

## Surfactants in Fertilizers

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Surface active agent adsorbed on the equipment used in measuring the surface tension of aqueous surfactant solutions was found to be a source of error in attempting to determine the extent of surfactant adsorption on the surface of suspended phosphate rock particles. The equipment used to measure surface tension of solutions by the drop-weight method was modified to eliminate contact of the solution with a small-bore glass tube and a new procedure based on the change in bubble volume with surface tension was developed. Anionic surfactants were more readily adsorbed on acidic surfaces, while cationic surfactants were more readily adsorbed on basic materials. Acidic surfaces were made hydrophilic by the anionic surfactants and hydrophobic by cationic surfactants. The results were reversed in the case of basic materials.

CERTAIN SURFACTANTS which were added in the acidulation step have been found to enhance the reactivity of washer-pebble phosphate rock with sulfuric acid, but had no appreciable effect on mixtures made with double-floated rock (3-5, 13). The cationic flotation reagent used in the second stage of the flotation process was assumed to be adsorbed on the rock and accounted for the difference in the behavior of floated and nonfloated rock (4). This was later confirmed by demonstrating that all types of surfactants were adsorbed from aqueous surfactant solutions by phosphate rock suspensions (6).

As the cationic reagent was added to float silica and clay residues, it was generally assumed in industry that this reagent was adsorbed mostly by this class of waste materials and that little if any was retained by the phosphate rock. That surfactants, adsorbed on surface tension measuring equipment, introduced errors into the results obtained by different procedures was soon recognized.

The first part of this article describes modifications made in the equipment used for measuring the surface tension of solutions by the drop-weight method and a new procedure based on variation in the size of bubbles with surface

tension of solutions, which was developed to reduce the errors due to adsorption of the anionic- and nonionic-type surfactants on surface tension metering equipment.

In the second part, differences in the amounts of a typical cationic surfactant adsorbed on different types of surfaces and by different kinds of solid materials associated with phosphate rock are described.

The last section covers observations made on a typical sample of commercially floated phosphate rock in comparison with experimental results obtained in this study.

## Evaluation and Modification of Methods for Measuring the Surface Tension of Aqueous Surfactant Solutions

The principal factor responsible for variations in the results of surface tension measurements made by different procedures was found to be the adsorption of surfactants in varying degrees on the walls of volumetric flasks and surface tension measuring equipment. The effects of such adsorption were at least threefold: (1) the reduction of the concentration of surfactant left in the solution, (2) the modification of the character of the surface on which the surfactant was adsorbed, and (3) the alteration of the actual dimensions of metering equipment, such as reducing the diameter of a capillary tube. The

height of the capillary rise of water in contaminated tubes exceeded that of pure water in the uncontaminated tubes by 10 or 15%. In the case of the capillary-rise method, consistent readings could not be obtained until equilibrium had been established between the surfactant in solution and that adsorbed on the walls of the capillary. Oftentimes, this required several hours because of slow diffusion of relatively large molecules up the long and narrow column of solution in the capillary tube. These difficulties and sources of error are not included among those discussed by Harkins (7), but are doubtless respon-

sible for the fact that the capillary-rise method, generally considered the most precise method for single-component systems, is not recommended for solutions. The drop-weight method (generally regarded as better suited for solutions, when long-time effects are not involved) offered little improvement over the capillary-rise method so long as the rate of drop formation was regulated by passing the surfactant solution through a capillary tube. In this case, the chief difficulties appeared to be the reduction of the concentration of the surfactant in solution and in the rate of drop forma-

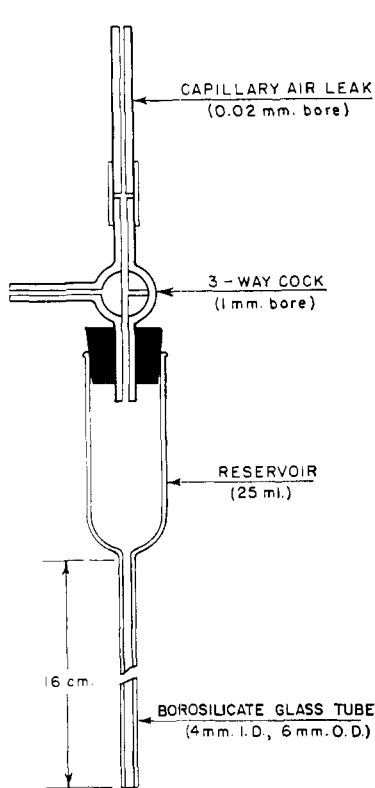


Figure 1. Apparatus for surface tension determination by modified drop-weight method

tion caused by surfactant adsorption on the capillary walls.

The magnitude of the errors caused by surfactant adsorption on solid surfaces varied with the type of surfactant in solution, the physical and chemical characteristics of the solid surface, and the ratio of the surface area to solution volume. Hence, the use of small-bore capillaries was not suitable for surface tension measurements of solutions of long-chain anionic, and nonionic-type surfactants, which have a high affinity for glass surfaces. Investigations herein reported cover a modified drop-weight method and an entirely new procedure, the bubble-volume method, which were designed to overcome most of the difficulties.

#### Modified Drop-Weight Method

The capillary tube for regulating the rate of drop formation was shifted to control the rate of admission of replacement air to the space above the solution in the reservoir as shown in Figure 1. The ratio of glass surface to solution volume in the critical area of the dropping tip was reduced by enlarging the bore of the tube. As a result of these changes in equipment design, errors due to surfactant adsorption on equipment surfaces were greatly reduced.

#### Bubble-Volume Method

As the weights of drops vary with the surface tension of solution, there should

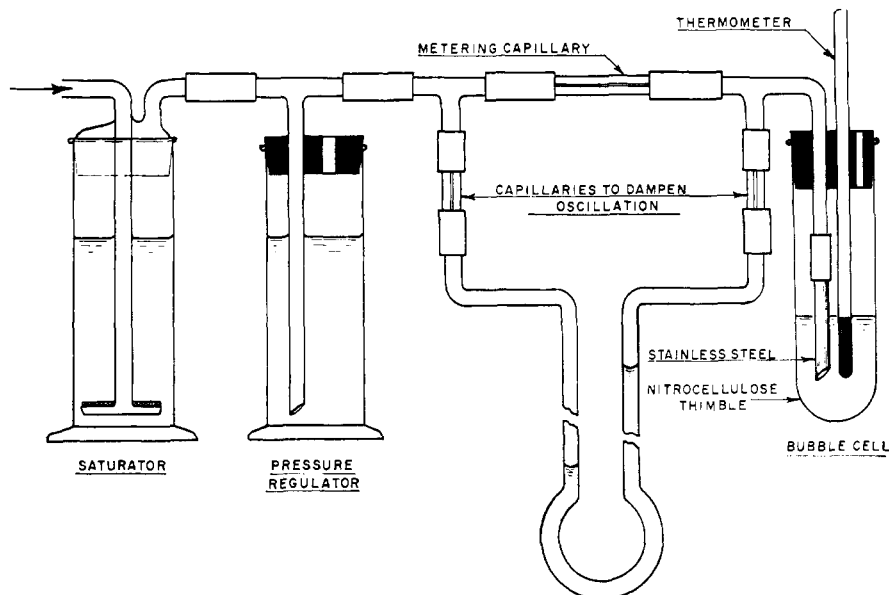


Figure 2. Apparatus for surface tension determination by bubble-volume method

be a corresponding variation in the size of gas bubbles formed beneath the surface of the solution under otherwise uniform conditions. Consequently, there should be a corresponding variation in the length of time required to form a bubble from a stream of air, or other gas, passed at a constant slow rate to a uniform depth below the solution surface. The rate of bubble formation

can easily be measured with the aid of a stop watch. Numerous observations would greatly reduce the probability of error due to false readings. Variations due to adsorption can be easily detected.

