of the treated rock.

In each of the treatments the surfactant solution was filtered off by suction after 10 minutes' contact with the rock, and the latter was washed with water to displace all the residual surfactant solution. After drying to remove water, the treated rock was extracted with 50 milliliters of water. The bars on the left in treatments 1 and 2 show the relative surface tensions of the surfactant solutions after contact with the rock. Surface tension of the solution after contact with the rock is lower in the second, than in the first treatment. This indicates that less surfactant was adsorbed by the rock in the second than in the first treatment. The bars on the right show the relative surface tensions of the aqueous extracts of the treated rock. The relative surface tension of the second extract is lower than that of the first, indicating that more surfactant was re-

moved from the rock in the second than in the first extraction. These observations indicate that the distribution of the surfactant between the solid and liquid phases is a function of the concentration of surfactant in solution and the amount of surfactant adsorbed on the surface of the rock.

**Phosphate Rock Capacity.** Relative capacities of phosphate rock for various surfactants shown in Figure 6(b) vary with the type, and with the molecular weight of the several surfactants. Thus, comparable estimates of the capacity of ground Florida land pebble show variations from about 4 pounds of the non-ionic and lower molecular weight anionic surfactants E, D, and K, to about 20 pounds of the high molecular weight anionic surfactant S and the cationic surfactant J and to about 36 pounds of surfactant I per ton of rock. Figure 1 and Table IV show variations in the capacity of ground nonfloated and unground and ground double-floated rock with various concentrations of surfactant J.

#### Discussion

The evidence of surfactant adsorption from aqueous solutions by phosphate rock suspensions presented, coupled with previously published data (7, 4) showing that double-floated rock during acidulation behaved like a surfactant-treated nonfloated rock from the same source, is strong presumptive evidence that the adsorbed cationic flotation agent is responsible for the observed differences in the acidulation phenomena between floated and nonfloated rock (3). Observations on the adsorption of the anionic-type surfactants are in line with the results of a previous investigation made on the presence of such reagents in single-floated rock (3).

Literature published by the producers of surfactants tends to create the impression that alteration of the surface tension of the solution phase is the most important role of these reagents in their application to fertilizer production. The fact that the surface tension of the aqueous solution is restored to that of pure water through adsorption of the surfactant by the rock from dilute solutions should dispel this opinion. Evidently, the surface tension of the aqueous solution used in the flotation process could have no effect on the acidulation phenomena of the floated rock. On the other hand, the surfactant adsorbed on the rock surfaces manifestly is carried into the rock-acid system where it can influence the reaction phenomena. Thus, a water-repellent surface film, such as the insoluble soap films produced by oleic acid, could interfere with the reaction between the rock and sulfuric acid—a complaint frequently made against single-floated rock in the early days of phosphate rock

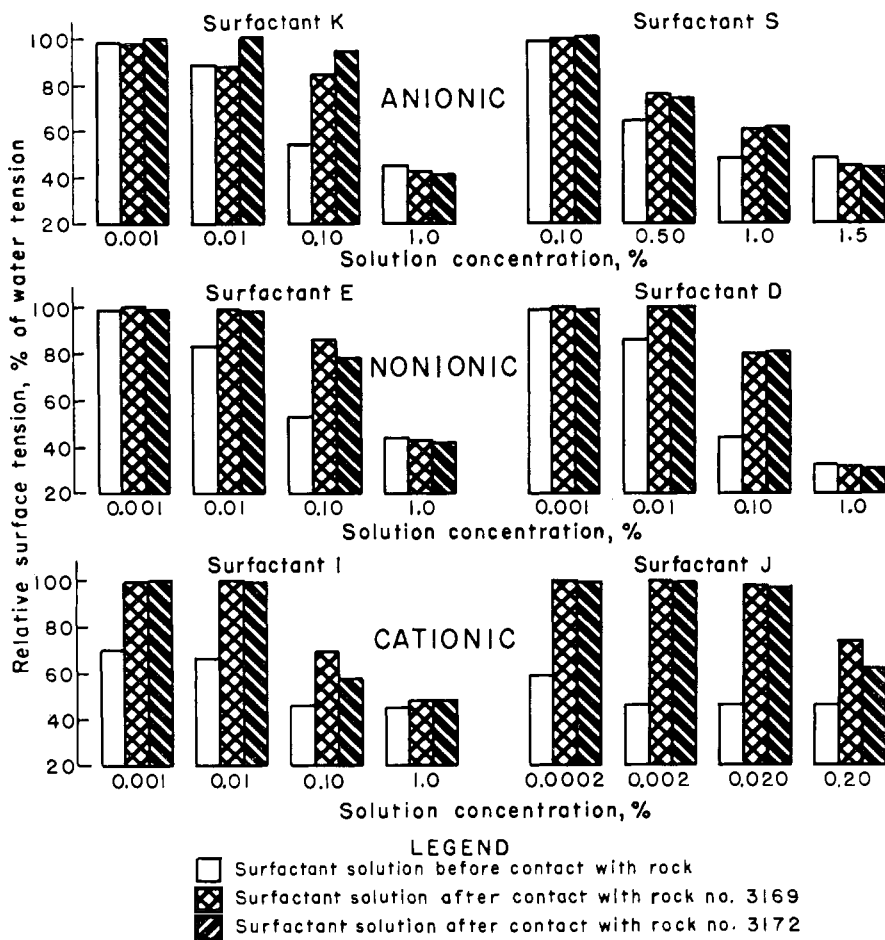


Figure 4. Effective ranges of concentration of various surfactants for measurements of sorption by nonfloated and double-floated Florida land pebble phosphate rock

