The Effect of Water Hardness on the Solubilizing Activity of Linear Alkylbenzene Sulfonate

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Abstract

The behavior of linear alkylbenzene sulfonate in hard water has been studied by solubilization, transmittance and pH. Maximum solubilization is reported at specific water hardnesses on the basis of the change in the micellar properties of the detergent. The water hardness at maximum solubilization increases as the concentration of the detergent or of sodium tripolyphosphate (STPP), sodium nitrilo triacetic acid (NTA) or sodium ethylene diamine tetra acetic acid (EDTA) increases, while it decreases with an increase in the alkyl chain length of the detergent. A linear relationship between the detergent concentration and the water hardness at maximum solubilization or transmittance was found. It seems that the effect of STPP, NTA and EDTA on solubilization of anionic detergent was mainly due to water softening.

Introduction

The mechanism of detergency may be regarded as consisting of emulsification, solubilization and other physico-chemical actions of detergents. In previous papers it was reported that maximum soil removal with an anionic detergent was obtained at the same water hardness, depending on the soil, detergent and concentrations of detergent and sequestering agent (1–3). Foam stability also showed a maximum value at the same water hardness using sodium dodecylbenzene sulfonate (4). It can be considered that these phenomena are the results of a change in the physico-chemical properties of detergents in hard water.

In recent years, a number of workers (5–7) have investigated the effect of water hardness on the solubilizing activity of anionic detergents, and found maximum values at certain hardnesses. It was suggested that solubilization behavior in hard water is an important factor in understanding the fundamental behavior of anionic detergents in soil removal.

In this work, the effect of water hardness on the solubilization of detergents was studied.

TABLE I
Isomer Distribution and cmc of Na-LAS

Carbon No.[a]	Isomer distribution (wt%) 2γ	3γ	4γ	5γ	6γ 7γ	cmc (wt%)
10 (Na-DBS)	39.72	23.59	19.16	17.53		0.141
13 (Na-TrDBS)	33.85	20.48	13.86	13.76	18.05	0.018
14 (Na-TeDBS)	31.81	18.03	12.91	14.26	22.99	0.009

[a] Alkyl chain length.

Experimental Procedures

Materials

Sodium linear alkylbenzene sulfonate (Na-LAS) was purified by extraction with ethyl alcohol and petroleum ether. Its isomer distribution and critical micelle concentration (cmc, determined from the surface tension-concentration curve using the du Noüy method at 25 C) are given in Table I.

Sodium tripolyphosphate (STPP, chemical grade) and sodium ethylene diamine tetra acetic acid (EDTA, reagent grade) were obtained from the Wako Junyaku Co., Japan. Sodium nitrilo triacetic acid (NTA, reagent grade) was obtained from the Tokyo Kasei Kogyo Co., Japan.

Yellow-OB (reagent grade) was purified by crystalization with ethyl alcohol-water 2:1.

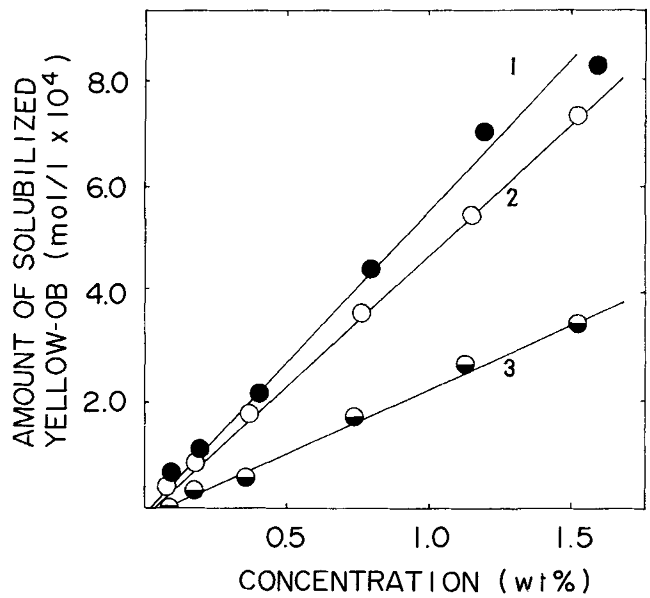

FIG. 1. The effect of the concentration of Na-LAS on solubilization. Na-TeDBS (1), Na-TrDBS (2), Na-DBS (3).