The equipment needed to make such measurements (Figure 2) consists of a train made up of a gas saturator, a pressure regulator, a flowmeter, and a

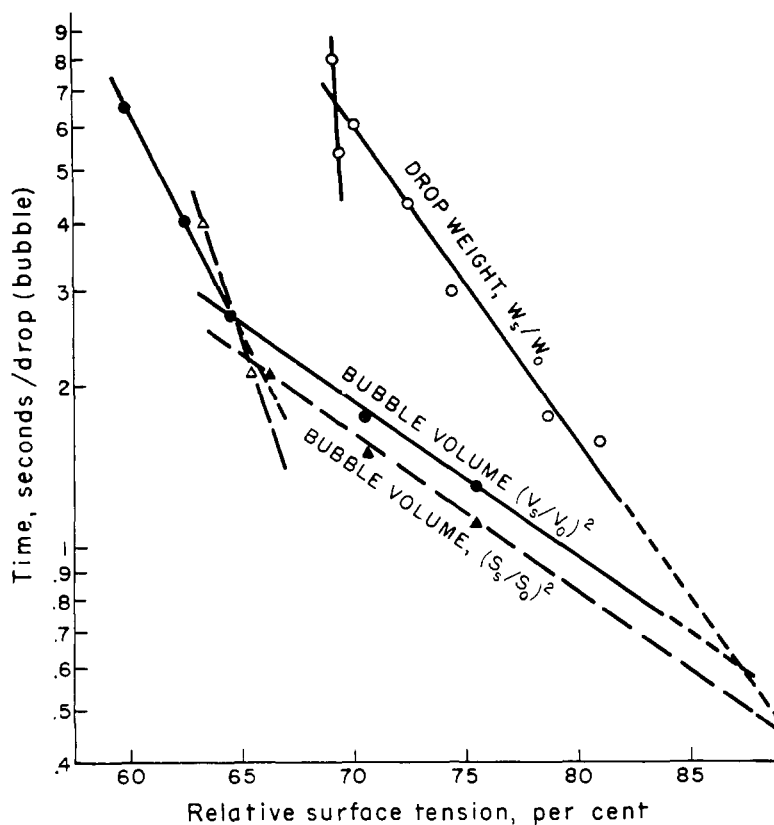


Figure 3. Influence of time of drop and bubble formation on surface tension measurements

**Table I. Surface Tension Measurements of Water Made by Bubble-Volume Method at Various Temperatures**

(Airflow at 25° C. = 1.48 ml./min.)

Temp., ° C.	S = Time, Sec./B	Correction Factors			γ H <sub>2</sub> O, Dynes/Cm.		100 γ <sub>c</sub> /γ <sub>c</sub> , %
		f' <sup>a</sup>	f'' <sup>b</sup>	f = f'f'' <sup>d</sup>	Calcd. <sup>c</sup>	Obsd. <sup>d</sup>	
10.65	4.16	0.9306	1.0150	0.9446	74.17	74.11	99.9
13.33	4.08	.9463	1.0123	.9579	73.78	73.71	99.9
16.17	4.01	.9559	1.0094	.9649	73.36	72.97	99.5
19.43	3.94	.9778	1.0060	.9837	72.87	73.10	100.3
23.20	3.86	.9904	1.0020	.9924	72.29	72.25	99.9
24.67	3.83	.9983	1.0004	.9987	72.07	72.14	100.1
26.57	3.78	1.0029	0.9984	1.0013	71.77	71.38	99.5
27.90	3.75	1.0168	.9969	1.0136	71.56	71.69	100.2
29.30	3.71	1.0252	.9953	1.0204	71.33	71.40	100.1
32.77	3.60	1.0492	.9916	1.0404	70.79	70.64	99.8
35.70	3.52	1.0673	.9883	1.0549	70.32	70.03	99.6
39.03	3.43	1.0955	.9842	1.0782	69.78	69.75	100.0
41.30	3.38	1.1126	.9839	1.0947	69.41	69.78	100.5
43.37	3.29	1.1344	.9794	1.1110	69.06	68.94	99.8
45.80	3.24	1.1525	.9765	1.1254	68.66	68.77	100.2
47.30	3.17	1.1745	.9748	1.1450	68.41	68.46	100.1
49.80	3.09	1.2020	.9727	1.1692	68.12	68.14	100.0

<sup>a</sup> Combined factor for change in gas volume, partial pressure, and density of H<sub>2</sub>O, (f' at 25° C. = 1).

<sup>b</sup> Factor equivalent to square root of change in surface tension.

<sup>c</sup> Calculated from Equation 3 (7).

<sup>d</sup> γ H<sub>2</sub>O (obs) = kf'S' = 18.86f'S' (Equation 4).

bubbling cell. The cell and beveled tip (45°) may be made of glass or other material. A nitrocellulose cell and stainless steel tip were used in the studies herein reported. Of the several materials tested, nitrocellulose and the steel tip seemed to affect the results the least.

**Theoretical Considerations**

Harkins (7) has shown that the weight, W, of the ideal drop is proportional to the surface tension:

$$W = Mg = 2\pi r\gamma \quad (1)$$

He has shown also that the resultant of the cohesive force, or surface tension, γ, may be considered as operating in a plane normal to the force, Mg, tending to detach the drop. As the weight of the pendant drop increases and exceeds the surface tension, a portion of it is pinched off and falls. The weight of the detached portion must equal the

force of surface tension at the point where the break occurs. Consequently, the relative surface tension of the solution must also be directly proportional to the relative weights of the drops,

$$\% RST = 100 W_s/W_o \quad (2)$$

The resultant of forces tending to detach the bubble formed at the 45°-angle tip in the bubble-volume method may be considered as operating in only one direction normal to the surface of the solution. Therefore the buoyancy of the bubble, which is directly proportional to its volume, must be proportional to the square root of the surface tension. Hence, the relative surface tension must be proportional to the square of the relative volume of the bubble and, therefore, to the square of the relative time of formation, if the rate of gas flow is constant and other conditions are uniform. The validity

of this postulate is supported by experimental evidence given in Table I, which shows the time in seconds per bubble of air formed in water as a function of temperature, by a constant flow of air, measured at 25° C. Correction factor f' covers changes in the volume of gas with the changes in temperature, partial vapor pressure, and density of water. Correction factor f'' is the square root of the change in surface tension of water with temperature calculated from the Harkins and Brown (7) equation:

$$\gamma_{H_2O} = 75.680 - 0.138t - 3.56 \times 10^{-4}t^2 + 4.7 \times 10^{-7}t^3 \quad (3)$$

