ment of LAS in river water with increasing distance downstream from a sewage treatment plant outfall. Table 6 shows a similar pattern for IL-MBAS and GC-LAS levels in four monthly samplings of stream sediments, with the data showing a much more rapid decrease of both levels with increasing distance downstream.

The IL-MBAS results shown in Table 7, although not necessarily specific for actual LAS, demonstrate that LAS was quantitatively carried through the concentration and clean-up steps of the methodology described in this paper.

Table 8 provides a comparison of the IL-MBAS and GC procedures applied to sludge samples. The results again show that LAS was quantitatively carried through the various operations of the described procedure. Converse to the findings for river water, stream sediment and effluent samples, the IL-MBAS results on sludge samples were essentially the same as the specific measurements of LAS provided by gas chromatography.

ACKNOWLEDGMENT

The internal standard used in this work was provided by R. D. Swisher. J. Quinlisk and B. Goodlander performed the chromatographic analyses.

REFERENCES

1. *Standard Methods for the Examination of Water and Wastewater* (APHA-AWWA-WPCF), 15th Edition, 530-532 (1980).
2. Swisher, R.D., *Surfactant Biodegradation*, Surfactant Science Series, Vol. 3, Marcel Dekker, Inc., New York, NY (1970).
3. Setzkorn, E.A., and A.B. Carel, *JAOCS 40*:57 (1963).
4. Swisher, R.D., *Ibid. 43*:137 (1966).
5. Waters, J., and J.T. Garrigan, *Water Res. 17*:1549 (1983).

[Received June 24, 1985]

New Amphoteric Surfactants Containing a 2-Hydroxyalkyl Group VIII. Synthesis and Surface Activities for Amphoteric Oligomeric or Polymeric Surfactants of β-Alanine Type

Masafumi Moriya[a], **Akira Nishimura**[a], **Kazuo Hosoda**[a], **Makoto Takai**[a] and **Hisao Hidaka**[*,b]
[a]Miyoshi Oil and Fat Co. Ltd., Tokyo, Japan, and [b]Meisei University, Tokyo, Japan

A series of amphoteric oligomeric and polymeric surfactants of poly(iminoethylene) (PIE) containing both a 2-hydroxyalkyl group (C_{12}-HA or C_{14}-HA) and a 2-carboxyethyl (CE) group as N-substituents was studied as follows: PIE having 1,000 or 20,000 molecular weight was treated with 1,2-epoxydodecane or 1,2-epoxytetradecane and subsequently methyl acrylate. The adducts were saponified to obtain amphoteric oligomeric surfactants (AO) or amphoteric polymeric surfactants (AP), poly{[N-(2-carboxyethyl)-N′-(2-hydroxyalkyl)]iminoethylene}. Various adducts of which the ratios of CE/HA for one unit of iminoethylene group are 2, 3.5, 8, 17 and 89 were synthesized.

Surface activities such as surface tension, solubilization of orange OT, and foaming power, and physicochemical properties such as turbidity, isoelectric point, and the dissociation constant, were studied. Particular attention was paid to the dependence of solubilization, viscosity and turbidity on pH value.

A series of amphoteric surfactants containing both β-alanine and hydroxyalkyl groups has been published by the authors (1-6). Because the application of the surfactants for commercial usages was restricted due to low molecular weights, we have developed new amphoteric high molecular surfactants containing both β-alanine and 2-hydroxyalkyl groups. Although a few papers have been reported on polyampholytes having polyethylenepolyamine skeletons and carboxylic groups, e.g. poly-N-ethyleneglycine (7), polyaminopolypropionic acid (8) and polydimethylaminoalkyl acrylates and similar polymers (9), these exhibit no or poor surface activities.

For this paper, new amphoteric oligomeric or polymeric surfactants, the sodium salts of poly {[N-(2-carboxyethyl)-N′-(2-hydroxyalkyl)]iminoethylene} were prepared. Poly(iminoethylene) was treated with 1,2-epoxyalkane and methyl acrylate, followed by saponification. The surface activities and physicochemical properties for these surfactants were studied.