flotation (3). A hydrophilic film, on the other hand, may promote reaction (2).

**Summary**

Investigation of the sorption of surface active agents from aqueous solutions by

Figure 5. Influence of variations in (a) contact time and (b) rock-surfactant solution ratio on sorption measurements of cationic surfactant J

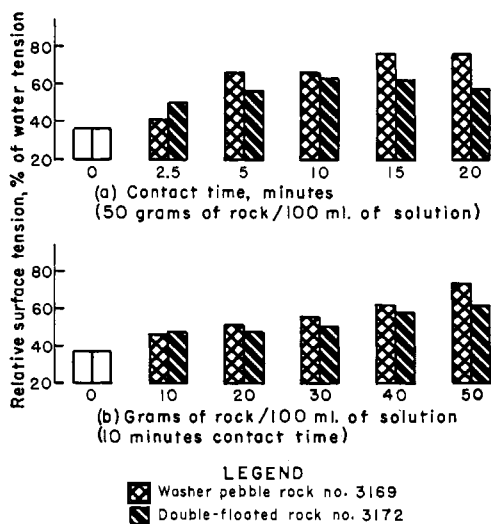
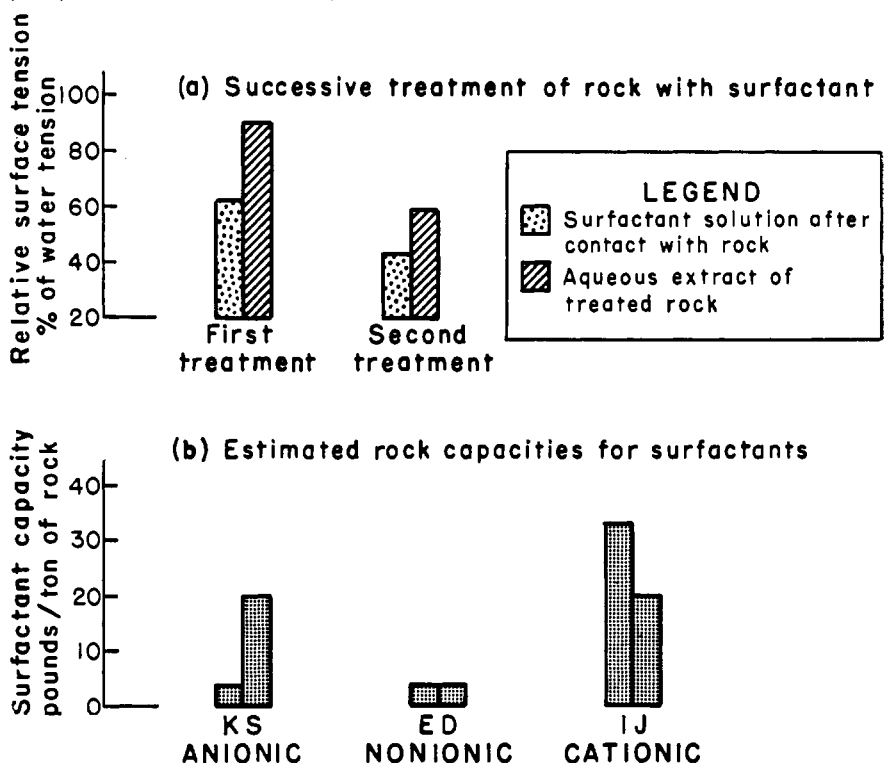


Figure 6. (a) Influence of degree of surface saturation on distribution of surfactant J between solid and liquid phases. (b) Estimated sorptive capacities of phosphate rock for different types of surfactants



phosphate rock suspensions has been made by measuring the relative surface tension of the surfactant solutions before and after contact with the rock by the capillary-rise method. Anionic, non-ionic, and cationic surfactants were adsorbed by the rock in varying amounts depending on the type and molecular weight of the surfactant, the particle size, and the previous treatment of the rock with flotation reagents. The cationic surfactants were more readily adsorbed by the rock than the anionic, or the nonionic types. Nonfloated rocks from different sources had approximately the same adsorptive capacity for various surfactants. Observations on the adsorption phenomena confirm previously observed evidence of the presence of the anionic type of flotation agent in single-floated, and the cationic type in double-floated phosphate rocks.

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