Surface tensions calculated from Equation 3 for the temperature are given in the sixth column. The fifth column shows the combined factors (f'f'' = f<sub>c</sub>) necessary to relate the time in seconds per bubble to the surface tension. The average value of the constant, k, in the equation:

$$\gamma_{H_2O} = k f_c S_o = 18.86 f_c S_o \quad (4)$$

was determined by dividing the surface tension of water by the observed time in seconds (S<sub>o</sub>), multiplied by the factor, f<sub>c</sub>. The average value of k thus found was 18.86 ± 0.04. Deviations from the mean were well within the limits of experimental error and without significant trend with variation in temperature. The observed surface tension, calculated by substituting the derived constant, k = 18.86, in Equation 4 is shown as dynes per centimeter in the seventh column and as percentage of the calculated tension in the last column.

Under normal operating conditions at constant temperature, the thermal factor, f', is equal to 1 and drops out, so that f<sub>c</sub> = f'' and

$$S_o = \gamma_{H_2O}/kfc = k'\sqrt{\gamma_{H_2O}} \quad (5)$$

and

$$\gamma_{H_2O} = k''S_o^2 \quad (6)$$

Comparison of the surface tension of a surfactant solution, γ<sub>s</sub>, with that of pure

**Table II. Variations with Time in Results Obtained by Drop-Weight and Bubble-Volume Methods**

Drop-Weight Method				Bubble-Volume Method							
H <sub>2</sub> O		0.025% solution K		% RST <sup>a</sup> =		H <sub>2</sub> O		0.025% solution K		% RST <sup>b</sup> =	
Sec./D	Mgs/D	Sec./D	Mgs/D	100 W <sub>s</sub> /W <sub>o</sub>	100 S <sub>s</sub> /S <sub>o</sub>	Sec./B	Ml./B	Sec./B	Ml./B	100 (V <sub>s</sub> /V <sub>o</sub> ) <sup>2</sup>	100 (S <sub>s</sub> /S <sub>o</sub> ) <sup>2</sup>
1.07	85.0	0.89	68.8	81.0	83.2	1.13	0.110	0.99	0.096	72.3	76.8
1.75	82.6	1.35	64.9	78.6	77.1	1.30	.104	1.13	.091	75.6	75.6
2.98	81.0	2.26	60.3	74.4	75.8	1.37	.103	1.17	.088	73.8	73.9
4.34	80.7	3.12	58.6	72.5	71.9	1.81	.106	1.52	.089	70.4	70.7
5.36	80.4	3.74	56.0	69.6	69.8	1.95	.103	1.65	.087	71.3	71.6
6.01	79.9	4.21	54.9	70.1	70.0	2.60	.104	2.12	.082	62.3	66.5
6.76	79.9	4.68	56.0	68.6	69.2	2.71	.097	2.19	.078	64.7	65.6
7.37	80.3	5.08	55.0	70.1	68.9	4.97	.095	4.03	.077	65.7	65.8

<sup>a</sup> % RST = 100 W<sub>s</sub>/W<sub>o</sub> = 100 S<sub>s</sub>/S<sub>o</sub>, where W<sub>s</sub> and W<sub>o</sub> represent weights of drops of solution and water, respectively.

<sup>b</sup> % RST = 100 (V<sub>s</sub>/V<sub>o</sub>)<sup>2</sup> = 100 (S<sub>s</sub>/S<sub>o</sub>)<sup>2</sup>, where V<sub>s</sub>, V<sub>o</sub> and S<sub>s</sub>, S<sub>o</sub> represent volume in milliliters, and time in seconds, respectively, per bubble in surfactant solution and in water, respectively.

water,  $\gamma_0$ , to obtain relative surface tensions, is given by:

$$100\% RST = 100 \frac{\gamma_s}{\gamma_0} = 100 \left( \frac{S_s}{S_0} \right)^2 = 100 \left( \frac{V_s}{V_0} \right)^2 \quad (7)$$

### Time Factor in Surface Tension Measurements

Table II shows variations in the weight of drops and in the volume of bubbles with time in seconds allowed for their formation in water and in a 0.025% surfactant K solution. The rate of drop formation was regulated by lengthening or shortening the capillary air leak controlling the flow of replacement air to the solution reservoir (Figure 1). The rate of bubble formation was controlled by varying the differential pressure on the flow meter by means of the pressure regulator (Figure 2).

Relative surface tensions of the 0.025% surfactant K solution, calculated from the data of Table II, are compared in Figure 3. Both the drop-weight and

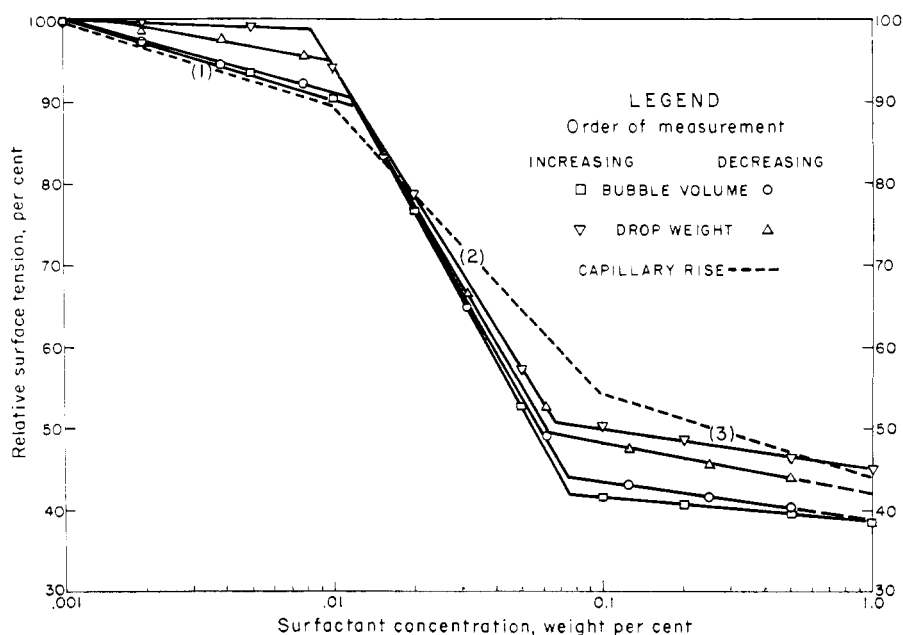


Figure 4. Comparison of surface tension measurements of aqueous solutions of anionic surfactant K made by different procedures