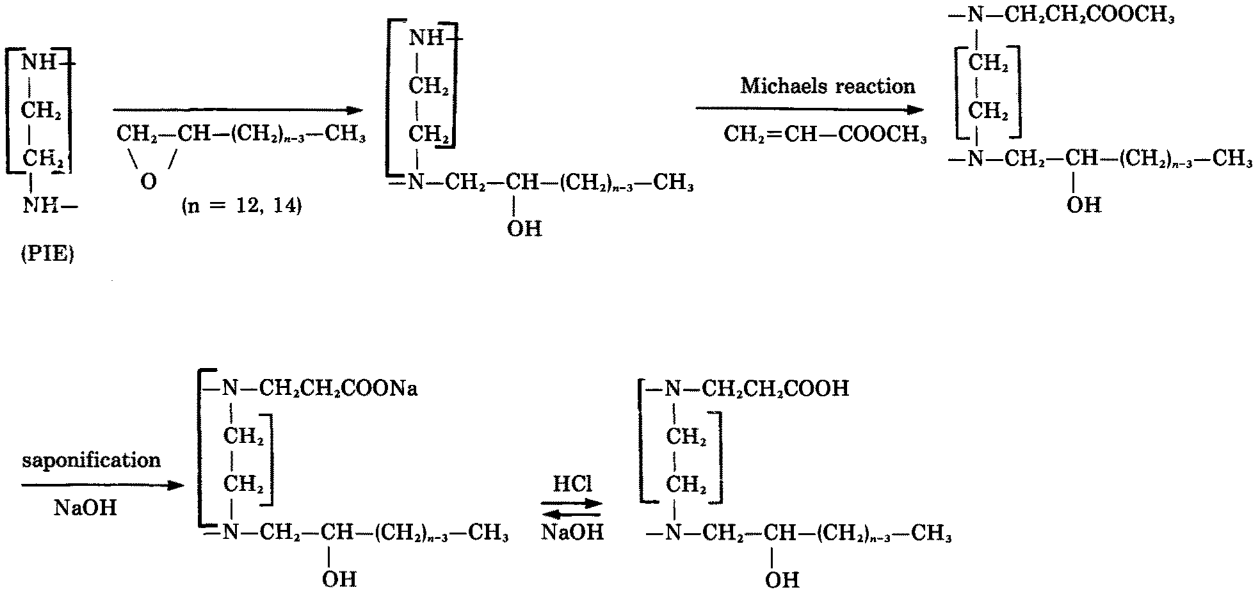
EXPERIMENTAL

Three series of amphoteric oligomeric surfactants (C_{12}-AO and C_{14}-AO) and amphoteric polymeric surfactants (C_{12}-AP) were synthesized as shown in the following scheme. The notations C_{12}- and C_{14}- placed in front of these abbreviations denote a 2-hydroxydodecyl group and a 2-hydroxytetradecyl group.

Scheme. Two series of oligomeric surfactants, C_{12}-AO or C_{14}-AO, were prepared by the addition of both 1,2-epoxydodecane or 1,2-epoxytetradecane and methyl acrylate to poly(iminoethylene) (PIE) having 1,000 molecular weight (iminoethylene unit number = ca. 23). Both C_{12}-AO and C_{14}-AO have an average calculated molecular weight of 2,500-3,500. While a series of polymeric surfactants (C_{12}-AP) was prepared similarly by the addition of 1,2-epoxydodecane and methyl acrylate to PIE having 20,000 mw (iminoethylene unit number = ca. 465). The average calculated mw of C_{12}-AP is 51,000-66,000. Where the additional molar ratios of CE/HA for one unit of the iminoethylene group are changed to be 0.6/0.3 = 2, 0.7/0.2 = 3.5, 0.8/0.1 = 8,

---

[*]To whom correspondence should be addressed at Meisei University, Faculty of Science and Engineering, 337, Hodokubo, Hino-shi, Tokyo 191 Japan.