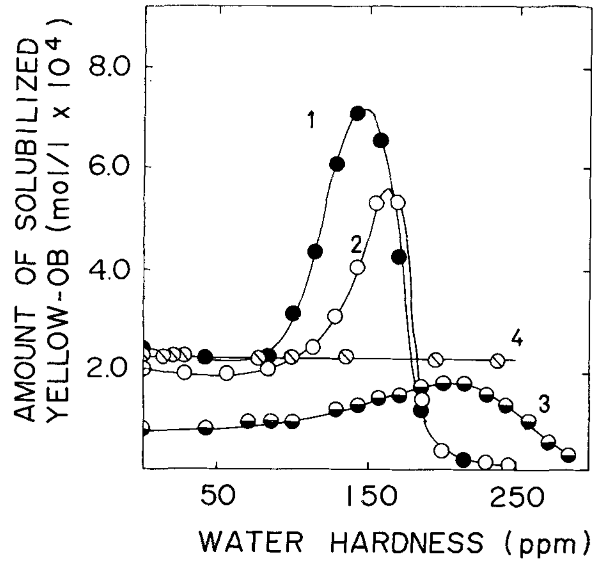

FIG. 2. The effect of the water hardness on solubilization. The concentration of Na-LAS is 0.4 wt%, Na-TeDBS (1), Na-TrDBS (2), Na-DBS (3). The concentration of PNE-10 (commercial material, Kao Soap Co., Ltd.) is 0.1 wt% (4).

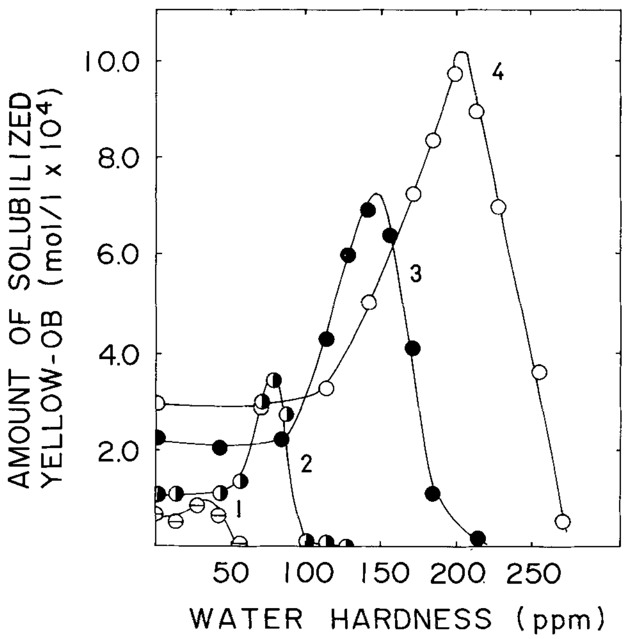

FIG. 3. The effect of the concentration of Na-TeDBS on solubilization in hard water. The concentration of Na-TeDBS is 0.1 wt% (1), 0.2 wt% (2), 0.4 wt% (3), 0.6 wt% (4).

The hard water was prepared from ion-exchange water using calcium chloride (reagent grade), and the calcium content was determined by EDTA titration.

Method

Solubilization was determined as follows. A test tube containing 10 ml of detergent solution with various water hardness and appropriate amounts of Yellow-OB was immersed in a thermostat at 30 ± 0.1 C and shaken for 16 hr. After equilibrium was attained, the unsolubilized Yellow-OB was separated with an ultracentrifuge (5,000 rpm, 10 min). Solubilized Yellow-OB solution was diluted by ethyl alcohol to a final concentration of ethyl alcohol-water 2:1. Then the optical density of the solution was measured at 447 mμ using a spectrophotometer (Hitachi Co.). The amount of solubilized Yellow-OB was calculated from the difference in the optical density before and after solubilization.