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	Alkylaryl sodium sulfonate, 37%
L	Alkylaryl sulfonic acid (unneutralized), 85%
M	Alkylaryl sodium sulfonate, 40%
N	Alkylaryl sodium sulfonate, 85%
O	Alkylaryl 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	Alkylphenoxy polyoxyethylene ethanol, 100%
Cationic	
I	Alkyl dimethyl benzyl ammonium chloride, 50%
J	Lauryl dimethylamine oxide, 20%
P	tert-Alkyl primary amine acetate
Q	Rosinamine-ethylene oxide condensation product
R	Imidazolium hydrochloride compound
U	C <sub>16</sub> and C <sub>18</sub> amines
V	C <sub>16</sub> and C <sub>18</sub> amine acetates
W	Amine acetate flotation reagent, commercial <sup>a</sup>

<sup>a</sup> Kerosine-water emulsion of C<sub>16</sub> and C<sub>18</sub> amine acetates.

Table IV. Derived Constants for General Equation 9<sup>a</sup>

Gas	Bubbles/Minute		Milliliters/Minute	
	a	b	a	b
H <sub>2</sub>	-3.7970	5.9887	-0.5523	0.6474
N <sub>2</sub>	-1.6184	3.5646	-0.1637	0.3514
Air	-1.3046	3.3822	-0.1508	0.3322
O <sub>2</sub>	-1.6525	3.1270	-0.1364	0.2964
CO <sub>2</sub>	-0.2342	3.6957	-0.2938	0.2922

<sup>a</sup>  $y = a + bx$ , where  $x = \text{cm. H}_2\text{O differential (Equation 9)}$ .

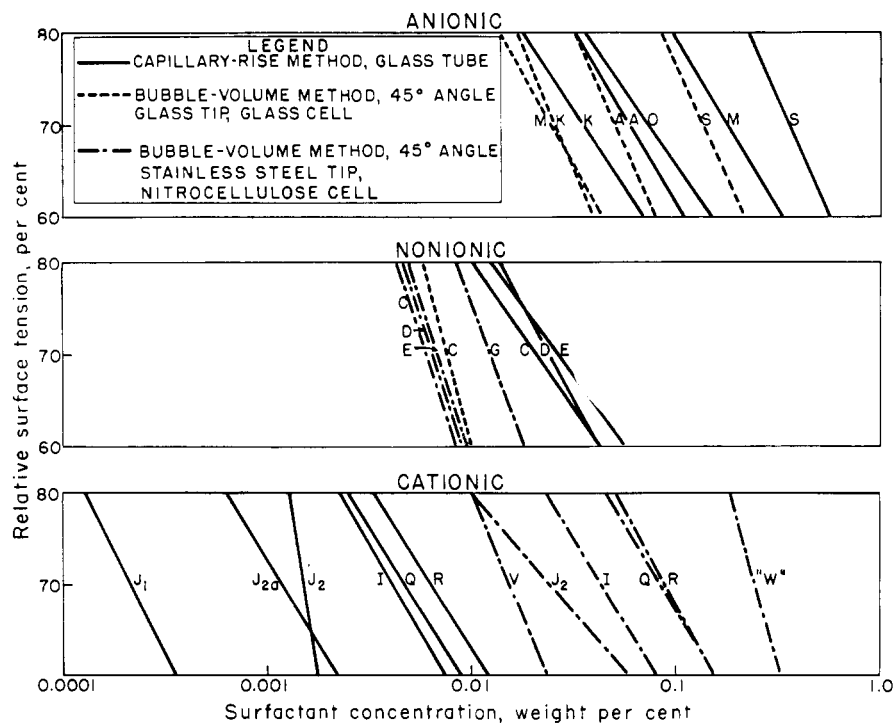


Figure 5. Comparison of results in the range 60 to 80% relative surface tension measurements of aqueous solutions of different surfactants made by bubble-volume and capillary-rise methods

bubble-volume methods will show increasing surface tension readings with decreasing time in seconds per drop or bubble. Extrapolation of the straight lines back toward zero time indicates that 100% relative surface tension readings would have been obtained at 0.1 to 0.2 second per drop or bubble, indicating that the changes resulting in surface tension lowering do not occur in the body of the solution, but develop with time at the surface boundary.

### Evaluation of Methods

A comparison of results obtained by the bubble-volume, the modified drop-weight, and the capillary-rise methods is shown in Figure 4 for a typical anionic surfactant (surfactant K, Table III). The curves all break into three segments, each of which may be expressed by the general equation:

$$\% RST = a + b \log c \quad (8)$$

where  $c$  represents the weight per cent of surfactant in solution. The difference between the results obtained by the several methods are attributable, prin-

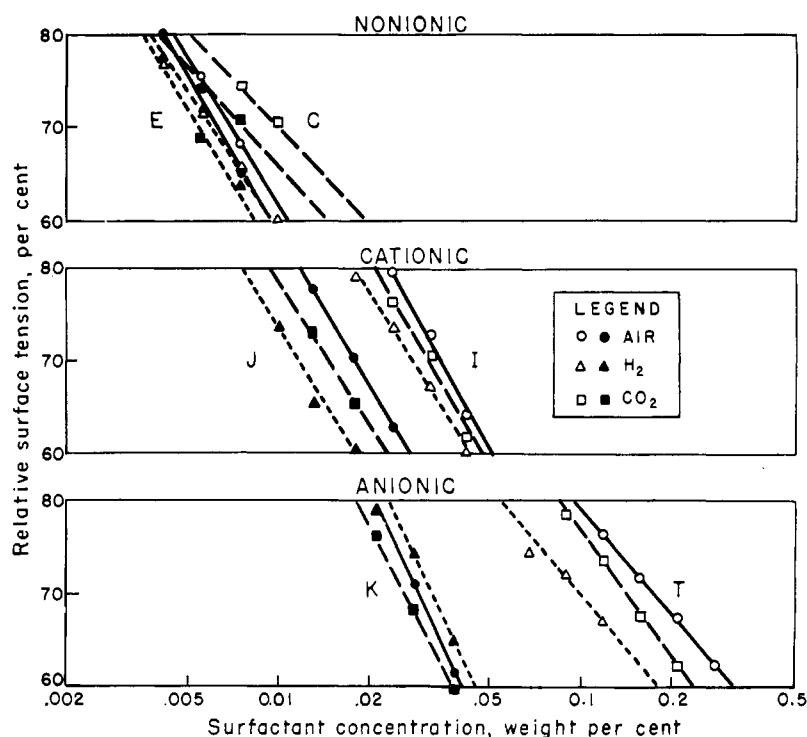


Figure 6. Influence of gas composition on relative surface tension measurements made by bubble-volume method

Table V. Comparative Data on Various Gases for 5 Cm. Differential

(Standard conditions of 5 cm. of H<sub>2</sub>O pressure differential)

Gas	Mol. Wt.	Relative Buoyancy	B/Min.	MI./Min.	V <sub>0</sub> = MI./B	S <sub>0</sub> = Sec./B	% RST <sup>a</sup>
H <sub>2</sub>	2	1.0004	26.15	2.68	0.1027	2.295	112.6
N <sub>2</sub>	28	1.0000	16.20	1.59	.0983	3.703	103.1
Air	28.8	1.0000	15.61	1.51	.0968	3.845	100.0
O <sub>2</sub>	32	0.9998	13.98	1.35	.0962	4.291	98.7
CO <sub>2</sub>	44	0.9994	18.71	1.17	.0624	3.206	41.5

<sup>a</sup> % RST = Relative buoyancy  $\times (V_0/V_a)^2$ , where  $V_0$  and  $V_a$  represent bubble volumes of gas and air, respectively, in water.