(C_{12}-AO, C_{14}-AO, C_{12}-AP) (C_{12}-AO-H, C_{14}-AO-H, C_{12}-AP-H)

REACTION SCHEME

0.85/0.05 = 17, and 0.89/0.01 = 89, the total addition molar ratio of CE and HA is 0.9 per one iminoethylene group.

Materials. Poly(iminoethylene) (PIE) of ca. 1,000 mw as a starting material was of commercial grade (SP-110, Japan Catalytic Chem. Ind. Co. Ltd.) and used without purification. The PIE having ca. 20,000 mw was also of commercial grade (210T, Sogo Pharmaceutical Co. Ltd.) with 4.23% moisture; it was dehydrated two times by an azeotropic distillation method with benzene. The composition ratio of primary amine:secondary amine:tertiary amine in PIE is 1:2:1. The 1,2-epoxydodecane and 1,2-epoxytetradecane used were from commercial sources of AOE X24 (Daisel Co., Ltd.) and distilled two times in vacuo. The boiling point of 1,2-epoxydodecane is 81-85 C/1 mmHg, and the purity is determined to be 92.75% according to gas chromatographic analysis. That of 1,2-epoxytetradecane is 92-95 C/0.6 mmHg, and the purity is 93.7%. Methyl acrylate (Kanto Chem. Co. Inc.) is distilled at bp. 70 C/608 mmHg.

Syntheses. PIE of 1,000 mw (63.3 g, 0.063 mol) was added with 1,2-epoxydecane (2.7 g, 0.015 mol) at 75-80 C for 6 hr. Subsequently, oligo[N-(2-hydroxydodecyl)iminoethylene] was added with methyl acrylate (112.8 g, 1.31 mol) at 80 C for 6 hr. After the addition, the saponification was carried out with 50% NaOH solution 1.1 times mol for methyl acrylate at 95-100 C for 3 hr to obtain C_{12}-AO. That followed the neutralization of C_{12}-AO with HCl to give the carboxylic acid type (C_{12}-AO-H). Again, C_{12}-AO-H was recrystallized with ethanol aqueous solution and acetone; this was repeated several times. C_{14}-AO was prepared similarly by the addition of 1,2-epoxytetradecane. C_{12}-AP was synthesized by adding 1,2-epoxydodecane (4.4 g, 0.024 mol), then methyl acrylate (170.7 g, 1.98 mol) to PIE of 20,000 mw (100 g, 0.005 mol) in benzene (100 g) at 80 C and subsequent saponification with 50% NaOH aqueous solution (158.6 g, 1.98 mol). Thus, the derivatives with individual composition ratio of CE/HA by changing the addition molar number of methyl acrylate and 1,2-epoxyalkane were prepared.

The elemental analysis of all surfactant derivatives (AO-H and AP-H) for C, H and N was within 2.5% of the calculated value. Further, the structures of the C_{12}-AO-H, C_{14}-AO-H, and C_{12}-AP-H series were confirmed by IR analysis; 3360 cm^{-1} (—OH), 1700 cm^{-1} (C=O), 1180 cm^{-1}, and 1576 cm^{-1} (—NH— bending).

Physicochemical and surface active properties. The surface tension was measured by Wilhelmy's method with a Shimadzu ST-1 tensiometer at 30 C. C_{12}-AO-H, C_{14}-AO-H or C_{12}-AP-H was dissolved in distilled water to prepare a test sample, of which alkalinity at pH 10 was controlled by adding 2N NaOH. The isoelectric point (pI) of these surfactants was determined from the mean value of the acid dissociation constant (pK_1) and the base one (pK_2), which was found by the potentiometric titration method (10). The electroconductivity was measured by using a Toa-Dempa CM-1DB conductometer. Turbidity was measured with a Nippon Precision Optical Instrument Co. SEP-PT-501 turbidimeter and by using a 10 mm length cell. The dye solubilization of orange OT was measured according to the Lambert-Buche method (11,12). The viscosity measurement was carried out with an Ubbelohde viscosimeter in a thermostat at 25 C. The foaming power for 0.5 wt% solution was measured at a fixed temperature according to the Ross-Miles method at pH 10 and 30 C. The foam height (mm) was recorded immediately after dropping the test sample and after standing for 5 min (1).