The transmittance and pH were determined using a spectrophotometer and pH meter at 30 C (Hitachi Co.).

Results and Discussion

Effect of Detergents on Solubilization

The effect of the concentration of Na-LAS on solubilization is shown in Figure 1. Some workers (8) have already reported the effect of the alkyl chain length of sodium alkylbenzene sulfonate on solubilization. We found that the amount of solubilized Yellow-OB increases with the increasing concentration or the alkyl chain length of Na-LAS; namely, the amount of Yellow-OB (mole) solubilized by sodium tetradecylbenzene sulfonate (gram, Na-TeDBS): 5.6 × 10^{-5} mole/g; by sodium tridecylbenzene sulfonate (gram, Na-TrDBS): 4.9 × 10^{-5} mole/g; by sodium decylbenzene sulfonate (gram, Na-DBS): 1.9 × 10^{-5} mole/g.

The effect of the water hardness on solubilization was determined using 0.4 wt% Na-LAS and 0.1 wt% polyoxyethylene (10) nonylphenyl ether (PNE-10).

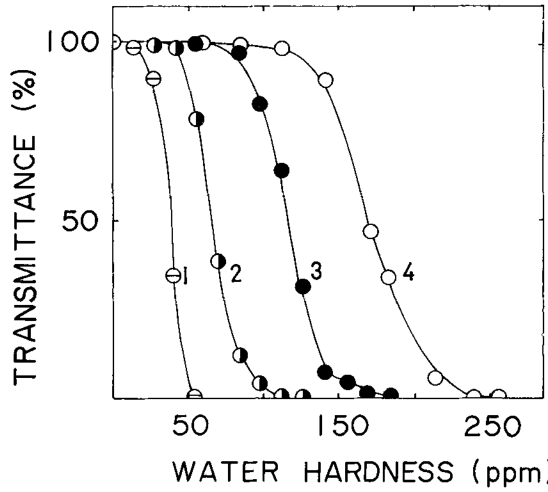

FIG. 4. The effect of the concentration of Na-TeDBS on transmittance in hard water. The concentration of Na-TeDBS is 0.1 wt% (1), 0.2 wt% (2), 0.4 wt% (3), 0.6 wt% (4).

The results are shown in Figure 2. In case of Na-LAS, the amount of solubilized Yellow-OB shows a maximum value at the same water hardness in spite of the constant concentration of detergents. The same phenomenon was observed on detergency of beef tallow-liquid paraffin soil with anionic detergents in hard water (1). Na-TeDBS showed the most solubilizing activity when the hardness of the water was 150 ppm; for Na-TrDBS, 164 ppm; and for Na-DBS, 207 ppm. The effect of water hardness on the solubilizing activity of Na-TeDBS is greatest, while with Na-DBS it is lesser. However, the relationship between the water hardness at maximum solubilizing activity for each detergent and alkyl chain length of detergent was parallel. From these results we thought it would be helpful to consider the hydrophile-lipophile balance of anionic detergents.

When the water hardness of a solution of an anionic detergent increases, it becomes turbid at some specific water hardness, just as nonionic detergents exhibit