Table VI. Time in Seconds per Bubble of Different Gases in Various Concentrations of Surfactant Solutions at 25° C.

(Pressure differential, 5 cm. H<sub>2</sub>O)

Surfactant Concentration, %	Surfactant C					Surfactant E				
	CO <sub>2</sub> 3.21	O <sub>2</sub> 4.29	Air 3.85	N <sub>2</sub> 3.70	H <sub>2</sub> 2.30	CO <sub>2</sub> 3.21	O <sub>2</sub> 4.29	Air 3.85	N <sub>2</sub> 3.70	H <sub>2</sub> 2.30
0.004	2.98	3.91	3.45	3.35	2.01	2.88	3.76	3.44	3.27	2.02
.006	2.88	3.76	3.34	3.18	1.94	2.76	3.62	3.19	3.12	1.95
.008	2.77	3.45	3.17	3.03	1.86	2.60	3.48	3.10	2.96	1.83
.010	2.60	3.32	2.96	2.83	1.78	2.47	3.19	2.90	2.81	1.72
.013	2.43	3.12	2.77	2.63	1.66	2.33	2.95	2.70	2.62	1.60
	Surfactant I					Surfactant J				
.013	2.99	3.91	3.67	3.35	2.10	2.74	3.37	3.39	2.96	1.86
.018	2.88	3.76	3.58	3.24	2.04	2.59	3.22	3.23	2.80	1.79
.024	2.80	3.64	3.43	3.14	1.97	2.53	3.06	3.05	2.71	1.72
.032	2.69	3.45	3.28	3.08	1.88	2.42	2.95	2.88	2.57	1.64
.042	2.52	3.29	3.08	2.91	1.78	2.35	2.85	2.75	2.51	1.58
	Surfactant K					Surfactant T				
.021	2.80	3.82	3.45	3.17	2.04	...	4.26	...	...	2.18
.050	2.38	3.22	2.83	2.65	1.74	3.03	3.93	3.67	3.48	2.07
.067	2.24	3.14	2.58	2.50	1.66	2.98	3.81	3.56	3.35	1.98
.090	2.19	2.95	2.58	2.45	1.61	2.84	3.72	3.47	3.22	1.95
.119	2.12	2.94	2.55	2.38	1.56	2.75	3.60	3.36	3.12	1.88
.211	2.07	2.79	2.45	2.32	1.52	2.53	3.33	3.16	2.84	1.78

cipally, to variations in the amounts of surfactant adsorbed on equipment surfaces.

Evaluation of the several methods (discussed in the second part) indicated that the bubble-volume method introduced less error due to surfactant adsorption on equipment surfaces, in the cases of the anionic and nonionic types (Figure 5), but not in the case of the cationic type, which showed little, if any, affinity for glass. The results obtained by the different methods of anionic surfactant K solution (Figure 4) are all in substantial agreement in the region of 0.01%, which coincided with the concentration in equilibrium with the monolayer as indicated by the intercept of segments 1 and 2 of the adsorption curves.

### Influence of Gas Composition

Harkins and others (72) have shown that the interfacial tensions of two immiscible liquids—e.g., mercury and water—are each affected by the chemical properties of the other. Likewise, the adsorption of surfactants from aqueous solution is affected by the chemical properties of the solid adsorbent as well as by the chemical composition of the surfactant in solution. The surface tensions of liquids are also modified by substances in solution, including dissolved gases, but there is a question as to the effect of gas composition on surface tension measurements of aqueous surfactant solutions as made by the bubble-volume method. Conceivably, the ori-

entation of surfactant molecules in the surface layer could be affected by the chemical composition of the gas in the bubble. The surface tension, in turn, might be influenced by the molecular arrangement in the surface layer at the gas-liquid interface (15). To test this possibility, surface tension measurements were made on varying concentrations of aqueous solutions of six surfactants including two each of the anionic, non-ionic, and cationic types (surfactants C, E, I, J, K, and T, Table III), using air, oxygen, nitrogen, hydrogen, and carbon dioxide as bubble forming gases.

Constants for the general equation:

$$y = a + bx \quad (9)$$

where  $y$  equals the rate of gas flow in bubbles (or in milliliters) per minute and  $x$  equals the scale reading for the pressure

differential in centimeters of water, derived by the method of least squares, are given in Table III. From these constants the number of bubbles per minute, (B/min.), the milliliters of gas per minute, (ml./min.), the volume in milliliters per bubble, (ml./B), and time in seconds per bubble (sec./B) for normal operation at a constant differential of 5 cm. of water were calculated as shown in Table V. The relative buoyancies of the gases in water, calculated from their several densities at 25° C., are given and the relative surface tension (% RST) of the aqueous solutions of these gases, as compared with air, is shown. A comparison of the % RST figures with the molecular weights of the gases shows that the relative surface tension of the water is inversely proportional to the molecular weight and to the solu-

bility of the gas with which it is in contact.

Table VI shows the time in seconds per bubble for the different gases when passed at constant rates under normal conditions of 5 cm. differential pressure on the flowmeter into various concentrations of the several surfactant solutions. Each recorded reading is an average of three or more observations that did not differ by more than 1%. Relative surface tensions for air, hydrogen, and carbon dioxide, calculated from the time in seconds,  $S_s$  (given in the body of the table) and  $S_o$  (shown at the head of each column) according to Equation 6, are shown in Figure 6. Graphical representation in the latter was limited to the range, 60 to 80% RST, to facilitate comparison of the results in a single graph.

## Influence of Adsorbed Surface Active Agents on the Physical and Chemical Properties of the Constituents of Phosphate Ore

### Materials

Table III lists the surfactants, and Table VII, the solid materials included in this study. Surfactants A to T, inclusive, were used in studies previously reported (6). Reagent W is

**Table VII. Test Adsorbents**

Lot No.	Description
2217	Fused phosphate rock, Commercial grade <sup>a</sup>
2335	Pembroke clay concentrate, experimental <sup>b</sup>
3169	Phosphate rock, Florida washer- pebble, commercial grind <sup>c</sup>
3172	Phosphate rock, double-floated concentrate, commercial grind <sup>c</sup>
3180	Phosphate rock, double-floated concentrate, unground <sup>c</sup>
22882	Limestone, agricultural, commercial grade
...	Quartz sand, commercial grind, acid-washed
...	Glaucosil, silica residue of New Jersey greensand, experimental (17)

<sup>a</sup> Produced by TVA.