RESULTS AND DISCUSSION

Surface activity for the CE/HA ratio in C_{12}-AO, C_{14}-AO and C_{12}-AP series. In order to investigate the evidence of micellization or aggregation, the relationship between

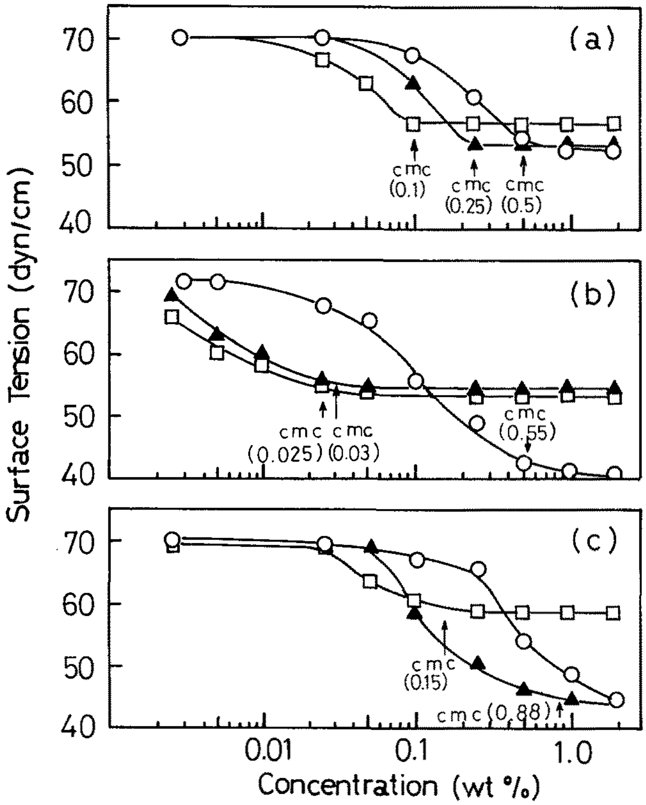


FIG. 1. Relationship between surface tension and log concentration (wt%) at pH 10 and 30 C. (a) C_{12}-AO; (b) C_{14}-AO; (c) C_{12}-AP. ○, CE/HA = 89; ▲, CE/HA = 8; □, CE/HA = 2.

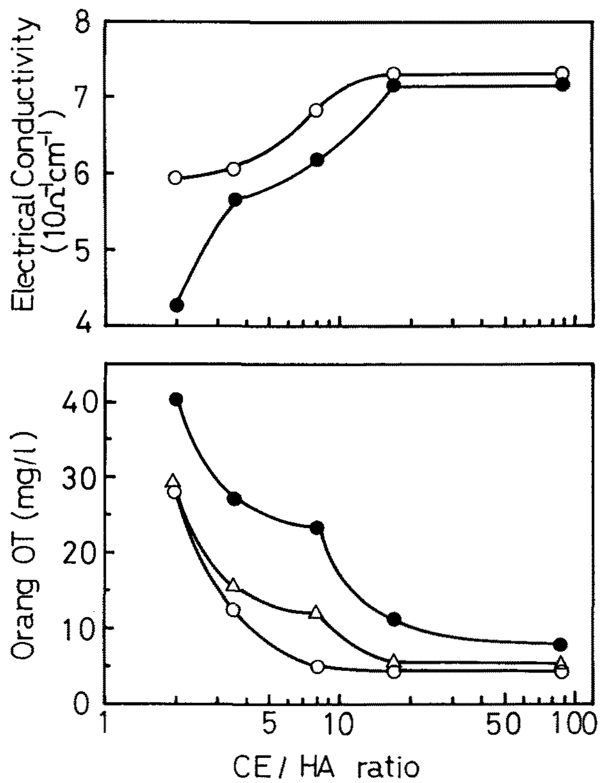


FIG. 2. Electroconductivity and solubilizing power of orange OT vs. CE/HA ratio for C_{12}-AO, C_{14}-AO and C_{12}-AP solutions (2 wt%) at pH 10 and 20 C. ○, C_{12}-AO; ●, C_{14}-AO; △, C_{12}-AP.

surface tension and log (concentration) was measured. Although a usual surfactant shows an obviously defined break, the slope of surface tension vs. log C for a polymeric surfactant does not exhibit an abrupt breakpoint (12). However, by analogy with a usual surfactant, we also define the breakpoint as the cmc for a polymeric surfactant.