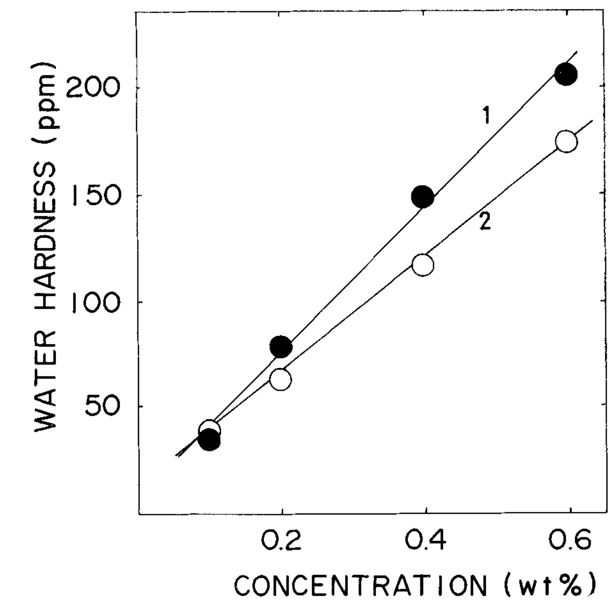

FIG. 5. The relationship between the concentration of Na-TeDBS and water hardness at maximum solubilization and 50% transmittance. Solubilization (1), transmittance (2).

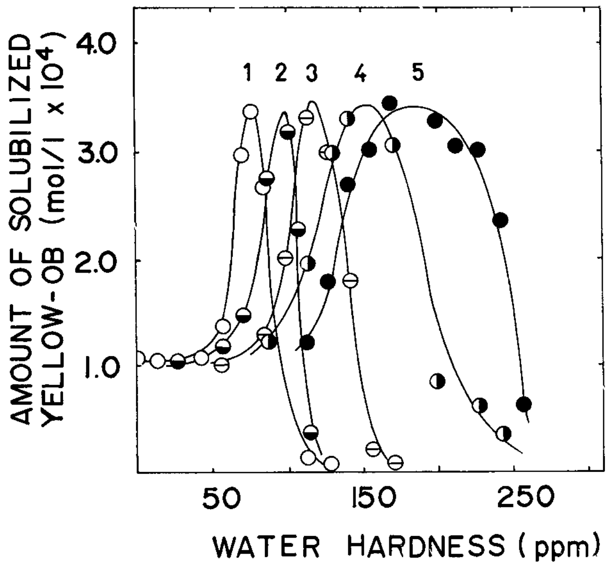

FIG. 6. The effect of the concentration of STPP on the amount of solubilized Yellow-OB vs. water hardness. The concentration of Na-TeDBS is 0.2 wt%. The concentration of STPP is 0 wt% (1), 0.02 wt% (2), 0.04 wt% (3), 0.06 wt% (4), 0.08 wt% (5).

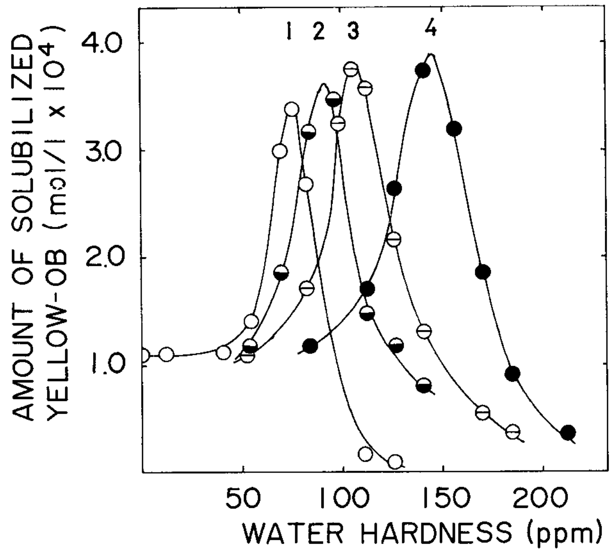

FIG. 8. The effect of the concentration of EDTA-2H₂O on the amount of solubilized Yellow-OB vs. water hardness. The concentration of Na-TeDBS is 0.2 wt%. The concentration of EDTA-2H₂O is 0 wt% (1), 0.02 wt% (2), 0.04 wt% (3), 0.08 wt% (4).