<sup>b</sup> Pembroke Chemical Corp., Pembroke, Fla. (17).

<sup>c</sup> Screen Analysis of phosphate rock:

Lot No.	Weight % Passing				
	Dry Screen				Wet Screen
	6- mesh	100- mesh	150- mesh	200- mesh	
3169	...	84.0	71.0	57.2	66.8
3172	...	86.0	74.7	54.3	67.3
3180	90.0	6.0	...	...	...

widely used commercially in the ore dressing of phosphate rock (7). It consists of a kerosine-water emulsion of the slightly water-soluble amine acetates of the C<sub>16</sub> and C<sub>18</sub> aliphatic hydrocarbons, of which surfactants U and V are the amine and the amine acetate salts, respectively. In addition to these materials, samples of the flotation cell effluent water and the commercially treated phosphate rock concentrate were examined and the results were compared with those obtained with other surfactants in this study.

Of the materials listed in Table VII, phosphate rocks 3169, 3172, and 3180 were included in investigations previously reported (6). Fused rock 2217 was selected to provide a vitreous surface without pronounced change in chemical composition. Pembroke clay 2335 represents that class of colloidal clay material usually associated with phosphate ore that is separated by flotation. Number 22882 was a typical commercial agricultural limestone. Glaucosil, the acid-insoluble silica residue of New Jersey greensand (17) was chosen to illustrate the class of porous materials having large internal, and relatively small external surface areas. Quartz sand is a common impurity of phosphate rock.

### Procedure

The solid materials were fractionated by screening them through Tyler Series screens Nos. 20, 35, 65, 150, and 270, the diameter of the openings of which are 0.833, 0.417, 0.208, 0.104, and 0.053

mm., respectively. Assuming a uniform distribution of sizes in each size class and a constant ratio between the actual outer surface and the geometric surface over the entire range of particle sizes, then the specific outer surface as well as the geometric surface areas in square meters per kg. of rock would be in the proportions of 1:2:4:8.

Surfactant adsorptions on the surfaces of the solid suspensions were determined by differences between the amounts of surfactants required to give relative surface tension lowerings to 70% (measured by the capillary-rise method) in the presence, and absence, of the solid suspensions, according to a procedure previously described (6).

Observations on the hydrophobic, or hydrophilic, nature of surfactant-coated solids and on the phenomena of bubble attachment were made. These qualities were largely, if not completely, determined by the type of surfactant and by the nature of the solid surface on which it was adsorbed.

The influence of surfactants on the rate of sedimentation of colloidal Pembroke clay suspensions (as shown in Figure 9) was measured by the procedure of shaking a weighed quantity of dry clay with equal volumes of 0.01%, by weight, of the various surfactant solutions or an equal volume of distilled water, to serve as a control. Eighteen hours later samples were taken with a pipet at 5 cm. below the surface. The relative degree of clarification was determined by light transmittance through these samples. These measurements were made with a Bausch and Lomb

spectrophotometer using a wave length of 1000 m $\mu$ . Transmittance through the freshly mixed control sample was taken as zero and through distilled water as 100% on the graphed scale.

### Experimental Results

In Figure 5, the results obtained by different methods of measuring the surface tension of aqueous solutions of various types of surfactants are compared. Only those portions of the relative surface tension curves falling in the middle range, 60 to 80%, are shown. This limitation was made in order to facilitate comparison and to focus attention on differences in the region where comparisons were ordinarily made.

Based on this comparison cationic surfactant J<sub>1</sub> was selected for a more extensive study of adsorption on the surface of the solid materials listed in Table VII. For this purpose, an additional supply of the reagent, J<sub>2</sub>, was secured from the producers. The new supply did not match the old one. The new lot was evidently more highly polymerized (16) or was made from higher molecular weight stock than the old one, as a considerably higher weight concentration of it in aqueous solution was required to produce the same degree of surface tension lowering. An attempt to depolymerize it by heating a 1.0% solution to the boiling point for several hours produced the change shown by curve J<sub>2</sub>. Despite these obvious differ-

ences, the amounts of surfactants adsorbed on ground phosphate rock No. 3169 at various surface tension readings were nearly the same (Table VIII).

The dependence of the amounts of cationic surfactant J<sub>1</sub> adsorbed by suspensions of different solids on the estimated geometric surface area of the various screen fractions, is shown in Figure 7. Figure 8 shows the dependence of the amounts of surfactant J<sub>1</sub> adsorbed by phosphate rock on the concentration of the surfactant in solution in sensible equilibrium with the rock suspensions. The influence of the various surfactants (Table III) on the rate of sedimentation of colloidal Pembroke clay suspensions is shown in Figure 9. Ionization as measured by the electrical conductance of surfactant solutions showed no correlation with the rate of sedimentation of the clay.

### General Observations

In addition to the quantitative measurements shown in Figures 7 to 9 inclusive, other pertinent observations of a qualitative nature included numerous tests for bubble attachment, made by shaking the solids with surfactant solutions in test tubes. Basic materials, including limestone and phosphate rock, could be floated with anionic-type surfactants. The acidic materials, such as fused rock, quartz sand, and ground glass, could be floated with cationic surfactants. Thus both anionic and

cationic surfactants may be considered as flotation agents for minerals of different composition or surface condition.

Basic materials (limestone and phosphate rock) surface-coated with anionic-type surfactants became hydrophobic, as did acidic materials (glass and silica-fused phosphate rock) surface-coated with cationic surfactants. By reversing the order of application, the solid surfaces could be made hydrophilic. Thus, basic materials like limestone and phosphate rock surface-coated with cationic surfactants were easily wetted and tended to repel air bubbles in aqueous suspensions. The same is true of acidic materials surface-coated with anionic surfactants. Consequently, both anionic- and cationic-type surfactants may also be considered as depressant reagents for minerals of different surface characteristics. Therefore, what constitutes either a flotation or a depressant reagent depends upon the physical and chemical nature of the solid in question as well as on the type of reagent. Thus, the same compound may be either a flotation reagent or a depressant, depending upon whether the surface of the solid to be treated is acidic or basic in character.