Figure 1 depicts the surface tension vs. log C for individual series of C_{12}-AO, C_{14}-AO and C_{12}-AP. When the CE/HA ratio of N-substituents in both oligomeric surfactants (C_{12}-AO and C_{14}-AO) and a polymeric surfactant (C_{12}-AP) increased, all cmc values were larger.

That is, when the addition number of 2-carboxyethyl group (CE) decreased and conversely the number of 2-hydroxyalkyl group (C_{12}-HA or C_{14}-HA) increased in all systems, each cmc was smaller and the aggregation behavior of micellization became more loose. Because the slope of surface tension vs. log C below the cmc exhibits a low gradient, the Gibbs isothermal equation also supports the conclusion that these oligomeric and polymeric surfactants have a larger occupied surface area. As aggregation behaviors are studied by the half-line width method of NMR spectroscopy, we will report in a subsequent paper.

In comparison with the C_{12}-AO and C_{14}-AO systems, C_{14}-AO shows considerably smaller cmc value than C_{12}-AO concerning the individual ratio of CE/HA = 2 and 8 except 89 in the N-substituents. The fact is due to the difference in chain length of the 2-hydroxyalkyl group. In analogy with the cmc of a common surfactant, the cmc decreased with an increase in alkyl chain length. Further, compared with the polymeric surfactant (C_{12}-AP) and the oligomeric surfactant (C_{12}-AO) having the same alkyl chain length, the cmc values of C_{12}-AP system are nearly equal to those of the C_{12}-AO system for individual ratio of CE/HA. The surface activities are the same in spite of the difference of skeleton of poly(iminoethylene) (PIE). Although it is obscure what state of solubilization is formed, the composition having more 2-hydroxyalkyl groups (HA) exhibited a well-defined breakpoint corresponding to the cmc. Because the C_{12}-AP system contains many cationic iminoethylene groups, it gave better solubility and the drop of surface tension was observed at a relatively higher concentration. The results of cmc values and surface tension are summarized in Table 1.

Figure 2 shows the electrical conductivity and the dye solubilization of orange OT for each addition ratio of C_{12}-AO, C_{14}-AO, and C_{12}-AP series at pH 10.

As the CE/HA ratio of N-substituents increased, the hydrophobic properties decreased. The solubilization of orange OT decreased with decreasing the hydrophobic HA group. The C_{14}-AO series exhibited the largest solubilization compared with the C_{12}-AO and C_{12}-AP series. This means that C_{14}-AO is more hydrophobic than C_{12}-AO and C_{12}-AP. On the other hand, as the ratio of the 2-carboxyethyl (CE) group increased, the ionic properties enhanced and the electrical conductivity increased. The CE/HA ratio reflects the balance of hydrophilic and hydrophobic properties. As mentioned below, it is closely related to the result of an isoelectric point.

Table 1

Comparison of Critical Micelle Concentration and Surface Tension

Amphoteric oligomeric surfactant (AO)	cmc (wt%)	γ(dyn/cm)[a]	Amphoteric polymeric surfactant (AP)	cmc (wt%)	γ(dyn/cm)[a]
C_{12}-AO (89)[b]	0.5	52	C_{12}-AP (89)[b]	(1.0 ∼ 2.0)	41
C_{12}-AO (8)	0.25	53	C_{12}-AP (8)	0.38	45
C_{12}-AO (2)	0.1	57	C_{12}-AP (2)	0.15	60
C_{14}-AO (89)	0.55	42			
C_{14}-AO (8)	0.03	55			
C_{14}-AO (2)	0.025	53			

[a] Surface tension at the cmc.