cloud points (see Fig. 4). In the case of Na-LAS, it is considered that a part of the Na-LAS in hard water may be converted to water-insoluble calcium linear alkylbenzene sulfonate (Ca-LAS), which has a higher krafft point than Na-LAS. Accordingly, detergent solution can be obtained with various Ca-LAS to Na-LAS ratios (that is, the detergent solution may have various HLB values or various krafft points). On the other hand, it is expected that as the water hardness in the solution of an anionic detergent increases, the cmc changes and the micellar weight increases (9), while the krafft point rises; that is, as the krafft point of the mixed detergent is raised more than the test temperature (30 C), the anionic detergent dissolves in hard water in molecular dispersion. Mankowich (10) found the existence of direct proportionality between micellar weight and Orange-OT solubilization using sodium dodecylbenzene sulfonate. Therefore, it can be expected that the micellar weight of Na-LAS in hard water shows a maximum value at the same water hardness which shows the maximum solubilizing activity.

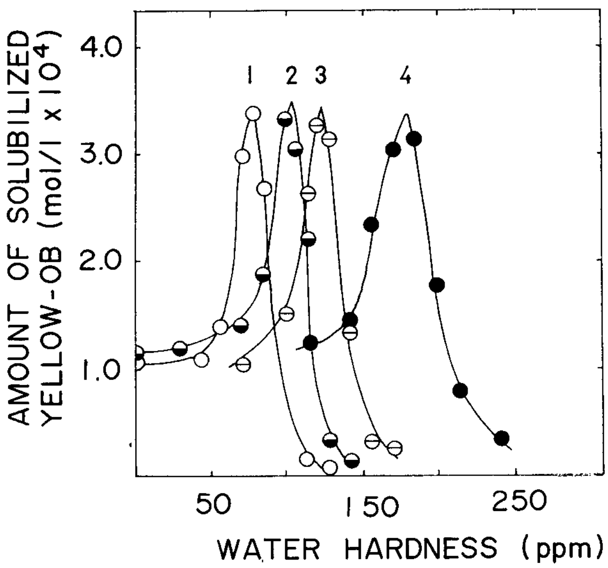

FIG. 7. The effect of concentration of NTA-H₂O on the amount of solubilized Yellow-OB vs. water hardness. The concentration of Na-TeDBS is 0.2 wt%. The concentration of NTA-H₂O is 0 wt% (1), 0.02 wt% (2), 0.04 wt% (3), 0.08 wt% (4).

On the other hand, the effect of calcium ion on the physico-chemical properties of nonionic detergents can be deduced from their cloud points (11). The cloud point of PNE-10 (0.1 wt%) was 64.5 C, and the effect of calcium ion on cloud point was too small to be neglected within the range of this study. Therefore, it is deduced that the micellar weight of PNE-10 does not change or it does so in a negligible amount (12,13). Accordingly, we consider that the amount of solubilization by PNE-10 did not influence water hardness (Fig. 2, Ref. 14).

The effect of the concentration of Na-LAS on solubilization in hard water has been determined using Na-TeDBS; the effect of water hardness on solubilization was most remarkable. The results are plotted in Figure 3. As the concentration increased, the amount of solubilization increased, and the water hardness at maximum solubilization increased. On the other hand, the relationship between the transmittance of Na-TeDBS to various water hardness solutions and water hardness is shown in Figure 4. From Figures 3 and 4, the relationship between the concentration of Na-TeDBS and water hardness at maximum solubilization or 50% transmittance is plotted in Figure 5. In Figure 5, it is clear that the relationship between the concentration of Na-TeDBS and water hardness at maximum solubilization is linear, and that the mole ratio of calcium ion to Na-TeDBS is 0.32; in case of transmittance, it is 0.25. Ginn et al. (5), and Kimura et al. (6) have measured the relationship between the solubilizing activities of some kinds of sodium dodecylbenzene sulfonate in hard water. They found that the ratio of calcium ion to sodium dodecylbenzene sulfonate at maximum solubilization with Orang-OT was about 0.4–0.5 molar ratio. These results can be explained by the hydrophilicity of anionic detergents from Figure 2.