### Discussion

Because of the influence exerted by different chemical substances on phenomena such as interfacial tension (12) and surfactant adsorption on solid

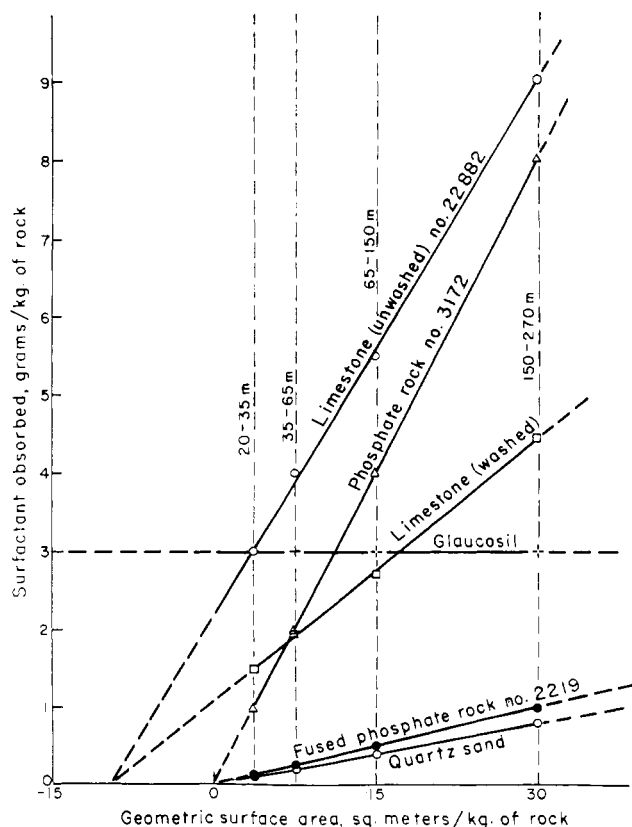


Figure 7. Surfactant J adsorption on surfaces of different types of solids in aqueous suspension

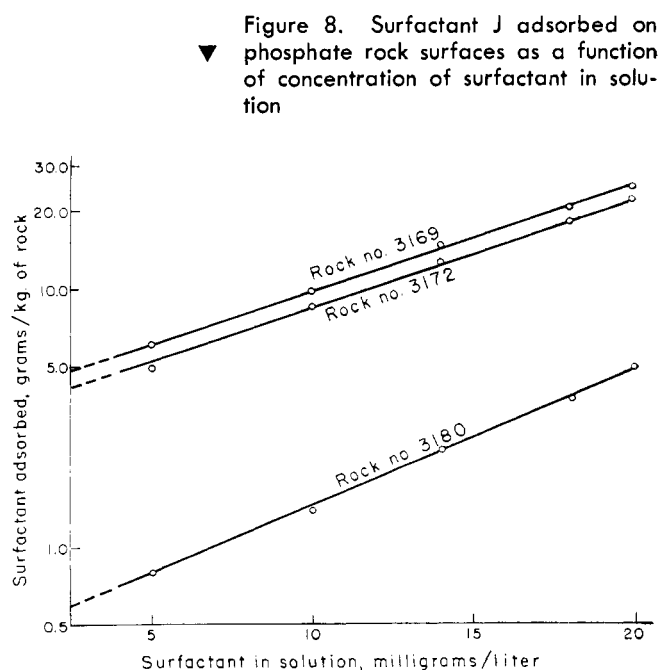


Figure 8. Surfactant J adsorbed on phosphate rock surfaces as a function of concentration of surfactant in solution

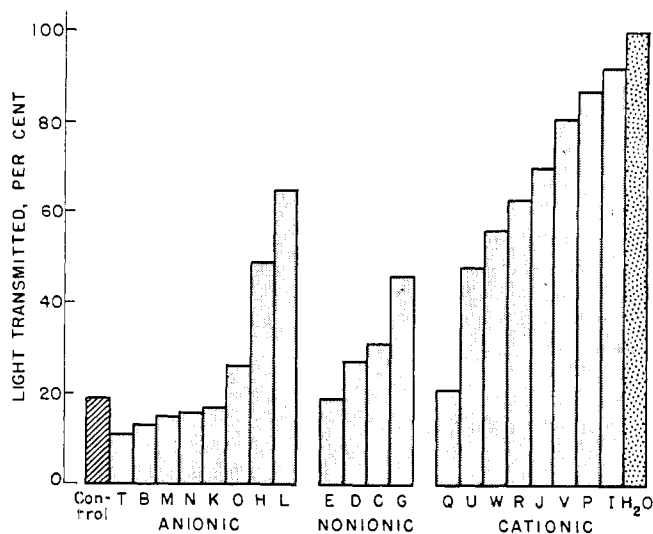


Figure 9. Influence of various surfactants on rate of sedimentation of colloidal Pembroke clay

surfaces, surface tension measurements made by the bubble-volume method might be expected to be affected by the chemical composition of the gas in the bubble.

Variations similar to those observed in the relative surface tension of the 0.025% surfactant K solution with time (shown in Figure 3), have been noted by others (8, 9, 12). That variations in the weight of drops of water and in the volume of air bubbles in water (Table II) occur with time, indicates that the phenomenon is independent of the solute. When taken together with a like trend in the surfactant solution, the only reasonable interpretation for these phenomena seems to be that the intermolecular rearrangement produced by the discontinuity of phase at the interface is a function of time. This shows that surface tension is not a colligative property of the solution, as it does not exist apart from the surface.

The capillary-rise method for measuring surface tension (Figure 5) requires considerably higher concentrations of anionic surfactants than the bubble-

volume method for equal surface tension lowering. The difference between results obtained by the two methods is attributable to the greater glass surface area exposed per unit volume of solution by the capillary-rise method and to the greater affinity between glass and the anionic-type surfactants. The same is true of the nonionic-type surfactants. This conclusion is supported by the shift to still lower surfactant concentration, on changing from a glass cell and tip to a nitrocellulose cell and stainless steel tip for the bubble-volume method. With the cationic-type of surfactants, the situation is completely reversed and the capillary-rise method requires far lower concentrations of surfactants than the bubble-volume method for equal surface tension lowering. This reversal in the relative position of the two methods for surface tension measurements is attributable to the lack of attraction between the glass surface and the organic cations of the surfactant. This is illustrated in Figure 7 by the low coefficients of adsorption of quartz sand and fused phosphate rock 2219 for cationic surfactant J<sub>1</sub>.

The pronounced difference between the adsorption coefficient of Florida pebble rock 3172 and fused rock 2219 (Figure 7) is largely attributable to a change in the character of the surface produced by fusion of the rock. If the alteration is only physical in character, it is evident that fusion produced an eightfold reduction in the external surface area of the rock. A reduction in total surface area of this magnitude would not be considered unlikely if large internal surface areas were involved in the adsorption. However, as the curves for quartz sand and fused and nonfused phosphate rocks (Figure 7) are alike, in

that all pass through zero geometric surface area, the amount of surfactant adsorbed is directly proportional to the external surface area of these materials only.

The glassy surface of calcium silicate formed by the fusion of calcium carbonate and silica in phosphate rock, like that of ordinary glass (Figure 5), has little affinity for the cationic-type surfactants by which both fused rock and quartz sand were floated. As the non-fused Florida rock did not show evidence of bubble attachment when treated with the cationic type of surfactants, the change produced by fusion was more chemical than physical.