[b] The addition molar ratio of CE/HA.

Figure 3 shows the turbidity for 2% aqueous solutions of these surfactants at pH 10. The turbidity is lowest at the neighborhood of CE/HA = 17. This fact is presumed to be correlated with the hydrophilic and hydrophobic balance. The turbidity for C_{12}-AP decreased steeply from the neighborhood of CE/HA = 3.5 to 17.

The foaming power for 0.5 wt% aqueous solutions of these surfactants is illustrated in Figure 4. When the CE/HA is less than 8, the foaming power lowered in the order of C_{12}-AO > C_{12}-AP > C_{14}-AO. On the contrary, they did in the order of C_{14}-AO > C_{12}-AP > C_{12}-AO in the range above CE/HA = 8. On the whole, the C_{14}-AO series having CE/HA = 17 exhibited the most excellent foaming power.

Dependence of physicochemical and surface active properties on pH value. Figure 5 shows the isoelectric point for individual components of these surfactants. The isoelectric point was determined from the relationship of $pI = (pk_1 + pk_2)/2$, where pk_1 and pk_2 are the minimum value in the differential titration curve. The C_{12}-AO-H and C_{14}-AO-H systems had higher isoelectric points than C_{12}-AP-H of a high molecular weight. The isoelectric point of C_{12}-AP-H lay at ca. pH 7. The point showed the minimum value for the derivatives containing the ratio of CE/HA = 17.

Figure 6 shows the dependence of dye solubilization of orange OT on pH value. C_{14}-AO-H has a relatively good solubilization in all pH ranges. The solubilization for

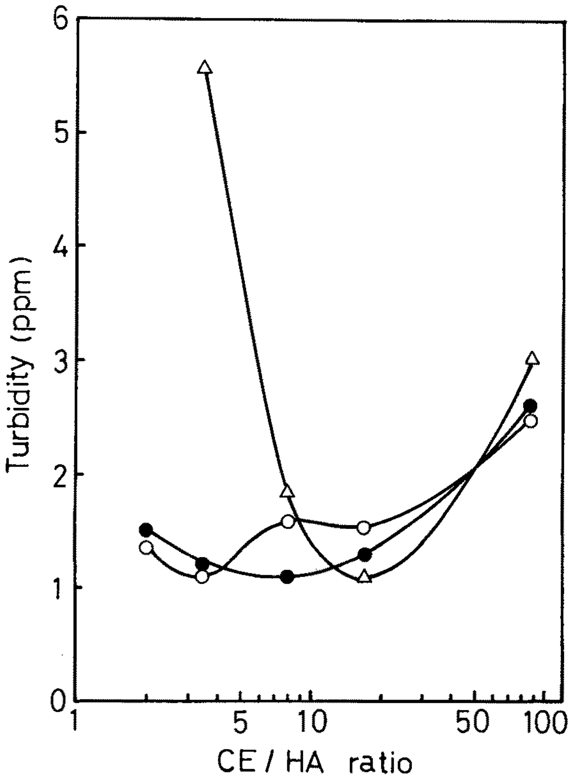


FIG. 3. Relationship between turbidity and CE/HA ratio for C_{12}-AO, C_{14}-AO and C_{12}-AP solutions (2 wt%) at pH 10 and 20 C. ○, C_{12}-AO; ●, C_{14}-AO; △, C_{12}-AP.