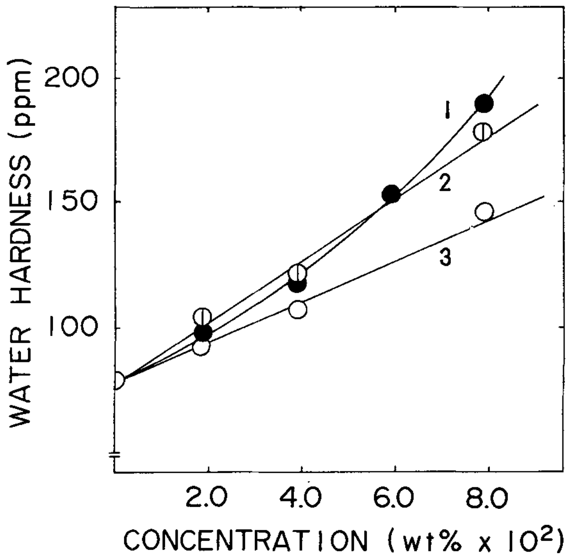

FIG. 9. The correlation between the concentration of builders and water hardness at maximum amount of solubilization. The concentration of Na-TeDBS is 0.2 wt% STPP (1), NTA-H_2O (2), EDTA-$2H_2O$ (3).

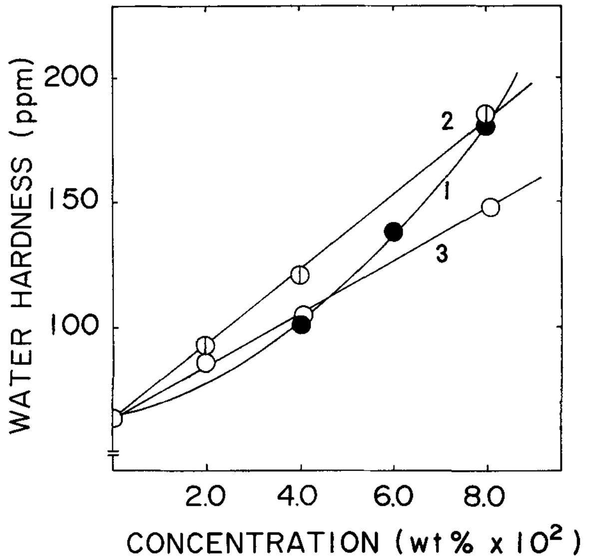

FIG. 10. The correlation between the concentration of builders and water hardness at 50% transmittance. The concentration of Na-TeDBS is 0.2 wt%. STPP (1), NTA-H_2O (2), EDTA-$2H_2O$ (3).

The Effect of Sequestering Builders

It was found that the amount of solubilized Yellow-OB showed a maximum value at some specific water hardness. Therefore, it was thought that it would be useful in understanding the role of the sequestering builder in anionic detergent solutions if we knew the effect of added sequestering builder on the water hardness at maximum solubilization. The mixture containing the added sequestering builder (STPP, NTA or EDTA) in various water hardness to Na-TeDBS (0.2 wt%) solutions was measured. The relationship between water hardness and the amount of solubilized Yellow-OB for each increment of the sequestering builder is shown in Figures 6, 7 and 8. In Figure 6, as the concentration of STPP increased, the water hardness at maximum solubilization increased. The maximum solubilization did not seem to be influenced greatly by the concentration of STPP. The same result was obtained for NTA and EDTA. From Figures 6, 7 and 8, it is interesting to note that the effect of added STPP on solubilization was different from that of NTA and EDTA; that is, as the concentration increased, the peak of the solubilization curve is lessened.

From the data in Figures 6, 7 and 8, the relationship between the concentration of the sequestering builder and water hardness at maximum solubilization is plotted in Figure 9. In the case of NTA and EDTA, the relationship between the concentration of the sequestering builder and the water hardness at maximum solubilization was linear, but in the case of STPP, as the concentration increased, the slope of the curve increased. The same behavior was observed in the relationship between transmittance of the Na-TeDBS in hard water containing STPP and water hardness. The relationship between water hardness at 50% transmittance and the concentration of builder was plotted in Figure 10.