The difference between surfactant adsorption on internal and external surfaces is illustrated by a comparison of the adsorption curves for glaucosil and quartz sand in Figure 7. In the case of glaucosil, substantially all of the surface area was internal (17). Fractionating this material into different screen sizes was analogous to chopping a sponge into small bits. No appreciable change in the total surface area was effected by so doing. Consequently, there was no appreciable difference in the amounts of surfactant adsorbed per unit weight of the different screen fractions. Assuming that glaucosil and quartz sand have the same coefficient of adsorption, an estimate of the total surface area of the glaucosil would be at least 112.5 square meters per kg. ( $3 \times 30/0.8$ ), equal to that of silt (2).

Differences in the amounts of surfactant J<sub>1</sub> adsorbed on phosphate rocks 3169, 3172, and 3180 (Figure 8) are attributable to differences in surface areas and to the presence of flotation reagent on rocks 3172 and 3180. Rock 3172 is the commercially ground double-floated rock 3180. The only difference between these two is that produced by grinding (footnote c, Table VII) (6). Roughly estimated, this would amount to a six- to eightfold increase in geometric surface area, which corresponds with the increase in the amount of surfactant adsorbed in equilibrium with 2 mg. of surfactant per liter of solution (Figure 8), which is in the region of the monolayer, where measurements were made for the data shown in Figure 7.

Rock 3169 is a commercial grind of washer-pebble rock of about the same screen analysis as rock 3172 (6). The most significant difference between these two is the presence of a small amount of cationic-flotation reagent (surfactant W, Table III) in the double-floated concentrate (rocks 3172 and 3180, Table VII). The presence of this reagent slightly reduced the capacity of rock 3172 for adsorbing more of the cationic type, but increased its capacity for the anionic type (6). These observations confirm the conclusions drawn from the data of

Table VIII. Differences between Lots of Surfactant J

Solution Tension, % RST	Surfactant J <sub>1</sub>		Surfactant J <sub>2</sub>	
	Mg./l. <sup>a</sup>	G./kg. <sup>b</sup>	Mg./l. <sup>a</sup>	G./kg. <sup>b</sup>
90	1.1	3.80	9.2	3.98
80	1.3	3.80	13.0	3.98
70	1.9	4.16	15.8	4.37
60	3.6	5.19	18.0	5.46
50	7.2	7.79	23.0	8.15

<sup>a</sup> Milligrams of surfactant per liter of aqueous solution.

<sup>b</sup> Grams of surfactant adsorbed per kilogram of rock 3169.



Figure 7 in that the surface involved in the adsorption of cationic surfactant J<sub>1</sub> on phosphate rock 3172 was external only and the correlation between the effective surface area and the calculated geometric area was very close.

Observations of interest concerning surfactant adsorption on limestone include: (a) its relatively high coefficient of adsorption for the cationic type of surfactant; (b) that the amount of surfactant adsorbed by the dust-coated unwashed limestone was double the amount adsorbed by the dust-free washed material; and (c) that both the washed and the unwashed samples adsorbed surfactant equivalent to about 10 square meters of surface area per kg. of rock that cannot be correlated with the geometric surface. The latter may be attributed to surfactant adsorption on the walls of cracks and crevices in the limestone that are too small to be affected by the process of screen fractionation. Surfaces of a like nature, but of a higher order of magnitude, were observed by Love and Whittaker (74) using other modes of measurement on similar limestone samples.

The difference between the washed and the unwashed limestone suggests that the dust particles, which carry electrostatic charges opposite to those on the gross particles, are uniformly distributed over the surface, and have a total area equal to that of the gross particles, including the cracks and crevices. When immersed, the charged particles are neutralized by hydrogen and hydroxyl ions derived from water and become alike in their adsorptive capacities for the surfactant. In any event, here is a striking confirmation of the need for wet screening of finely ground materials to remove the dust electrostatically held on the surface of larger particles.

That both anionic and cationic surfactants behave more or less alike on the sedimentation rate of Pembroke clay (Figure 9), in that some (including nonionics) promote sedimentation while others do not, may be explained by the amphoteric nature of the clay. The results shown in Figure 9 illustrate differences between surfactants of the same ionic type. Anionic surfactants T, B, M, N, and K are all sodium salts of sulfonic acids, of which surfactant K is the sodium salt of the unneutralized sulfonic acid, L. The neutralization of L to produce K greatly reduced the capacity of the original acid to cause flocculation and sedimentation of the clay. Such phenomena give some clarification as to the nature of the bond between the solid surface and the surfactant adsorbed thereon. To quote from Bayer (2),

... flocculation of clays is intimately related to the potential of the

particle and the magnitude of the potential increases with the ease with which an ion is exchanged. It should be obvious, therefore, that flocculation is closely associated with exchange reactions.

If the sorption phenomena herein described are primarily due to chemisorption, as appears to be the case, then the physical and chemical properties of the solid surface, as well as the surfactant, must be considered as factors affecting the distribution of the surfactant adsorbed thereon. Modification of the electrostatic charge or surface potential by the surfactant adsorbed thereon then becomes the primary function of flotation reagents. The cationic surfactant used to float siliceous material from phosphate rock is almost completely adsorbed, not on the silica or siliceous material, but on the basic phosphate rock by virtue not only of its greater adsorption coefficient, but also of the preponderance of the rock in the flotation-cell feed.

### Commercially Floated Rock

The presence of kerosine in the commercial reagent W complicates the picture in so far as the action of cationic amine acetate is concerned. However, the amine acetate (surfactant V, Table III) behaved in every essential respect like the other cationic surfactants, except as to its limited solubility in water (about 0.10%).

The sample of double-floated concentrate, still wet when opened at the laboratory, smelled strongly of kerosine, while the effluent water from the flotation cell had scarcely any odor of kerosine. Measurements of the tension of the effluent water were equal to those of distilled water, showing that there was no evidence of surfactant remaining in solution. On drying in air at room temperature, the freshly dried rock retained a strong odor of kerosine. The surface of the rock was also decidedly hydrophobic, as was evidenced by drops of water standing up on the surface of the rock pile. The water-drop test was repeated a few weeks later, after the odor of kerosine had disappeared, and the water readily spread out and wetted the surface of the rock, as it should have from the nature of the surfactant absorbed thereon.

Evidently the kerosine was used primarily as a vehicle to increase the solubility of the surfactant in the oil-water mixture. Its adsorption along with the surfactant on the surface of the rock was responsible for the temporary hydrophobic quality of the freshly dried rock surface. It may also have enhanced the floatability of the siliceous material,

but it had no significant effect on the flotation of phosphate rock, as the rock was not floated in this stage of the ore dressing process (7). Hence, flotation, and therefore bubble attachment, does not depend on a hydrophobic surface (70), as is generally presumed. The two phenomena are usually concomitant, but not interdependent.

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