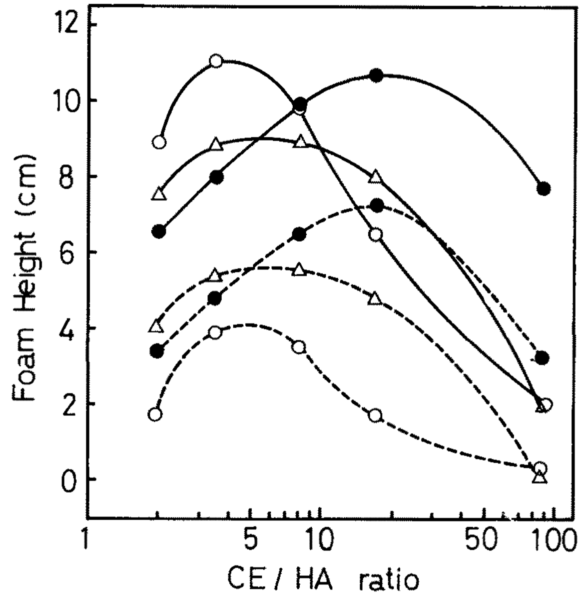


FIG. 4. Foaming power vs. CED/HA ratio for C_{12}-AO, C_{14}-AO and C_{12}-AP solutions (0.5 wt%) at pH 10 and 30 C. ○, C_{12}-AO ●, C_{14}-AO; △, C_{12}-AP. Solid line: height immediately after dropping the test sample. Dotted line: height after standing for 5 min.

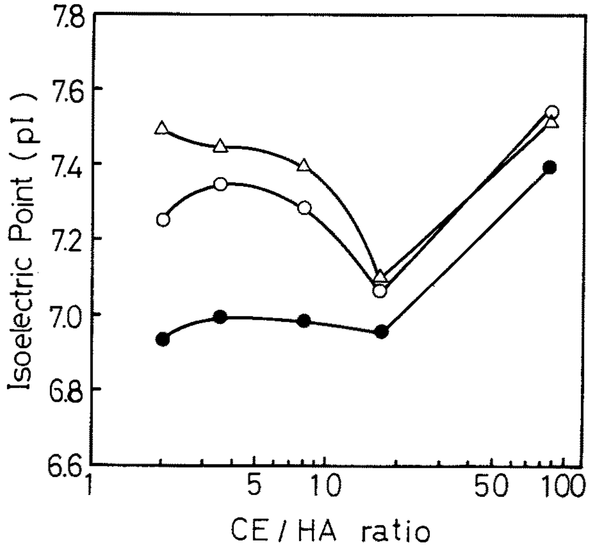


FIG. 5. Isoelectric ponts vs. CE/HA ratio for C_{12}-AO-H, C_{14}-AO-H and C_{12}-AP-H solutions (1 ~ 1.25 wt%) at 20 C. ○, C_{12}-AO-H; △, C_{14}-AO-H; ●, C_{12}-AP-H.

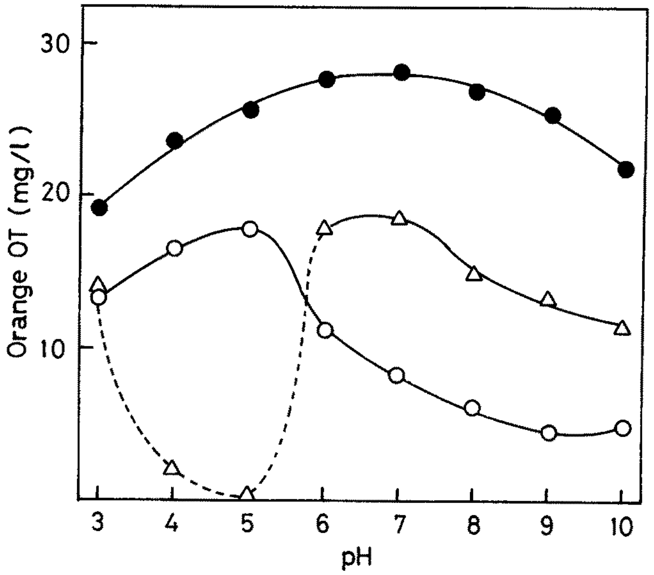


FIG. 6. Dependence of solubilizing power on pH value for C_{12}-AO-H, C_{14}-AO-H and C_{12}-AP-H solutions (0.5 wt%) at 20 C. ○, C_{12}-AO-H, CE/HA = 8; ●, C_{14}-AO-H, CE/HA = 8; △, C_{12}-AP-H, CE/HA = 8.