Sequestering activity was determined by pH in builder to water hardness systems. The results are plotted in Figure 11. It was found that the effect of added STPP in hard water was different from NTA and EDTA as indicated by the solubilization or transmittance data in Figures 9 or 10.

From Figures 9, 10 and 11, sequestering activity was calculated. The results are given in Table II.

From the preceding results, it is clear that the effect of STPP, NTA and EDTA on the solubilization of Na-LAS was mainly due to water softening. Moreover it seems that we can obtain useful information concerning the role of builders in detergency from such studies. Table II indicates that the sequestering activity obtained by solubilization and detergency methods is lesser than that from the

TABLE II
The Sequestering Activity of Builders of Various Methods

Builder	Sequestering activity (mole ratio of Ca^{2+}/builder)			
	Solubilization	Transmittance	pH	Detergency (2)
STPP	0.97–1.76	0.87–2.47	Not clear	1.70
NTA	0.86	1.04	1.1	......
EDTA	0.82	1.11	1.0	......

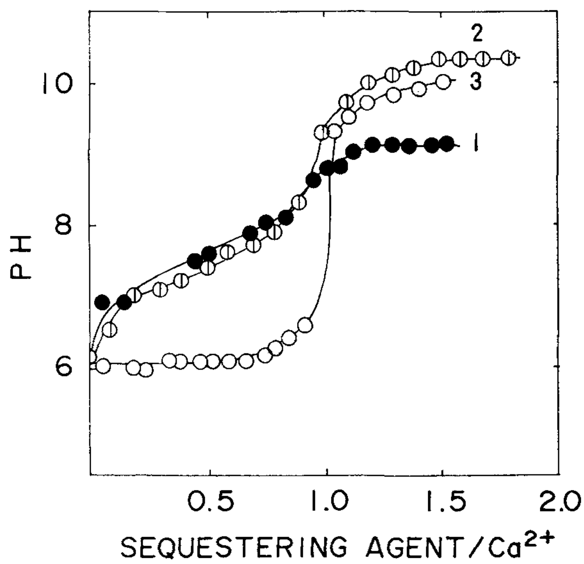

FIG. 11. The relationship between the effect of sequestration and pH. STPP (1), NTA-H_2O (2), EDTA-$2H_2O$ (3).

transmittance and pH method. It is our intention to carry out further studies to account for this.

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REFERENCES

1. Arai, H., JAOCS *43*, 312–314 (1966).
2. Arai, H., I. Maruta and T. Kariyone, Ibid. *43*, 315–316 (1966).
3. Arai, H. and M. Aoki, J. Chem. Soc. Japan, Ind. Chem. Sec. *71*, 99–104 (1968).
4. Arai, H., M. Aoki and I. Maruta, Colloid Symposium, Japan October, Saporo, 1967.
5. Ginn, M. E., F. B. Kinney and J. C. Harris, JAOCS *36*, 332–336 (1959).
6. Kimura, Y., S. Tanimori and T. Shimo, J. Oil Chem. Soc. Japan *13*, 656–661 (1964).
7. Pearson, J. T., and A. S. C. Lawrence, Trans. Faraday Soc. *63*, 488–494 (1967).
8. Mankowich, A. M., Ind. Eng. Chem. *44*, 1151–1159 (1952).
9. Corkill, J. M., and J. F. Goodman, Trans. Faraday Soc. *58*, 206–214 (1962).
10. Mankowich, A. M., Ind. Eng. Chem. *47*, 2175–2181 (1955).
11. Arai, H., J. Colloid Interface Sci. *23*, 348–351 (1967).
12. Becher, P., and H. Arai, Ibid. *27*, 634–641 (1968).
13. Arai, H., Ibid. *29*, 167 (1969).
14. Saito, H., and K. Shinoda, J. Colloid Interface Sci. *24*, 10–15 (1967).

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