C_{12}-AO-H decreased in the range above pH 5. C_{12}-AP-H exhibited an abnormal value at pH 4~5 due to the condensation effect for orange OT dye. However, the solubilization was excellent at the neutral and alkaline range above pH 6.

Figure 7 displays the dependence of viscosity on pH value at 25 C. The viscosity for 1 wt% solutions of the derivatives containing CE/HA = 8 was measured. C_{12}-AO-H exhibited the lowest viscosity at pH 4.5 and

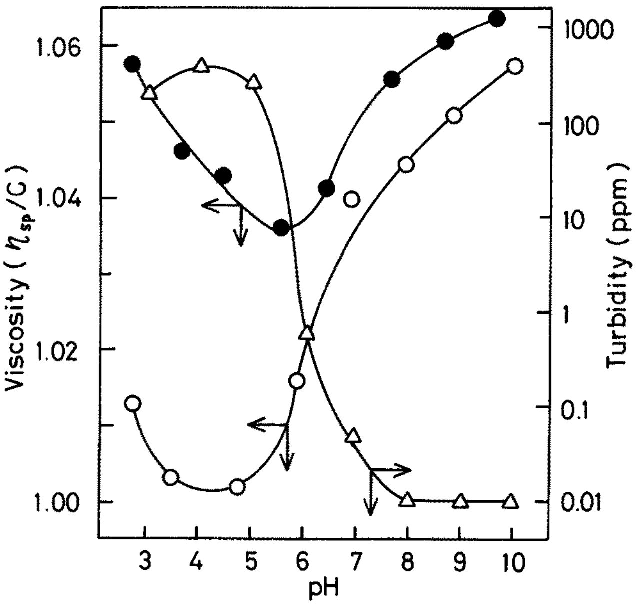


FIG. 7. Dependence of viscosity (1 wt% solutions at 25 C) and turbidity (0.1 wt% solutions at 30 C) on pH value. ○, C_{12}-AO-H, CE/HA = 8; ●, C_{14}-AO-H, CE/HA = 8; △, C_{12}-AP-H, CE/HA = 8.

C_{14}-AO-H at pH 5.5. On the other hand, the viscosity was high at the alkaline side and increased again at the neighborhood of pH 3. As for C_{12}-AP-H having high molecular weight, the aggregation appeared for the pH change and so turbidity was measured. The solution became turbid steeply below pH 5. The pH value where the carboxylic anions of C_{12}-AP change to the acid type was found to lie in the range of 4.5–5.5.

REFERENCES

1. Takai, M., H. Hidaka and M. Moriya, *J. Am. Oil Chem. Soc. 56:*537 (1979).
2. Hidaka, H., M. Moriya and M. Takai, *Ibid. 56:*914 (1979).
3. Takai, M., H. Hidaka, S. Ishikawa, M. Takada and M. Moriya, *Ibid. 57:*382 (1980).
4. Takai, M., H. Hidaka, S. Ishikawa, M. Takada and M. Moriya, *Ibid. 57:*183 (1980).
5. Hidaka, H., S. Yoshizawa, M. Takai and M. Moriya, *Yukagaku 31:*489 (1982).
6. Hidaka, H., H. Kubota and S. Yoshizawa, *Ibid. 32:*213 (1983).
7. Gregor, H.P., D.H. Gold and G.K. Hoeschele, *J. Am. Chem. Soc. 77:*4743 (1955).
8. Werdehausen Achim and Dohr Manfred, German Patent 1,770,160 (1971).
9. Melamed, S., U.S. Patent 2,980,657 (1961).
10. Hidaka, H., Y. Kawajiri and S. Noro, *Yukagaku 28:*190 (1979).
11. Mikumo, J., T. Asahara, and T. Imai, *Sekken Kaimenkasseizai,* Nikkan Ind. Newspaper Press (1975), p. 185.
12. Kame, M., S. Kishima, H. Koda and Y. Danjo, *Yukagaku 12:*173 (1963).
13. Wessling, R.A., and D.M. Pickelman, *J. Dispersion Sci. and Tech. 2:*281 (1981).

[Received January 25, 1985]